

California Biobutanol Multimedia Evaluation

Tier I Report

Prepared

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For the

**California Environmental Protection Agency
Multimedia Working Group**

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1. Executive Summary

1.1. Scope

Butamax™ Advanced Biofuels, LLC¹ is seeking to commercialize biobutanol² for use in blends with gasoline to be offered for sale within the State of California. Under California law, a necessary prerequisite for this commercialization is completion of a Multimedia Assessment. This report has been prepared as Tier I of that Multimedia Assessment.

Butanol-Gasoline blends of up to 3.7wt% Oxygen (approximately 16vol%) and meeting certain additional requirements are approved by the US EPA as substantially similar to baseline gasoline under terms of the Octamix Waiver³ issued under §211(f) of the Clean Air Act Amendments. US EPA Regulations also require completion of health effects testing (§211(b)) prior to commercialization; Butamax™ is currently working to complete this requirement.

The scope of this Multimedia Assessment is limited to gasoline/biobutanol blends containing 3.7wt% Oxygen (approximately 16vol%) in the form of iso-butanol and meeting other requirements of the Octamix Waiver and applicable California reformulated gasoline requirements. While many other fuel formulations fall within the scope of the Octamix Waiver, they are not within the scope of this Multimedia Assessment.

1.2. Background

In 2006, BP and DuPont first announced their joint efforts to develop biobutanol as a new biofuel component for use as a gasoline blendstock. The motivation for this multi-year effort is to develop a fuel that can be economically produced from renewable feedstocks and which provides superior performance and consumer value with the existing and future vehicle fleet.

Compared to ethanol, biobutanol offers several potential advantages –

- Biobutanol can be produced from the same feedstocks as ethanol through modest retro-fits of existing corn and sugarcane ethanol assets. This will allow production to be ramped up quickly by existing ethanol producers without impact

¹ Butamax™ Advanced Biofuels, LLC is a 50:50 joint venture of BP and DuPont which was formed in July 2009 for the purpose of commercializing biobutanol technology that has been jointly developed by BP and DuPont.

² For the purposes of this document, the term “biobutanol” is used to refer to all isomers of butanol produced from biomass. BP and DuPont are working specifically to commercialize the production of iso-butanol, one of the possible isomers. Inclusion of data on other isomers of butanol is for reference only.

³ 53 FR 3636 (2/8/88).

to feedstock producers. As technology develops for production of ethanol from lignocellulosic feedstocks, biobutanol technology will be extended to include those feedstocks as well.

- Biobutanol’s chemical properties allow it to be blended at 16vol% in gasoline while maintaining compatibility with the existing E10-capable vehicle fleet and offering equivalent performance on criteria pollutant emissions.
- Biobutanol has a higher energy density than ethanol, allowing the iso-butanol in a 16vol% blend to displace about 13.6%⁴ of the hydrocarbon gasoline, while the ethanol in a 10vol% blend displaces only about 6.8%⁵ of the hydrocarbon gasoline.
- The water-solubility and corrosivity of biobutanol is sufficiently low that biobutanol/gasoline blends can be transported in existing pipelines without risk of phase separation.
- Biobutanol has a blending RVP⁶ of 5.2psia, considerably lower than that of ethanol (blending RVP of 19 psia). As a result, biobutanol offers enhanced value to refiners who are typically RVP-constrained during summer blending season.

$$^4 \frac{16\text{vol}\% * (95500/115600)}{[84\text{vol}\% + 16\text{vol}\% * (95500/115600)]} = 13.6\% , \text{ where iso-butanol energy content is } 95,500 \text{ BTU/gal and gasoline energy content is } 115,600 \text{ BTU/gal.}$$

$$^5 \frac{10\text{vol}\% * (75700/115600)}{[90\text{vol}\% + 10\text{vol}\% * (75700/115600)]} = 6.8\% , \text{ where ethanol energy content is } 75,700 \text{ BTU/gal and gasoline energy content is } 115,600 \text{ BTU/gal.}$$

⁶ The blending Reid Vapor Pressure (RVP) of iso-butanol is 5.2 psia compared to CARB Phase 3 gasoline with a summertime RVP of 7.00 psia. (RVP is defined as the vapor pressure of an air-saturated sample at 100°F and a 4:1 vapor:liquid ratio.)

The blending value (vapor pressure or octane) of a component (e.g. ethanol) determines the effect a blending component will have on a gasoline blend when it is blended into the base gasoline. A blending value of a component is not necessarily the same as that property of the pure component. Blending values are often functions of the blend composition.

Example 1:

For example, the Research and Motor Octane numbers for pure ethanol are 109 and 90, respectively, with a (R+M)/2 = 99.5. However, when blended at a 10% volume into a base gasoline, ethanol blending octane numbers are 129 and 103, respectively, with a (R+M)/2 = 116. To calculate the (R+M)/2 value of 10% ethanol blended into a base gasoline with a (R+M)/2 of 88.5, the blending value of ethanol can now be used in the following simple equation:

$$(10\%)*(116) + (90\%)*(88.5) = 91.25$$

The benefits of biobutanol as an Alternative Fuel are recognized through its explicit mention in the renewable fuels components of the Federal Energy Independence and Security Act of 2007 (EISA 2007). The categorization of a specific source of biobutanol under EISA will be determined by the choice of feedstock (e.g., corn, sugarcane or lignocellulosic matter) and the lifecycle greenhouse gas benefit calculation.

The various butanol isomers have been used in the chemicals industry for a number of years and the potential health effects have been well-studied. While commercial butanol production has largely been through petrochemical pathways, health impacts are a property of the molecule that will be substantially unchanged for butanol produced through biological mechanisms. Additional studies to be undertaken in support of this multi-media assessment will focus on release pathways characteristic of the fuels lifecycle.

(Vol. % ethanol in blend)*(Blending Value of Ethanol) + (Vol. % gasoline)*(Value of Gasoline)= Final Property of Blended Gasoline

Example 2:

For example, the vapor pressure of pure ethanol at 100 F is 2.3 psia. Blending 10% ethanol into a base gasoline with a vapor pressure of 8.0 psi does not cause the vapor pressure of the gasoline to decrease to 7.43 ($10\% * 2.3 + 90\% * 8.0 = 7.43$). Instead the final vapor pressure of the blend is actually close to 9.1psia, meaning that the blending vapor pressure of ethanol at 100 F is actually 19 psia! ($10\% * 19.0 + 90\% * 8.0 = 9.1$).

2. Biobutanol Background Information

2.1. Introduction

Butanol or butyl alcohol is an aliphatic alcohol with a four-carbon structure and the molecular formula of C₄H₁₀O. There are four isomeric structures for butanol; 1-butanol

Table 2-1. Properties of Butanol Isomers

(* Average Blending Values; source: BP)

	1-butanol	iso-butanol	2-butanol
RON ⁷	94*	109*	110*
MON ⁸	81*	90*	93*
R+M/2 ⁹	87	100	102
Density, 20°C [kg/m ³]	810	801	808
Boiling point (°C)	118	108	100
Heating value [MJ/L]	27.0	26.6	26.8
% heating Value of Gasoline	84	83	83
Oxygen (% w/w)	21.6	21.6	21.6

(or n-butanol), iso-butanol, 2-butanol (or sec-butanol) and tert-butanol. With the exception of tert-butanol, the isomers occur naturally as a product of fermentation of carbohydrates. Several properties of the butanol isomers that can be produced via fermentation are presented in **Table 2-1**.

1-butanol is by far the most utilized of the butanol isomers. 1-Butanol is typically used as both an industrial solvent and an intermediate feedstock for the manufacture of other chemicals

including butyl acetate and butyl acrylate. These derivatives are used either as solvents or as monomer components for surface coatings. There currently is no significant usage of any butanol isomers for fuels.

In more recent years, there has been increasing interest in the potential use of biobutanol as an advanced biofuel component. This interest has been driven by the following characteristics:

- A higher energy density than ethanol (26.6 MJ/L for biobutanol vs 21.1MJ/L for ethanol) offering improved fuel consumption
- Greater water stability than ethanol, facilitating the introduction of biobutanol into the supply chain and the option of transporting gasoline/butanol blends by pipeline

⁷ Research Octane Number – one of two key measurements of gasoline ignition quality, defined by ASTM D2699

⁸ Motor Octane Number – one of two key measurements of gasoline ignition quality, defined by ASTM D2700

⁹ The numerical average of RON and MON. This is the octane rating that is required to be posted on retail gasoline dispensers in the US.

- A lower blending vapor pressure than ethanol facilitating the blending of Biobutanol into gasoline, with ethanol having a blending RVP of 19 psia, and Biobutanol having a blending RVP of 5.2 psia.

2.2. History of Biological Production of Butanol

To date, the biological pathway to butanol has primarily been via co-production with acetone and ethanol in a fermentation process (known as the ABE process for **A**cetone **B**utanol **E**thanol) using the *Clostridia* bacteria strain with various feedstocks such as wheat and corn. The ABE route was chiefly displaced during the 1950s by more economical petrochemical routes to manufacture butanol. However, in recent years, there has been a resurgence in the technology, particularly in China, due to high oil prices and increasing demand in the chemicals market. The butanol isomer produced by the ABE process is 1-butanol.

As a result of the increasing penetration of biofuels and the opportunity butanol presents, a number of companies have announced initiatives, via both existing and novel technological processes, to develop butanol pathways that are cost-competitive with ethanol.

BP and DuPont have been working together since 2003, leveraging DuPont's biotechnology and bio-manufacturing capabilities with BP's fuels technology expertise and fuels market know-how. In 2006 the companies announced the creation of a partnership to develop, produce and market a next generation of biofuels, with the first planned commercialization being biobutanol. Under the partnership, there are currently more than 70 patent applications in the areas of biology, fermentation processing, chemistry and end uses for 1-butanol, iso-butanol and 2-butanol. While the BP and DuPont have secured various patents on different butanol isomers, it is iso-butanol that has been selected for commercialization. BP and DuPont have recently formed a joint venture, Butamax™ Advanced Biofuels, for the purpose of commercializing this technology.

A technology demonstration facility in Hull, North-East UK is currently under construction and due to start up in 2010. This facility is being designed to process grain (corn and wheat) and sugar (sugarcane juice and molasses) feedstocks. Sugars derived from these feedstocks will be fermented using the organism being developed by Butamax™ and the product purified with the intended commercial purification scheme. The facility will produce iso-butanol from all the designed feedstocks; distiller's grains will be co-produced when operating on grain feedstocks. Nominal production capacity of this facility will be approximately 5000 gallons/year at expected operating rates; as this is a pilot unit it will be operated primarily to develop process design data with fuel production secondary.

2.3. Legislative Incentives for Biobutanol

Federal law has established several incentives for biobutanol –

1. The Energy Independence and Security Act of 2007 (EISA 2007) significantly increases biofuel mandates to 36 billion gallons by 2022. The act also requires that “Advanced Biofuels”, defined as fuels that reduce lifecycle greenhouse gas emissions by at least 50%, constitute at least 21 billion gallons of the total. Butanol’s potential as a biofuel is apparent in the acts clear inclusion of “butanol or other alcohols as produced through the conversion of organic matter from renewable biomass” in the Advanced category description¹⁰.
2. EISA defines all corn starch based ethanol as a conventional biofuel regardless of GHG performance. Corn based butanol with preferred GHG characteristics would be able to qualify for the Advanced Biofuel category, provided that it was able to meet the 50% reduction in lifecycle GHG performance from gasoline.
3. Blender’s Credit. Whereas ethanol receives a \$0.45/gal blender’s credit, butanol and other alcohols are granted a \$0.60/gal credit. This credit is set to expire at the end of 2010.
4. In addition, EPA regulations promulgated to implement the Energy Policy Act of 2005 (EPAct 2005) assigned biobutanol an Equivalence Value of 1.3 RINs relative to conventional ethanol’s 1.0 RINs. This means that every physical gallon of butanol blended counts as 1.3 gallons for compliance purposes. The EPA intends to carry over this provision into the new rules.
5. The 2008 Farm Bill included a \$1.01 per gallon production tax credit for all cellulosic biofuels. Cellulosic butanol will qualify on a volume basis for this tax credit.

Iso-butanol produced using the process under development by Butamax™ Advanced Biofuels also offers enhanced value for gasoline blenders in California -- while it has a carbon intensity (per megajoule) equivalent to ethanol when produced from the same feedstock, it can be included at higher blend levels in gasoline while maintaining compatibility with the existing car fleet (*i.e.*, vehicles compatible with 10vol% ethanol will also be compatible with 16vol% butanol blends). This allows a greater proportion of fossil fuel to be displaced by renewable fuel without requiring turnover of the existing vehicle fleet. As a result, iso-butanol facilitates compliance with the California LCFS by allowing higher biofuel penetration to be accommodated in the existing vehicle fleet while using existing distribution and retail infrastructure.

3. Production of Iso-Butanol

3.1. Iso-Butanol Production Process

The iso-butanol to be sold in California will either be manufactured from a corn or from sugarcane initially. Longer term, production of iso-butanol from lignocellulosic

¹⁰ Section 201(1)(B)(ii)(VI) of the EISA legislation.

feedstocks is expected. This report focuses on corn and sugarcane routes as they are much better defined at this time.

The process to produce iso-Butanol from corn has five major process steps:

- 1) Feedstock processing and saccharification which converts the corn starch to fermentable sugars. The unit operations involved in this step are identical to those in the Corn to Bio-ethanol process.
- 2) Fermentation to convert the sugars to iso-butanol using a proprietary microorganism. The unit operations involved in this step are similar to those in the Corn to Bio-ethanol process, substitution of the microorganism is the primary change.
- 3) Purification to recover the iso-butanol product from the fermentation. The unit operations involved in this step are different from those in the Corn to Bio-ethanol process.
- 4) Solid/liquid separation to remove solids from the process for disposal. The unit operations involved in this step are identical to those in the Corn to Bio-ethanol process.
- 5) Water treatment operations to allow water recycle to saccharification and concentration of insoluble materials to remove them from the process for disposal. The unit operations involved in this step are identical to those in the Corn to Bio-ethanol process.

The process to produce iso-butanol from sugarcane has four major process steps:

- 1) Feedstock processing and the crushing of the sugarcane to release the sugar juices. The unit operations involved in this step are identical to those in the Sugarcane to Bio-ethanol process.
- 2) Fermentation to convert the sugar to iso-butanol using a proprietary microorganism. The unit operations involved in this step are similar to those in the Sugarcane to Bio-ethanol process, substitution of the microorganism is the primary change.
- 3) Purification to recover the iso-butanol product from the fermentation. The unit operations involved in this step are different from those in the Sugarcane to Bio-ethanol process.
- 4) Generation of electrical power and steam to operate the process from the waste bagasse generated during the sugarcane crushing. The unit operations involved are identical to those in the Sugarcane to Bio-ethanol process.

3.1.1. Feedstock Processing

The feedstock processing operations for iso-butanol production are identical to those for Bio-ethanol. A brief summary is given below:-

Corn to iso-Butanol

In the Corn to iso-butanol process the corn is milled and ground into flour. Fresh water is mixed with water recycled from the distillation section of the process and added to the flour along with a mix of enzymes. The enzymes convert the starch in the corn into sugars. This process is identical to that used in the corn to Bio-ethanol process. The mix of solids, sugars and water is then ready to be fermented into iso-butanol.

Sugarcane to iso-Butanol

In a sugar mill, sugarcane is washed, chopped, and shredded by revolving knives. The shredded cane is repeatedly mixed with water and crushed between rollers; the collected juices contain 10–15 percent sucrose. This process is identical to that used in the sugarcane to Bio-ethanol process. The juices are fed to a fermentation vessel for conversion into iso-butanol.

With either corn or sugarcane feedstocks, the amount of water required is proportional to the amount of feedstock consumed. The iso-butanol process produces the same number of megajoules of fuel per unit of feedstock as the bio-ethanol process. Accordingly, the amount of water consumed for feedstock processing, per MJ of fuel produced, is the same for bio-ethanol and iso-butanol produced from the same feedstocks.

3.1.2. Fermentation

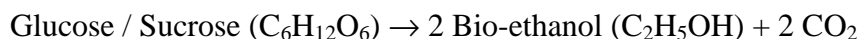
The fermentation processes used to make iso-butanol is similar to the Bio-ethanol process. The principle difference is that a proprietary organism is used to convert the sugar to iso-butanol rather than the yeasts used to make Bio-ethanol.

The sugars, solids (in the case of Corn to iso-butanol) and water from the feedstock processing area are fed into the fermentation vessels (the fermentation vessel design is similar to that used in Bio-ethanol production). The iso-butanol organism is added to the fermentor and the conversion of sugar to iso-butanol takes place as per the following equation –



Theoretically, 1kg of glucose will yield 0.411kg (0.513L @ 0.801kg/L) of iso-butanol with an energy content of 13.7MJ (@ 26.6MJ/L).

The corresponding equation for the production of bio-ethanol –



Theoretically, 1kg of glucose will yield 0.511kg (0.644L @ 0.794kg/L) of ethanol with an energy content of 13.6MJ (@ 21.1MJ/L).

3.1.3. Product Purification

The purification section for a Corn to iso-butanol facility and that for Sugarcane to iso-butanol facility are very similar though differ from their respective bio-ethanol counterparts due to the unique characteristics of iso-butanol vs bio-ethanol. The iso-butanol purification process employs traditional unit operations that provide for competitive energy usage rates and cost-competitive product purification rates.

On a Corn to iso-butanol plant the process for separating the solids and water from the fermentation product and recycling water back to the saccharification section is identical to that on a Corn to Bio-ethanol plant.

On Sugarcane to iso-butanol plants the process for handling the water recovered from the fermentation product is identical to that on a Sugarcane to Bio-ethanol plant.

3.1.4. Managing the Fermentation Process

The fermentation process on an iso-butanol production facility will be managed in an identical manner to that on a bio-ethanol facility. The iso-butanol process will employ a genetically modified micro-organism (GMM) for the fermentation. Additional process controls necessary for management of the GMM are addressed in **Section 9.4**.

3.2. Overview of iso-Butanol Feedstocks

3.2.1. Primary Feedstocks for Multimedia Review

The feed stocks used to manufacture iso-butanol will be the same as those used to manufacture Bio-ethanol. In particular the following feedstocks will be used:-

- Corn
- Sugarcane
- Ligno Cellulosic Feedstocks (longer term only)

Corn and Sugarcane will form the feedstocks for the first generation of iso-butanol processing facilities. The technology will be extended to include lignocellulosic feedstocks as technology required for the production of sugars from LC feedstocks (the same technology required for LC ethanol production) is developed.

3.2.2. Feedstock Characteristics

The characteristics for the feed stocks are shown in Table 3-1 below:

Feed Stock	Crop Description	Growing Conditions	Crop Yield	Ethanol Yield	iso_Butanol Yield
Corn (US Midwest)	Annual Cereal Food Crop	Sub tropical and temperate region. Very wide range of growing conditions from semi-arid to humid	150 bu/acre or 9.4 tonne/ha	420 gal/acre or 1040 gal/ha (83 GJ/ha)	330 gal/acre or 820 gal/ha (83 GJ/ha)
Sugarcane (Brazil)	Tropical ratoon grass. Once planted can be harvested annually for up to 7 years before re-planting	Around the equator, high water input, Grows best in deep, well drained soil of medium fertility.	85 tonne/ha	770 gal/acre or 1910 gal/ha (152 GJ/ha)	610 gal/acre or 1510 gal/ha (152 GJ/ha)
LC Feedstock (miscanthus)	Fast growing perennial grasses on agricultural land	Vary regionally – different species	15 tonne/acre	1375 gal/ac or 3340 gal/ha (266 GJ/ha)	1070 gal/ac Or 2640 gal/ha (266 GJ/ha)

Table 3-1. Ethanol and iso-Butanol Feedstocks

3.2.3. Feedstock Economic Considerations

The cost of production of iso-butanol is heavily influenced by the feedstock cost. The following factors are key drivers in feedstock economics:-

Crop Yield

Increasing the yield of the crop reduces the area of land that has to be farmed and harvested to provide the feed stock to the processing facility. This lowers the cost contribution from leasing the required land and can minimize direct and indirect land use change impacts. In addition increasing crop yield reduces the transport distance and hence logistic cost and fuel consumption in moving the feedstock to be processed.

Iso-butanol production yields the same number of megajoules of fuel per unit (bushel, tonne, etc) of feedstock as does bio-ethanol produced from the same feedstock. As a result, direct and indirect land use impacts will be the same, per MJ of fuel, as that for bio-ethanol produced from the same feedstocks.

Fertilizer and Water Requirements

Decreasing the requirement for fertilizer and water for the crop reduces the overall cost of the crop. Reduced fertilizer usage also improves lifecycle greenhouse gas balance and reduces the risk of water pollution due to fertilizer run-off. Reduced water use also leaves more water available for other crops, wildlife and human consumption.

Iso-butanol production yields the same number of megajoules of fuel per unit (bushel, tonne, etc) of feedstock as does bio-ethanol produced from the same feedstock. As a result, water and fertilizer use requirements for agriculture will be the same, per MJ of fuel, as that for bio-ethanol produced from the same feedstocks.

3.3. Iso-Butanol Standardization and Fuel Quality

Table 3-2 below compares some of the basic gasoline properties to ethanol and iso-butanol. Of note is the relatively high Research Octane Number (RON), and Motor Octane Number (MON) of both iso-butanol and ethanol compared to gasoline. However, the RON and MON of pure iso-butanol is lower than that of pure ethanol. At the 16vol% blend level iso-butanol provides nearly the same octane uplift as a 10vol% ethanol blend.

One of the advantages of iso-butanol is its higher heating value compared to ethanol. This is primarily due to the lower oxygen content of iso-butanol compared to ethanol, and this allows higher volumes of iso-butanol than ethanol to be blended into gasoline for any given oxygen content, *e.g.*, a 16 volume% iso-butanol blend has an oxygen content of 3.7 wt % and an ethanol and gasoline blend with the same oxygen content only has 10 volume % ethanol.

Many of the above properties are discussed below in more detail.

	Gasoline	Ethanol	Iso-Butanol
RON*	92	129	109
MON*	82	103	90
Anti-knock Index* (R+M)/2	87	116	100
RVP* (psia)	7.00 psia (summer)	19	5.2
Density, 20 °C [kg/m³]	720-775	794	801
Boiling point (°C)	<210	78.3	108
Heating value [MJ/L]	32.2	21.1	26.6
% heating Value of Gasoline	100	66	83
Oxygen (%w/w)	≥2.0 [†]	34.7	21.6

Table 3-2. Fuel Properties

* blending values (*source: BP*)

[†] CARB Phase 3 gasoline is typically 2.0wt% oxygen (5.7vol% ethanol) through 2009, increasing to 3.5-3.7wt% oxygen (10vol% ethanol) in 2010

Octane and Vapor Pressure for Iso-butanol Blends

The effect of blending iso-butanol into an unleaded regular gasoline (ULR) and an E10 ethanol blend were investigated. **Table 3-3** shows the effect of this blending on two key

Material, wt%	Fuel 1	Fuel 2	Fuel 3	Fuel 4
ULR	100	83	90	73
Iso-butanol	0	17	0	17
Ethanol	0	0	10	10
Research Octane Number	95.6	97.8	98.8	101
Motor Octane Number	85.5	86.2	86.9	87.6
Reid Vapor Pressure, psi	8.67	8.24	9.82	8.64

fuel properties, octane and Reid Vapor Pressure (RVP). From Fuel 2 in the table, it can be seen that iso-butanol increases the Research Octane Number (RON) and Motor Octane Number (MON) when blended into the ULR base, Fuel 1. Iso-butanol also possesses the very favorable property of decreasing the RVP of the ULR when blended at 17wt%.

Table 3-3. Octane and RVP Blending Data

From Fuel 3 in the table, it can be seen that while ethanol at a 10% blend also increases RON and MON, it has the disadvantage that it increases the RVP of the base fuel. However, blending 17wt% iso-butanol and 10wt% ethanol actually lowers the RVP to essentially the same RVP as the original ULR fuel. This synergic property of iso-butanol can be seen with Fuel 4 in the table¹¹.

¹¹ Fuel 4 is included in this table for illustration only. It’s oxygen content exceeds that currently allowable under EPA regulations.

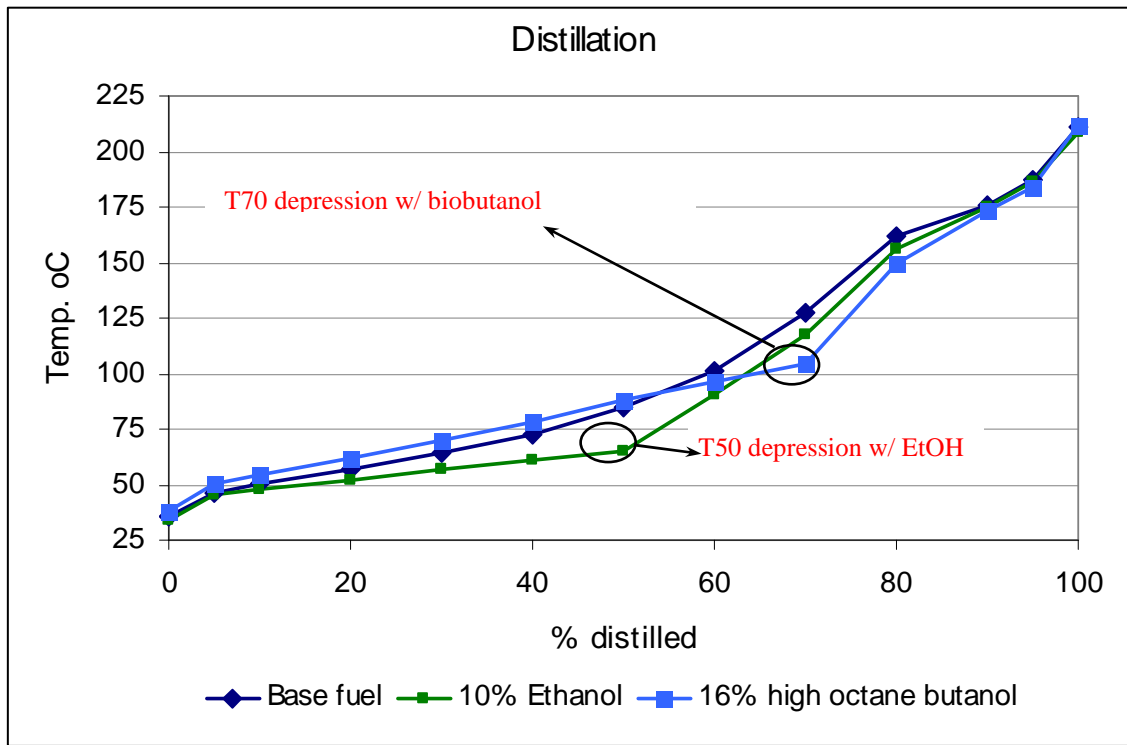


Figure 3-1. Distillation Impacts

Distillation

Figure 3-1 shows distillation curves for a base gasoline, a 10vol% ethanol blend and a 16vol% iso-butanol blend produced from this base gasoline. Of note is the similarity of the base gasoline low end volatility compared to the 16 vol% iso-butanol blend (This is indicated by the close overlap of the two distillation curves between 0 and 50% distilled). The E10 curve indicates increased low end volatility (the E10 curve is below the other two between 0 and 50% distilled). Normally this would indicate good cold start performance. However, in the case of E10, the greater low end volatility is caused by the formation of low boiling azeotropes composed of ethanol and hydrocarbons. These azeotropes are rich in ethanol and depleted in hydrocarbons, creating a more lean fuel/air mixture. At cold start conditions, an enriched fuel/air mixture is needed for good ignition; this shift in composition makes the vapor less ignitable than if it were all hydrocarbons, resulting in reduced cold start performance. By contrast, the iso-butanol blend has low-end volatility similar to the hydrocarbon base gasoline and the low-end vapor is not rich in iso-butanol content; iso-butanol azeotropes form at higher temperatures, as indicated in this data by the depression of T70. This T70 suppression is not important for cold start driveability performance.

Oxidation Stability of iso-Butanol Blends

Oxidation stability of gasoline blends containing iso-butanol showed some differences compared to base fuel.

Standard oxidation stability tests (ASTM D525) were performed on blends of iso-butanol in an unleaded regular gasoline containing refinery additives but no deposit control additive. Results shown in

Table 3-4 indicated that iso-butanol did not have a negative impact on this property at 15 wt% blend level, nor does ethanol show a negative impact on the oxidation stability at 10% blend level. However, a blend containing both iso-butanol (15%) and ethanol (10%) did show some non-linear effects¹². Specifically, iso-butanol/ethanol showed a slight decrease in stability (shorter induction period). It is well known that gasoline oxidation stability is highly dependent on blend components and that stability can be improved by the addition of antioxidant additives.

The data for Fuel 3 in

Table 3-4. Oxidation Stability shows that this iso-butanol blended fuel meets the current ASTM specification for gasoline without the use of anti-oxidants. However, if the fuel did not meet the >240 minutes induction period, then it is anticipated that the stability of the fuel could be increased using current technology anti-oxidant additives.

Material, wt%	3	4	7	8
ULR	85	90	75	100
iso-Butanol	15	0	15	0
Ethanol	0	10	10	0
ASTM D525 induction period (minutes)	255.8	297.0	178.8	251.6

Table 3-4. Oxidation Stability

Iso-butanol Water Tolerance and Phase Separation without and with Ethanol

Scoping water tolerance and phase separation tests of iso-butanol - gasoline blends were conducted at 65 °F. Blends of gasoline containing 0 to 25vol% iso-butanol were mixed with water and equilibrated at 65 °F. Although any level of water could have been used, a level of 1.3% was a convenient amount that resulted in sufficient volumes of aqueous and hydrocarbon phases that could each be analyzed. The hydrocarbon and aqueous phases were separated and analyzed for iso-butanol, and the hydrocarbon phase

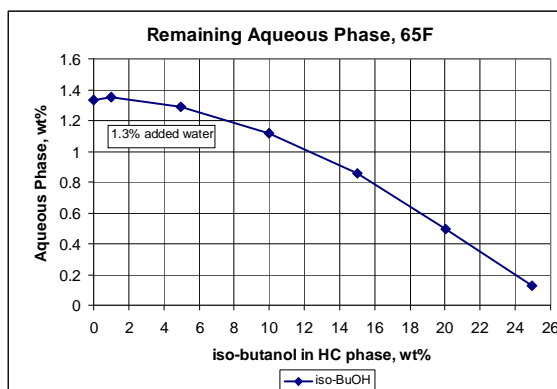


Figure 3-2. Water Absorption of iso-Butanol/Gasoline Blends

¹² This blend was tested for illustration only. It is not compliant with Federal or California regulations as it exceeds permissible oxygen levels.

was analyzed for water. **Figure 3-2** shows that as the level of iso-butanol was increased, the amount of water that the gasoline blend was able to absorb also increased (*i.e.*, the remaining aqueous phase decreased) and **Figure 3-3** shows the concentrations of iso-butanol in the aqueous phase for each iso-butanol/gasoline blend tested. From **Figure 3-2** and **Figure 3-3** at an iso-butanol concentration of 17 wt%, the level of water absorbed is approximately 0.6 wt%¹³. **Figure 3-4** shows the water concentration in the corresponding hydrocarbon phase.

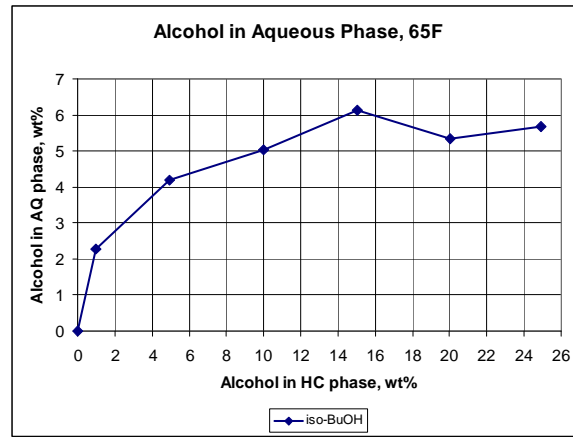


Figure 3-3. iso-Butanol Extraction from Gasoline into Water

The distribution of iso-butanol between the hydrocarbon and aqueous phases was calculated from the concentration data. Results are displayed in **Figure 3-5** as the distribution coefficient. Iso-butanol’s overall low water sensitivity indicates that its gasoline blends have the potential for pipeline shipment.

Scoping water tolerance and phase separation tests were also conducted on iso-butanol - ethanol - gasoline blends at 65 °F. Increasing amounts of iso-butanol were mixed with E10 gasoline and then either 1.3% or 2.6% water were added to all of the blends.

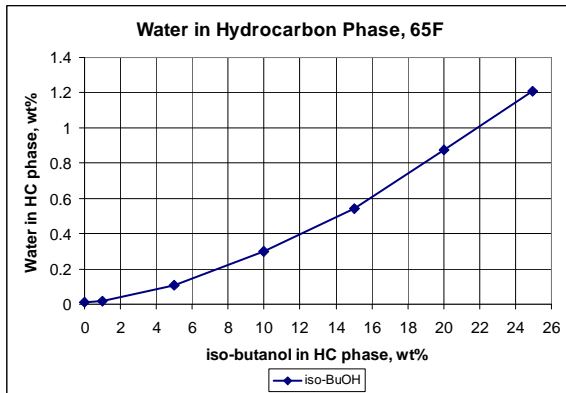


Figure 3-4. Water Solubility in iso-Butanol / Gasoline Blends

E10 gasoline and then either 1.3% or 2.6% water were added to all of the blends. Again, these levels of water are convenient amounts for this series of experiment. The water needed to be increased to 2.6vol% for some blends because gasoline blends containing ethanol absorb larger amounts of water and 1.3% water was not always sufficient to induce the formation of separate aqueous and hydrocarbon phases for analysis (*i.e.*, the 1.3vol% water was completely absorbed by the higher iso-butanol blends). This can be seen in

Figure 3-6 where 1.3 vol% was sufficient to cause two phases until the amount of iso-butanol in E10 reached 5vol%, but for 10vol% iso-butanol in E10, the level needed to be increased to 2.6vol% water to induce phase separation.

¹³ water added (1.3%) minus water remaining (aqueous phase **Figure 3-2** (0.7) * water concentration in the aqueous from **Figure 3-3** (1.00 - 0.06 = 0.94)): 1.3 wt% - 0.7wt%*0.94 ≈ 0.6 wt% . ,

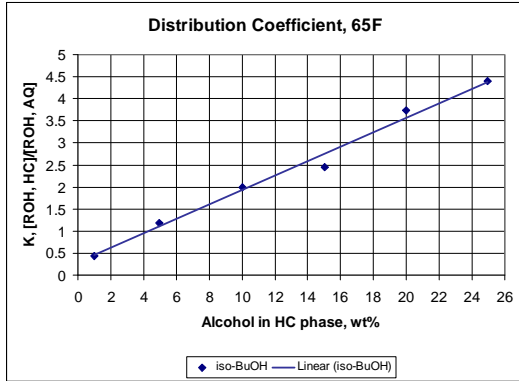


Figure 3-5. Distribution of iso-Butanol Between Water and Gasoline

The resulting hydrocarbon and aqueous phases were analyzed for iso-butanol, ethanol and water. **Figure 3-7** shows the amount of water in the hydrocarbon phase increased as the iso-butanol concentration increased. Comparing **Figure 3-4** and **Figure 3-7**, it can be seen that the absorbed water concentration was higher with ethanol present. Referring back to **Figure 3-6**, it can be seen the remaining aqueous phase was higher at low concentrations of iso-butanol, but decreased at higher concentrations of iso-butanol. From **Figure 3-8**, it is seen that the amount of ethanol extracted into the aqueous phase decreased with increasing iso-butanol concentration. These observations indicate that iso-butanol acts as a co-solvent for ethanol. **Figure 3-9** shows that iso-butanol in the aqueous phase reached a peak of about 12% when the iso-butanol was at a 5wt% concentration, and then it plateaued to about 6wt% at higher levels of iso-butanol in the hydrocarbon.

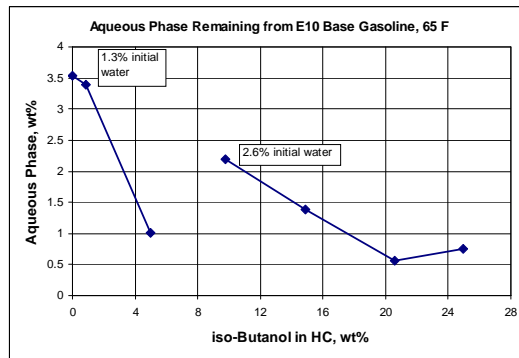


Figure 3-6. Absorbition of Water into E10 / iso-Butanol / Gasoline

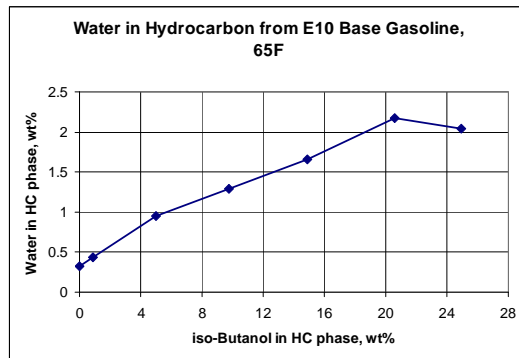


Figure 3-7. Water Solubility in E10 / iso-Butanol / Gasoline Blends

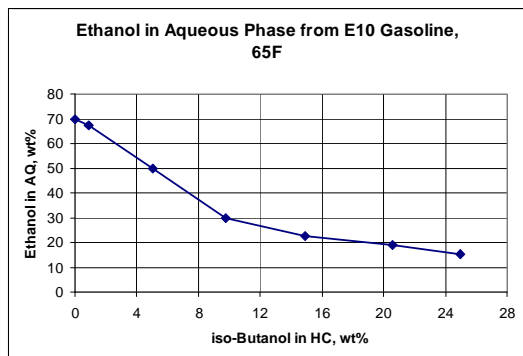


Figure 3-8. Ethanol Extraction to Aqueous Phase with E10 / iso-Butanol / Gasoline Blends

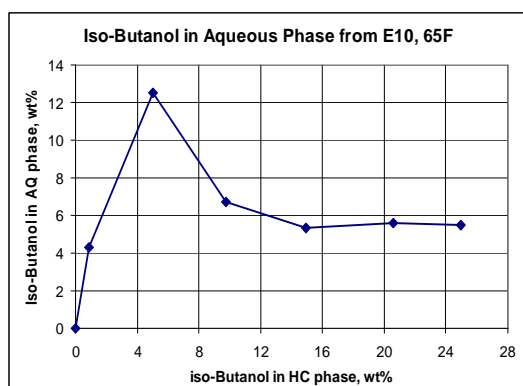


Figure 3-9. Iso-Butanol Extraction to Aqueous Phase with E10 / iso-Butanol / Gasoline Blends

3.3.1. Iso-butanol Fuel Energy Content

As cited above in **Section 3.3**, the fuel energy content of pure iso-butanol is approximately 95,400 BTU per gallon (26.6 MJ/l). This is 83% of the energy density of gasoline, while the energy density of ethanol is only 66% that of gasoline.

The fuel energy content of a 16 volume% iso-butanol blend is approximately 112,300 BTU per gallon, and this is comparable to the energy content of an E10 blend which has an energy content of 111,500 BTU per gallon. This comparison of energy content between E10 and 16vol% iso-butanol implies that consumers will experience slightly better (<1%) fuel economy with the butanol blend compared to E10.

4. Storage and Distribution of Iso-butanol

4.1. Material Compatibility

4.1.1. Iso-Butanol Elastomer Compatibility

Elastomer compatibility testing for chemical grade iso-butanol blended at 20% in unleaded regular gasoline showed slightly more ($\leq 1\%$) swelling than the ULR itself.

Elastomer swelling tests were conducted by soaking specimens of elastomer in fuel at ambient temperature for two weeks. Density and Durometer hardness tests were performed before and after soaking in fuel. Results are shown in **Figure 4-1**. Elastomer Swell Effects and **Figure 4-2**. Elastomer Hardness Effects.

Butamax™ Advanced Biofuels has not tested for elastomer compatibility with mixtures of ethanol and iso-butanol in CARB gasoline.

This testing has evaluated representative elastomers for swell and hardness impacts due to exposure to mixtures of ethanol and iso-butanol blended CARB gasolines as percentage changes. For all four elastomers tested: CPE = chlorinated polyethylene, epichlorohydrin, Hypalon™ and Viton™ B, a blend of 20% iso-butanol in unleaded regular gasoline (ULR) showed more swelling change than the base ULR. However differences between ULR and the iso-butanol blend were small, <1%. Compared to ethanol blends at 10% and 20%, results varied depending on the elastomer, but differences were small <3%. Hardness changes were generally inversely related to swelling (i.e. increased swelling gave decreased hardness) as typically observed. The differences observed for gasoline blends containing iso-butanol are not expected to have a negative impact on the vehicle systems. However because of the wide variety of materials used in vehicles, additional testing in vehicles is planned.

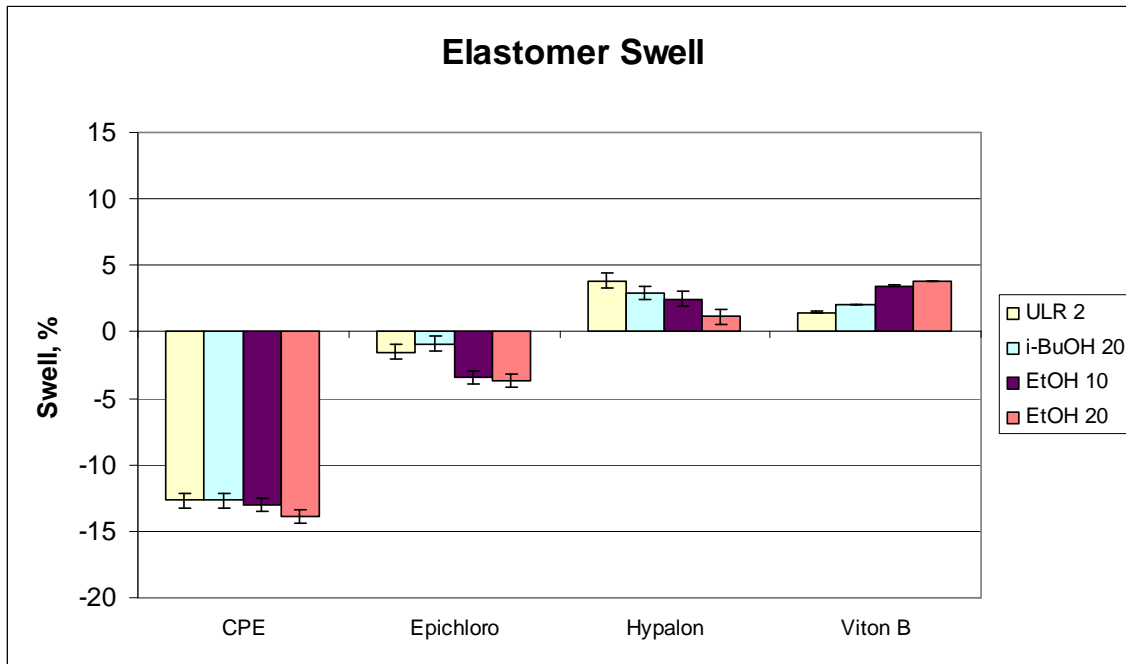


Figure 4-1. Elastomer Swell Effects

- **Test representative elastomers for swell and hardness impacts due to exposure to mixtures of ethanol and iso-butanol blended CARB gasolines.**

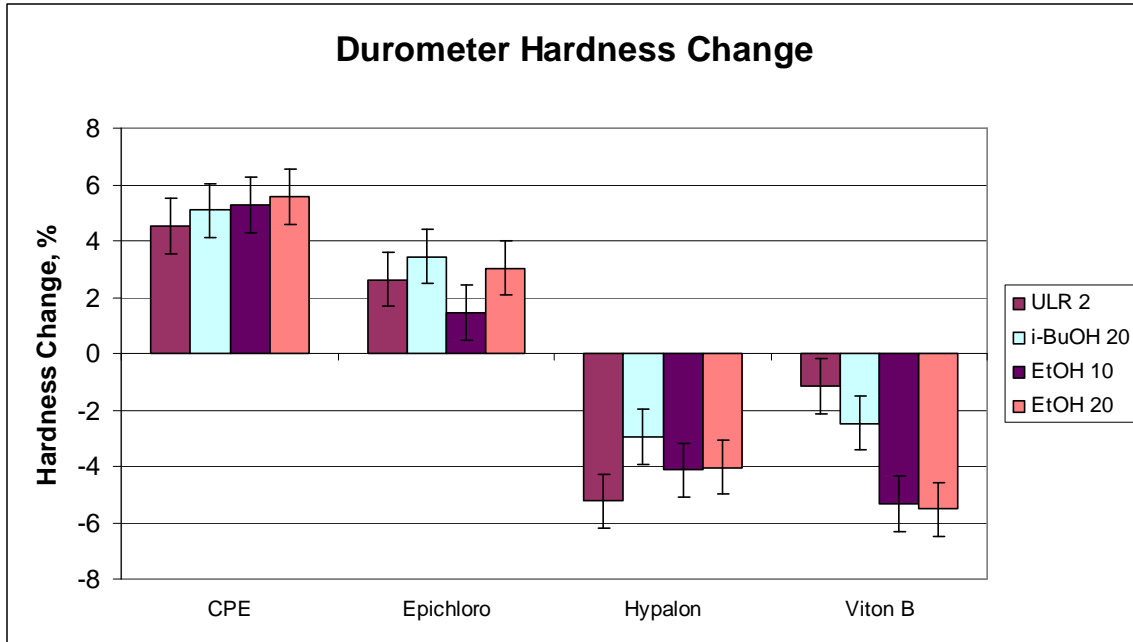


Figure 4-2. Elastomer Hardness Effects

4.1.2. Butanol Material Compatibility – Literature Search

Butamax™ Advanced Biofuels has not located any literature data on iso-butanol compatibility with fiberglass tank resins and sealants.

➤ **Test for compatibility of California gasoline blended with iso-butanol with fiberglass tank resins and sealants.**

It is known to the industry that ethanol blended gasoline can have a detrimental effect on automotive materials and components^{14,15}.

However, for several years automotive manufacturers and their suppliers have manufactured vehicles tolerant to E10 blends, including several million flexible fuel vehicles which are compatible with E85 fuel.

The effect of iso-butanol on automotive components is less well known. A literature search was conducted to shed light on this topic, and the search returned two articles that are somewhat relevant to this topic.

The first of these papers is a German language paper that reviews the use of alcohols and ethers on fuel properties and material compatibility¹⁶. While this paper did highlight the

¹⁴ R. Pierce and P. Moses, Effects of Fuel Exposure on Physical Properties of Selected Plastics, SAE International, International Congress and Exposition (1990), 900632.

¹⁵ Shiotani, Kinoshita, Goto, Saito, Research about Applicability of Biomass Ethanol for Motor Fuel, Society of Automotive Engineers of Japan, Academic Lecture Meeting, May 20, 2005.

effect of butanol on gasoline volatility properties, it only mentioned that alcohols can have a negative effect on material compatibility without citing any experimental data.

The second paper investigated aluminum corrosion with alcohol and alcohol blends. The author found that alcohols (C₂-C₄) will react with aluminum to form alkoxides¹⁷. These alkoxides can then go into solution and result in a fresh aluminum surface susceptible to further corrosion. In addition, the author found that a minute level of water inhibits this reaction, and he determined the minimum water content (MWC) needed to prevent this corrosion in alcohols and their mixtures. The results indicate that pure ethanol and butanol have the same MWC to prevent corrosion. He also found that alcohol mixtures have a higher MWC needed to prevent corrosion than pure alcohols alone.

MWC for Ethanol, Butanol, and a 50/50 Mixture Each

Ethanol – 0.3 volume % (at 120°C)

Butanol – 0.3 volume % (at 120°C)

Ethanol and Butanol (50/50 vol. % blend) – 1.2 volume % (at 120°C)

Unfortunately, the paper did not investigate the influence of gasoline on this corrosion mechanism. As a result, it cannot be inferred that aluminum corrosion will occur by this same mechanism when ethanol and/or butanol are blended with gasoline.

BP's theory for explaining how MWC inhibits aluminum corrosion is as follows. When aluminum is exposed to a water and alcohol solution, the water will react with the aluminum surface to form aluminum oxide. This aluminum oxide is an adherent layer, and it does not dissolve into the alcohol, but instead acts as a protective skin that inhibits the alcohol from reacting with the aluminum. When the MWC is reached or exceeded, the protective layer is sufficient to completely inhibit the alkoxide reaction.

4.2. Storage and Storage Stability

Iso-butanol and its gasoline blends are stable under normal conditions of storage and use. During BP's multi-year study of iso-butanol blended fuel, no blend in underground storage, vehicle tank, or laboratory vessel ever demonstrated instability. One measure of this is the induction period oxidation test results of >240 minutes which indicate one year stability to gum formation at ambient temperatures, see Table 3-4.

¹⁶ A. Marhold and A Lanik, Alternative Kraftstoffkomponenten – Anwendungseigenschaften und Verhalten in Motoren, Erdoel-Erdgas-Zeitschrift, 98. Jg., May 1982.

¹⁷ T. Tsuchida, Corrosion Behavior of Aluminum in Mixed Alcohol Solutions, Corrosion Engineering 53, 71-80 (2004)

Hazardous polymerization will not occur, nor should hazardous decomposition products be produced. In **Section 3.3**, it was noted that oxidation stability testing demonstrated that the iso-butanol did not significantly impact the oxidation stability of gasoline.

Additional precautions for storage and handling of iso-Butanol/gasoline blends are substantially the same as recommended practices for gasoline and ethanol/gasoline blends. Specific examples follow --

- As with gasoline and ethanol blends, avoid all possible sources of ignition (spark or flame) and excessive heat. In addition, avoid highly reactive materials such as oxidizing and reducing agents.
- Store iso-butanol and its gasoline blends in segregated and approved areas.
- Light hydrocarbon vapors can build up in the headspace of tanks. These can cause flammability/explosion hazards even at temperatures below the normal flash point (note: flash point must not be regarded as a reliable indicator of the potential flammability of vapor in tank headspaces). Tank headspaces should always be regarded as potentially flammable and care should be taken to avoid static electrical discharge and all ignition sources during filling, ullaging and sampling from storage tanks.

The flammability range of biobutanol blends (and also ethanol blends) at moderate levels of oxygenate (i.e. $\leq 20\%$) is dominated by the gasoline component. The lower and upper flammability limits of these blends are expected to be the same as gasoline. (e.g., The upper flammability limit of gasoline is exceeded at temperatures above about $-40\text{ }^{\circ}\text{F}$. Therefore confined vapor spaces over the liquid at or above this temperature are not ignitable.) Consequently, biobutanol blends are expected to possess the same fire hazards as gasoline. BP knows of no situations where iso-butanol blend is expected to pose a greater fire hazard than gasoline or moderate ethanol gasoline (E10) blends.

Bio-produced iso-butanol itself is expected to have essentially the same fire hazards as industrial grade iso-butanol. Iso-butanol's fire hazard is well known and its MSDS gives appropriate handling, storage and fire fighting information.

- When the product is pumped (e.g. during filling, discharge or ullaging) and when sampling, there is a risk of static discharge. Ensure that the equipment used is properly earthed or bonded to the tank structure.
- Electrical equipment should not be used unless it is intrinsically safe (i.e. will not produce sparks.)
- If product comes into contact with hot surfaces, or leaks occur from pressurized fuel pipes, the vapor or mists generated will create a flammability or explosion hazard.

- Empty containers represent a fire hazard as they may contain flammable product residues and vapor.
- Never weld, solder or braze empty containers.

4.3. Distribution and Blending of Iso-butanol

Iso-butanol and its gasoline blends can be distributed in the same manner as ethanol, gasoline, and their blends. However, due to the inherently better water tolerance for iso-butanol blended gasoline compared to ethanol blended gasoline, the potential exists to ship iso-butanol blended gasoline through pipelines. This water tolerance can be seen below in **Figure 4-3**. This figure shows the water tolerance at multiple temperatures for iso-butanol blended gasoline at several different concentrations, including 16vol% iso-butanol. As the temperature increases from -40 °F to 65 °F, the saturation level of water in the iso-butanol blended fuel increases. For the 16vol% iso-butanol blend, the saturation level at -40 °F is approximately 2.5 wt%, and this increases to approximately 5.5 wt% at 65 °F. In contrast a typical E10 fuel in the marketplace today will undergo a phase separation when it reaches is saturated level of approximately 0.4 wt%.

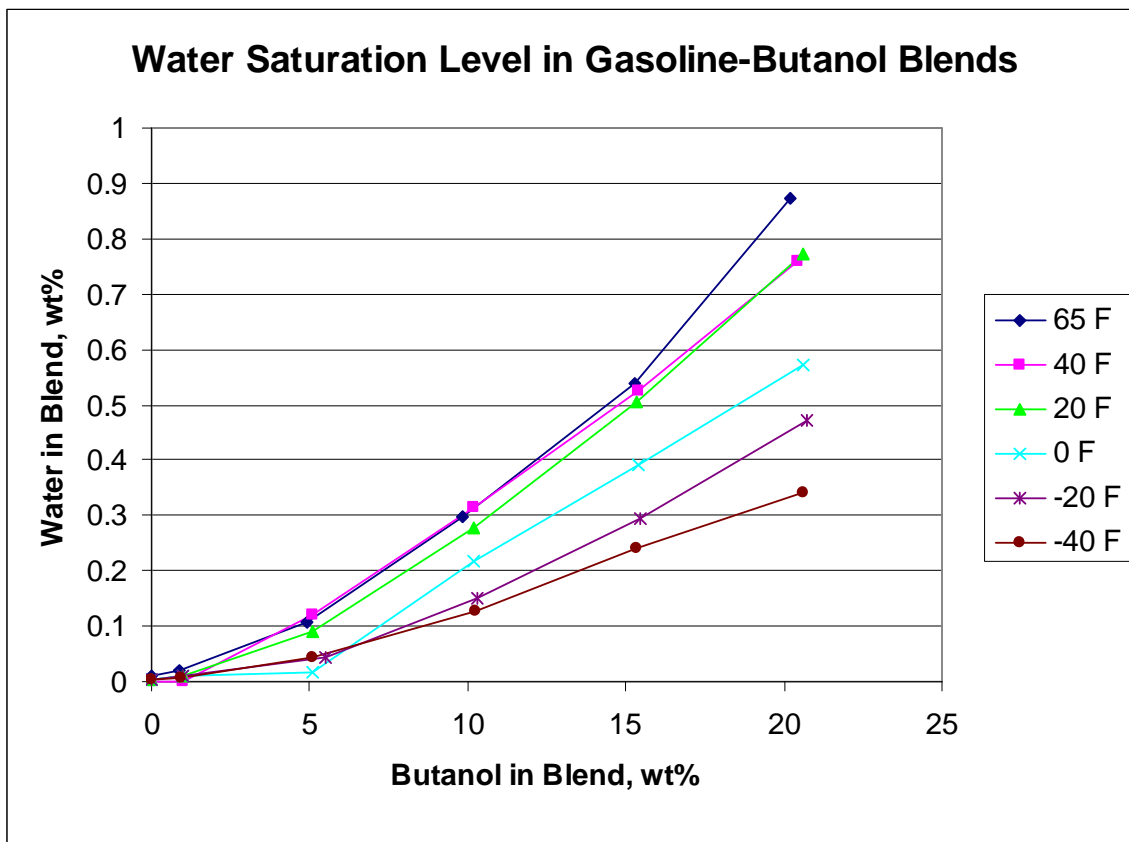


Figure 4-3. Water Saturation – Impact of Temperature

Corrosion is also a concern for pipeline shipments. The OCTAMIX waiver requires a specified corrosion inhibitor to assure protection of vehicles. Pipeline specifications include a test of corrosion performance, the NACE test. BP’s experience in the preparation of gasoline/iso-butanol blends for its test programs has shown that the NACE

specification can readily be achieved with typical industry practices for the use of commercial corrosion inhibitors.

4.3.1. Conductivity

The conductivity for pure ethanol and iso-butanol can be found in the literature¹⁸. Pure ethanol has a conductivity of 135 pS/m, and pure iso-butanol has a conductivity of 950 pS/m. However, several factors will influence the conductivity of final E10 and 16vol% iso-butanol blended gasolines. These include the purity of the alcohols after fermentation and distillation, the type of denaturant (in the case of ethanol), and the gasoline base fuels. The conductivity of E10 and 16vol% iso-butanol gasoline is a knowledge gap that will be addressed in the Tier II plan.

- **Determine the electrical conductivity of E10 and 16vol% iso-butanol/gasoline blends.**

4.4. Retail Site Equipment

Equipment used for dispensing of fuel into motor vehicles is regulated by a number of agencies. Different agencies regulate different pieces of equipment consistent with their missions, including fire prevention, human exposure, water and soil pollution and air pollution.

- **UST Rules** – Covers underground storage tanks and piping with focus on protection of ground water resources. Regulated by U.S. EPA under 40 CFR Part 280. Part 280.32 of these regulations requires that equipment have demonstrated material compatibility with the substances being stored and handled. The EPA will accept equipment listed by a nationally recognized testing laboratory (NRTL) such as Underwriter's Laboratories (UL) or third party testing as proof of this requirement.
- **Human Exposure** – OSHA regulations 1910.106(g), 1910.303 and 1910.307 cover dispensers, nozzles, breakaways and pumps. These regulations require equipment listed by a nationally recognized testing laboratory (NRTL) such as Underwriter's Laboratories (UL).
- **Vapor Recovery Requirements** – Subject to EPA regulation under the 1990 Clean Air Act and California ARB regulation. ARB certifies equipment for conformance with vapor recovery requirements and will only test equipment listed by a nationally recognized testing laboratory (NRTL) such as Underwriter's Laboratories (UL).
- **Weights and Measures Approvals** – BP has met informally with California DMS metrology staff and has been advised that their primary concern is whether blended fuel will conform to ASTM D4814. Butamax™ Advanced Biofuels believes that 16vol% iso-butanol blends can be made within D4814 specification requirements. It

¹⁸ International Critical Tables of Numerical Data, Physical Chemistry and Technology (1st Electronic Edition) Edited by Washburn, E.W. Originally published from 1926-1930, and released by Knovel in 2003

is likely that NTEP (National Type Evaluation Program, an activity of the National Council on Weights and Measures) approval would be required before the fuel can be commercially sold.

- **Leak Detection Equipment** – Leak detection equipment is developed and tested under guidance of the NWGLDE (National Working Group on Leak Detection Equipment). Third party testing will be required by the CA State Water Control Board to demonstrate that the leak detection equipment will function as required by State and Federal rules.
- **Fire Codes** – Enforced by state fire marshals. Fire codes set by NFPA/IFC and require UL listed equipment. In CA, IFC is the model code on which CA State Fire code is based. Per these rules, iso-butanol blends will require NRTL “listed” tank, pipes, pumps, shear/impact valves, dispensers, vapor recovery equipment, hose breakaways, hose swivels, hoses, nozzles, electrical leak and level sensors, pressure/vacuum valves and vapor flow meters.

Gasoline with iso-butanol levels at 16 vol% currently does not have UL certification for retail station equipment. This includes the underground storage tanks, pumps, dispensers, and break away valves as outlined above. UL approval is generally required as a pre-requisite for new equipment to achieve certification for conformance with applicable regulatory requirements. There is no established process for achieving approval of legacy equipment. UL has stated publicly that it will not retroactively list legacy equipment.

BP will work with its equipment vendors and UL to gain approval for a 16 vol% iso-butanol blend. This will not be easy. One potential path forward is to use the testing protocols currently being used by industry to gain approval for E10+ blends. At this time, the UL approval path for iso-butanol blended gasoline is not fully defined, and BP will communicate progress as this approval path is defined and executed.

4.5. Storage Emissions from Terminals (Vapor recovery)

It is anticipated that the same vapor recovery practices and equipment currently used for ethanol and its gasoline blends can be used for iso-butanol and its gasoline blends.

- **BP will perform a review of applicable terminal vapor recovery requirements.**

4.6. Fire Fighting Protocol

The fire fighting protocol for iso-butanol and its gasoline blends is the same as that for ethanol and its respective blends. In case of a fire, water fog, alcohol resistant foam, dry chemical, or carbon dioxide extinguisher can be used. Use of a water jet is not an appropriate extinguishing media.

Both the liquid and vapor from these alcohols and their gasoline blends are flammable, and the vapor may cause a flash fire. Further the vapors may accumulate in low or confined areas, and travel a considerable distance to a source of ignition.

Combustion products may include the following: carbon oxides (CO, CO₂) (carbon monoxide, carbon dioxide) and other hazardous substances. Exposed firefighters must wear MSHA/NIOSH approved positive pressure self-contained breathing apparatus with full face mask and full protective clothing.

5. Use of iso-Butanol

5.1. Performance Characteristics

5.1.1. Low Level Blends

In its early stages of butanol research, BP conducted vehicle testing on a variety of butanol isomers at several different concentrations. This discussion on low level blends includes data from vehicles fueled with 11.5 and 16.8 vol% iso-butanol (Phase 1 and Phase 2, respectively). Although BP does not plan to commercialize an 11.5 vol% blend, these data are included below with the data on 16.8 vol% iso-butanol for completeness.

Iso-butanol (11.5 and 16.8 vol%)-gasoline blends were used to fuel four vehicles. Monitoring of gross driving performance; inspection of engine cleanliness; emissions and fuel economy testing were conducted. No gross material incompatibilities were observed. Engine cleanliness of intake valves, fuel injectors, throttle plate and oil filler cap were not negatively impacted. Emissions and fuel economy testing showed the expected reduction in total hydrocarbon emissions and fuel economy, and these data are presented in Section 5.3.2.

Vehicles and Inspections

Characteristics of the four vehicles selected for the fleet are given in **Table 5-1**. The Toyota, 4TO1, and the Chevrolet, 4CV1, were premium recommended vehicles. (The vehicle ID numbers are explained below in **Table 5-1**) The accumulated mileage includes both Phase 1, exclusive iso-butanol gasoline blend, and Phase 2, rotation with retail fuels. Prior to start of testing the following inspections were made:

- Intake-valve deposit (IVD) ratings were made on the assembled engine with a boroscope using the standard CRC (Coordinating Research Council) scale.
- Throttle plate and oil filler cap sludge ratings were performed on the parts removed from the engine using a CRC rating scale.
- Injector flow and spray ratings were performed on the injectors dismantled from the engine on the standard flow rig using Stoddard solvent as the fluid.

Following Phase 1, these inspections were repeated to determine changes after exclusive use of the iso-butanol blend. Vehicles were driven on local roads under prevailing weather conditions by BP employee drivers for both phases. Operational and performance problems, if any, were reported by each driver.

Table 5-1. Fleet Vehicle Characteristics

Make / Model	Engine Fuel System	Odometer, Initial/Final	Accumulated Mileage	Start Date, Phase 1	ID
Chrysler / Concorde 2004	2.7 L, 6-cyl, DOHC	69,828 / 73,689	3861	26 April 2007	4CHY2
Ford / Focus 2004	2.0 L, 4-cyl	75,719 / 79,098	3379	28 March 2007	4FO1
Toyota / Celica 2004	1.8 L, 4-cyl, DOHC, WT-i	59,087 / 61,291	2204	3 April 2007	4TO1
Chevrolet / Monte Carlo 2004	3.8 L, 6-cyl, supercharged	53,447 / 61,291	2896	9 May 2007	4CV1

Iso-butanol Fuel Blend

Properties of the iso-butanol gasoline fuel blends are given in **Table 5-2**. The fleet initially began using a 11.5 volume % blend and then was changed to a 16.8 volume% blend. The base gasoline was a retail, summer grade non-oxygenated gasoline with added n-butane to adjust Reid vapor pressure (RVP).

Table 5-2. Fuel Inspection

Property	Iso-butanol Blend (11.5 vol%)	Iso-butanol Blend (16.8 vol%)
Research Octane No.	94.2	97.1
Motor Octane No.	83.6	85.9
Antiknock Index	88.9	91.5
API Gravity	58.33	56.32
Specific Gravity, 60/60	0.7454	0.7534
Reid Vapor pressure, psi	11.49	8.75
Initial Boiling Pt, °F	74.2	79.0
10% Distilled, °F	103.2	131.0
30% Distilled, °F	148.9	173.0
50% Distilled, °F	188.3	199.1
70% Distilled, °F	222.9	216.8
90% Distilled, °F	340.5	312.1
Final Boiling Pt, °F	399.7	380.7
AP-NA4M additive, g/gal	0.48	0.48

Results and discussion

No driveability problems were reported during either Phase 1 or 2, 11.5vol% iso-butanol and 16.8vol% iso-butanol, respectively.

Engine Inspections

Table 5-3 shows the results of IVD ratings and their changes. The results are presented as least square means (LSM) of the ratings because the engines do not all have the same number of valves. The LSM statistic is used to make comparisons as if all engines had the same number of valves.

Table 5-3. IVD Ratings

Vehicle	Number of Valves	Initial IVD CRC Rating*, LSM	Final IVD CRC Rating*, LSM	Change ± 95% CI
4CHY2	12	8.22	9.12	0.90 ± 0.23
4FO1	8	8.92	9.32	0.40 ± 0.28
4TO1	8	8.24	8.55	0.31 ± 0.28
4CV1	6	9.37	8.82	-0.55 ± 0.33
Fleet		8.69	8.95	0.27 ± 0.14
* CRC rating scale: 10 = clean; 1=extremely dirty				

The fleet average results showed a slight increase in cleanliness. It should be noted that the one vehicle that did not show a cleanliness improvement had a supercharged engine and its initial CRC rating was much higher than the other vehicles (i.e. it started the test in a very clean condition).

Table 5-4 shows results of fuel injector ratings. No significant changes in flow variation were observed. Also all spray patterns were normal and no injectors showed leaks.

Table 5-4. Fuel Injector Ratings

Vehicle	Number of Injectors	Initial Flow Variation*, LSM	Final Flow Variation*, LSM	Change ± 95% CI
4CHY2	6	-0.3	0.7	1.0 ± 1.3
4FO1	4	2.1	0.7	-1.4 ± 1.6
4TO1	4	-1.6	-1.1	0.6 ± 1.6
4CV1	6	-0.2	-1.2	-1.0 ± 1.3
Fleet		0.0	-0.2	-0.2 ± 0.71
* Percent variation compared to standard injector				

Table 5-5 shows results of fleet average sludge ratings. For the 4FO1 vehicle the area above and below the throttle plate was black plastic so it could not be rated. These area ratings are based on the other three vehicles. No statistically significant changes in sludge ratings were observed.

Table 5-5. CRC Sludge Ratings, Fleet Average

Rating Area	Initial Rating*, average	Final Rating*, average	Change ± 95% CI
Above throttle plate	9.91	9.83	-0.08 ± 0.30
Below throttle plate	8.90	8.99	0.09 ± 0.19
Top of plate	9.87	9.87	0.00 ± 0.01
Bottom of plate	9.27	9.20	-0.07 ± 0.16
Oil fill cap	9.71	9.92	0.21 ± 0.59
* CRC scale: 10 = clean; 1 = heavy sludge.			

Use of blends of iso-butanol in gasoline up to 16.8% showed no gross negative impacts on vehicle operation or engine cleanliness.

5.1.2. High Level Blends

While initial commercialization plans focus on a 16vol% iso-butanol blend, a limited amount of work has been performed to begin assessing the feasibility of higher blend levels. This work provides an initial indication that there is potential to expand iso-butanol to higher blend percentages. This Tier I report does not purport to cover all of the items that would need to be addressed before approval of a higher level blend could be achieved.

The purpose of this scoping-level program was to define a preliminary, operability-based limit on the maximum butanol concentration that can be used in gasoline for conventional (i.e., non-FFV) vehicles. The study was to focus only on short-term operability factors (e.g., driveability, acute vehicle malfunctions, etc). Two critical operability factors were identified for the study, as described in the principle objectives:

- Determine the threshold iso-butanol concentration in gasoline for conventional (non-FFV) vehicles above which air/fuel ratio (AFR) excursions exceed acceptable limits and cause the vehicle to display dashboard malfunctions indications (MILs) due to excessive fuel oxygen.
- Determine the limits of iso-butanol concentration and ambient temperature where cold-start and warm-up driveability performance of conventional (non-FFV) vehicles is degraded due to the volatility reduction which results from splash-blending butanol into conventional gasoline.

The adaptability of vehicle AFR control systems was investigated in on-road and chassis dynamometer driving tests which required the control systems to adapt to fuels with 61 to 78 volume % butanol (14 to 17.5wt% oxygen, or four to five times the oxygen content of E10). The study found that the closed-loop fuelling / AFR control systems of modern vehicles are remarkably robust, adapting to the oxygen levels of high-butanol fuels without malfunction over a wide range of driving conditions.

The driveability investigation employed US industry-standard CRC methods to assess the cold-start and warm-up driveability of gasolines splash-blended with 5 to 60 vol% iso-butanol; both summer and winter base fuels were included in the study. The investigation found that cold-start and warm-up driveability performance of splash-blended high-butanol fuels was remarkably good; 20 vol% blends were virtually indistinguishable from base gasoline, and 30 vol% blends were acceptable over the majority of test temperatures. A practical limit near 40 vol% was apparent, as driveability performance began to degrade rapidly above this level. A notable exception to this conclusion was the single direct-injection car in the study, which for low test temperatures experienced unacceptable driveability at concentrations in the range of 20 to 30 vol% iso-butanol. Even considering the most severe car in the study, the results indicate that a commercial offer for splash-blended high-butanol fuels is a practical possibility worthy of continued investigation.

Splash blending experiments, while instructive, are limited as they do not permit any tailoring of the hydrocarbon portion of the fuel to match the increasing volume of iso-butanol. Future experiments, with fully-blended fuels would be expected to show even less impact from increasing butanol content. Additional studies are required on emissions and durability before commercialization of such high level blends can be considered. Butamax™ Advanced Biofuels is not seeking approval for high blends at this time.

5.2. Use of Additives

Butamax™ Advanced Biofuels does not foresee iso-butanol and its gasoline blends to need any additive chemistries that are not already commercially available for ethanol and its gasoline blends. Testing to date has shown that additive requirements for iso-butanol blended gasoline are essentially the same as for ethanol blended gasoline. This can be seen in the IVD data presented in **Section 5.1.1**, where the tests were run at typical level of detergent, 1.1x LAC.

5.3. Potential Impacts during Fuel Use

5.3.1. Iso-butanol Impact on Air Quality

Any projected impacts of iso-butanol on air quality will need to be assessed based on completion of emissions studies undertaken as part of this multimedia assessment.

5.3.2. Exhaust Emissions

The vehicle fleet trial discussed in **Section 5.1.1** also included emissions and fuel economy testing. Following Phase 2 of the fleet test the vehicles were fueled on 11.5% iso-butanol gasoline blend and driven for a few weeks in normal operation until emissions testing could be scheduled. The standard Federal Test Procedure (FTP) and the highway driving cycle emissions and fuel economy tests were performed using an 11.5 volume % iso-butanol blend and the corresponding all hydrocarbon base gasoline. **Table 5-6** and **Table 5-7** show the respective results as percentage changes from the base fuel. The dynamometer load setting for vehicle 4FO1 was lower, about 20%, than standard for this vehicle when testing both fuels. This difference does not influence the

results because the load conditions were the same for both fuels that were compared. On an absolute basis the FTP emissions and fuel economy will not correspond to the exact FTP protocol. For this small fleet, statistically significant fleet average reductions of total hydrocarbon emissions were observed for both FTP and highway cycle tests. These results are in accord with expectations of a general reduction of THC emissions when oxygenates are present in gasoline. No other emissions changes were statistically significant. Statistically significant fleet average reductions in fuel economy were observed for both the FTP and highway cycle tests. The magnitude of the reductions was approximately in accord with the lower energy content of the fuel blend (2.7%).

Table 5-6. FTP Emissions and Fuel Economy Results*

Vehicle	CO % Change ± 95% CI	THC % Change ± 95% CI	NO _x % Change ± 95% CI	FE % Change ± 95% CI
4CHY2	13 ± 24	11.0 ± 6.0	6.5 ± 20	1.6 ± 2.2
4FO1**	26 ± 20	4.6 ± 20	-5.1 ± 23	3.2 ± 1.6
4TO1	-1 ± 28	11 ± 8.3	5.8 ± 21	5.0 ± 1.7
4CV1	-6 ± 29	5.1 ± 15	-5.8 ± 23	2.4 ± 2.4
Fleet	9 ± 24	9.2 ± 5.0	0.5 ± 11	3.2 ± 0.97

* Statistically significant differences in **bold**. Positive numbers are reductions compared to hydrocarbon base fuel. Percentages are based on g/mi for emissions and mi/gal for fuel economy.
 ** Dynamometer settings lower than standard for both fuels.

Table 5-7. Highway Emissions and Fuel Economy Results*

Vehicle	CO % Change ± 95% CI	THC % Change ± 95% CI	NO _x % Change ± 95% CI	FE % Change ± 95% CI
4CHY2	8 ± 15	10.2 ± 6.1	1.4 ± 22	1.8 ± 1.9
4FO1**	13 ± 15	3.6 ± 17	-4.9 ± 24	2.9 ± 1.5
4TO1	-3.3 ± 17	10 ± 8.4	4.8 ± 21	4.3 ± 1.6
4CV1	3 ± 18	2.6 ± 15	-21 ± 27	2.2 ± 2.1
Fleet	5.4 ± 8.2	7.9 ± 4.9	-4.7 ± 12	2.9 ± 0.86

* Statistically significant differences in **bold**. Positive numbers are reductions compared to hydrocarbon base fuel. Percentages are based on g/mi for emissions and mi/gal for fuel economy.
 ** Dynamometer settings lower than standard for both fuels.

Use of blends of iso-butanol in gasoline up to 11.5vol% showed no gross negative impacts in emissions. Fuel economy reduction was within the range expected for the lower energy content of the blend.

- **Perform exhaust emissions testing for 16vol% iso-butanol blends in California reformulated gasoline versus 10vol% ethanol blends in California reformulated gasoline to determine whether any adjustments to the Predictive Model are required to model 16vol% iso-butanol blends. Determine impact on Ozone Reactivity and Potency-weighted Toxics emissions.**

5.3.3. Effects on Toxic Air Pollutants

The impact of iso-butanol on toxic air pollutant emissions from motor vehicles will be evaluated per Federal EPA CAA Section 211(b) requirements for fuel additive registration. The Tier I vehicle emissions evaluation is fully defined in 40CFR 79.52, and requires the identification of combustion emissions. These include hydrocarbons with twelve 12 or fewer carbon atoms. Aldehydes and ketones with eight or fewer carbon atoms, and ethers and alcohols with six or fewer carbons atoms. This evaluation needs to be conducted both with and without exhaust aftertreatment.

This evaluation has not been completed, and it is currently a knowledge gap that will be addressed in the Tier II report. The toxic emissions for a CARB gasoline blended with 16vol% iso-butanol needs to be compared to a CARB gasoline blended with 10vol% ethanol.

- **Determine toxic air pollutants in automotive exhaust using EPA Section 211(b) methodology with California reformulated gasolines blended with 10vol% ethanol and with 16vol% iso-butanol.**

5.3.4. Evaporative Emissions

The impact of iso-butanol on vehicle evaporative emissions has not been determined. No substantial change is anticipated for 16vol% iso-butanol blends compared to 10vol% ethanol blends at the same RVP.

- **Determine the composition of the headspace of 10vol% ethanol and 16vol% iso-butanol blended California reformulated gasoline blends over a range of temperatures and calculate differences in potency-weighted toxics and reactivity. Headspace samples to be generated using the methodology attached as Appendix F¹⁹.**

The impact of iso-butanol on permeation emissions from vehicle fuel systems is currently being determined. A first phase of testing has recently been completed with data evaluation currently in progress. The program compared the permeation impact of 9vol% iso-butanol blends against that of a 6vol% ethanol blend on vehicle fuel systems from three high volume models. In addition, a 50:50 mix blend of the 9vol% Isobutanol and 6vol% blends were also tested to examine the impact of mixing the oxygenates. Test

¹⁹ This methodology was used by ARB for work published on Ethanol Fate, Transport, and Health Risk Analysis and published as Appendix 7 to Analysis of the Air Quality Impacts of the Use of Ethanol in Gasoline on October 4, 1999 (<http://www.arb.ca.gov/fuels/gasoline/ethanol/ethfate/ethfate.htm>)

fuels were blended to meet California CARB phase 3 specifications and the testing followed the CRC E-65^{20,21} protocol used to determine ethanol’s fuel permeation.

Phase 2 of the permeation study will repeat the process evaluating 7 vehicle fuel systems on 16 vol% Isobutanol, 10 vol% Ethanol and a 50:50 blend mix. The goal of phase 2 is to demonstrate no-harm from the use of 16 vol% Isobutanol in CARB Gasoline. The Scope of Work document for the Phase 2 study is attached to this document as **Appendix D**.

- **Determine permeation emissions of 16vol% iso-butanol relative to 10vol% ethanol in CARB gasoline per the program described in Appendix D.**

5.3.5. Iso-butanol Impact on Drinking Water Quality

The perceptibility of iso-butanol in drinking water has recently been evaluated in a human-panel study conducted by TRC, Inc. (2007). The study measured the human odor detection and taste detection thresholds of neat butanol in drinking water using a standard protocol identical to that previously used to evaluate MTBE (TRC, 1993).

In the above study the odor detection threshold for neat iso-butanol is reported to be 29ppm. The taste detection threshold is reported to be 9ppm. These values are more than 700 times and more than 200 times greater than the respective odor and taste detection thresholds reported for MTBE.

Odor detection threshold values for neat ethanol in drinking water are reported to range from 0.2 ppm to 100 ppm²². Taste detection threshold data for neat ethanol in drinking water were not located in the published literature.

Iso-butanol is substantially less potent than MTBE in its odor and taste properties and falls within the reported range of odor threshold values for ethanol.

	OD	OR
Conventional Gasoline	0.94	1.24
B10	0.66	0.86
E10	0.34	0.50

Table 5-8. Odor Detection and Odor Recognition Thresholds

Odor threshold values for finished fuels, including B10 and E10, were also compared in the human-panel study conducted by TRC, Inc (2007). Mean odor detection (OD) and recognition (OR) threshold values (ppm) for conventional gasoline, B10, and E10 are listed **Table 5-8**.

²⁰ Haskew, H., Liberty, T.F. and McClement, D., “Fuel Permeation From Automotive Systems”, CRC Project No. E-65, **2004**.

²¹ Haskew, H., Liberty, T.F. and McClement, D., „Fuel Permeation from Automotive Systems: E0, E6, E10, E20 and E85“, CRC Project No. E65-3, **2006**.

²² ASTM, Compilation of Odor and Taste Threshold Values Data, Committee E-18, ASTM Data Series DS 48A, 1978.

6. Release Scenarios

6.1. Defining Release Scenarios

Fuel releases may occur during the production, transportation, storage, handling, distribution, and use of fuel-grade iso-butanol or gasoline blended with iso-butanol. In this chapter, a variety of potential fuel release scenarios are presented. These scenarios follow a life-cycle approach using examples as provided in the report on “Potential Scenarios for Ethanol-Containing Gasoline Released into Surface and Subsurface Waters”²³.

Figure 6-1 and **Figure 6-2** illustrate the life-cycle phases of bulk iso-butanol production, transportation, storage, and blending, as well as the distribution and use of the blended gasoline/iso-butanol fuel. The potential release scenarios during each phase are summarized in Table 6-1. Each scenario includes brief description of release assumptions, site characteristics, likelihood of occurrence, risk assessment issues, and risk management. The similarities between iso-butanol and ethanol, a reference fuel, are also listed for each release scenario.

6.2. Normal Releases

Iso-butanol will be biologically produced from grains, sugarcane, or cellulosic materials. The biomass pretreatment, fermentation, separation, and refining processes for fuel-grade iso-butanol production will be very comparable to those for ethanol. However, the microorganisms used in the production may be different species than those used to produce ethanol. Details on the production process are described in **Section 3.1**. Controls necessary for managing the organisms employed in the fermentation process are addressed in **Section 9.4**.

Production process impurities may be present in bulk fuel-grade iso-butanol. These will typically be generated as byproducts from fermentation and will generally consist of other three to five carbon alcohols. Unlike ethanol, fuel-grade iso-butanol does not require the addition of toxic or noxious denaturants to make it unfit for human oral consumption. Therefore, those harmful denaturant compounds associated with typical fuel ethanol releases may not be observed in soil and water impacted with bulk fuel-grade iso-butanol.

²³ Rice, D.W., S.E. Powers, and P.J.J. Alvarez. 1999 UCRL-AR-135949

6.3. Off-Normal Releases

6.3.1. Storage, transportation, and distribution of bulk fuel-grade iso-butanol

At the production plant, the refined bulk fuel-grade iso-butanol will typically be stored in large capacity, above ground storage tanks (ASTs). Because iso-butanol can be transported through pipelines, blending with gasoline at refineries is preferred. In this case, bulk iso-butanol transport to refineries would primarily be through marine cargo or railway tanker cars. The bulk iso-butanol will be stored in ASTs at refineries. It is also possible that terminal blending will be required in some locations, in which case, transportation modes will be identical to ethanol. Bulk iso-butanol would be transported to terminals through marine cargos, rail cars, and tanker trucks. The bulk iso-butanol would likewise be stored in ASTs at these facilities.

Releases may occur from these ASTs, associated AST piping, distribution pipelines, and the various transport vehicles.

6.3.2. Storage, transportation, and distribution of blended gasoline/iso-butanol fuel

Blended gasoline-iso-butanol fuel will be stored in ASTs at refineries, and possibly at terminals where and if it is blended at those facilities. From refineries, the blended fuel will be transported through pipelines to distribution terminals in the same manner as is done for gasoline fuel. Distribution of the blended fuel to retail sites will likewise be similar to current methods through tanker trucks. At the retail site, the fuel will be stored in underground storage tanks (UST), generally 10,000 and 20,000 gallons in volume, and eventually dispensed at the fueling pumps.

The transportation, storage and dispensing of blended gasoline-iso-butanol fuel will not be materially different from the way ethanol fuel is handled. This includes releases from ASTs, associated AST piping, distribution pipelines, tanker trucks, USTs, and dispensing equipment. These releases of iso-butanol fuel can impact the environment, particularly soil and groundwater.

Aromatic hydrocarbons: benzene, toluene, ethylbenzene, and xylene isomers (BTEX) are common groundwater pollutants associated with the petroleum hydrocarbon releases. Iso-butanol blended with gasoline will contain these constituents. Groundwater modeling studies indicated that the rapid ethanol biodegradation in the subsurface may slow down BTEX biodegradation and, therefore, result in a prolonged dissolved BTEX plumes. It is expected that iso-butanol may also impact the environmental fate of BTEX compounds, but to a lesser degree than ethanol. Ongoing environmental fate studies (see Appendix E: Environmental Fate Studies Scope of Work) are examining the effects of iso-butanol on BTEX biodegradation and comparing to the effects of ethanol.

- **Complete environmental environmental fate studies currently in progress (described in Appendix E).**

6.4. Use

During the use of iso-butanol fuel in vehicles and watercraft, releases to the environment may occur through two types of emissions -- exhaust and evaporative. Exhaust emissions are the uncombusted iso-butanol fuel exiting the tailpipe, and the evaporative emissions are those volatilized and leaked from the vehicle/watercraft fuel trains. The emissions from an individual vehicle or watercraft are relatively low. The extent of the releases from all the vehicles or watercraft in California, however, may be more significant but scattered. The characteristics of the emission releases associated with the use of iso-butanol fuel are discussed in **Section 5.3**.

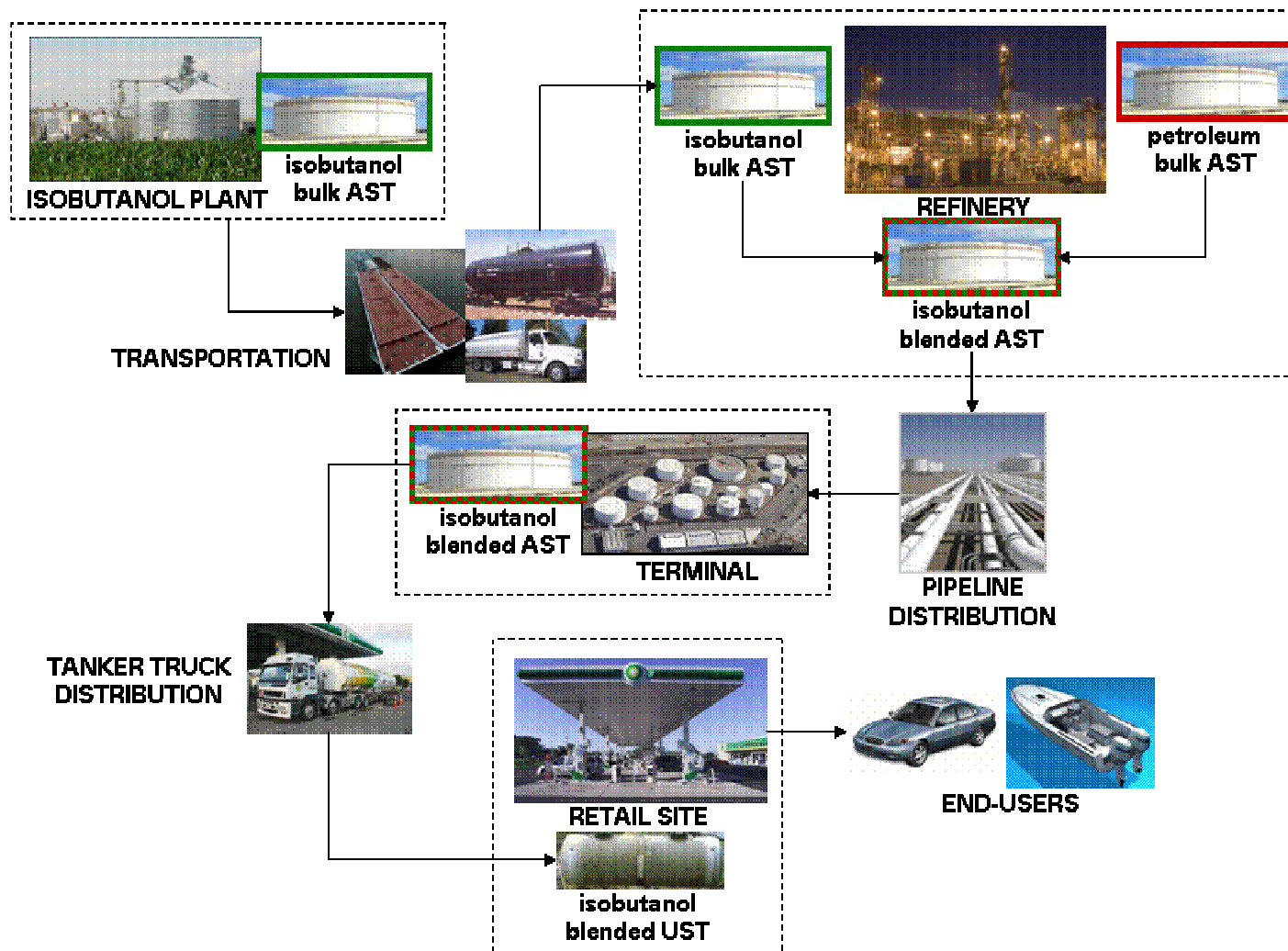


Figure 6-1. Lifecycle Use of Iso-butanol - Refinery Blending

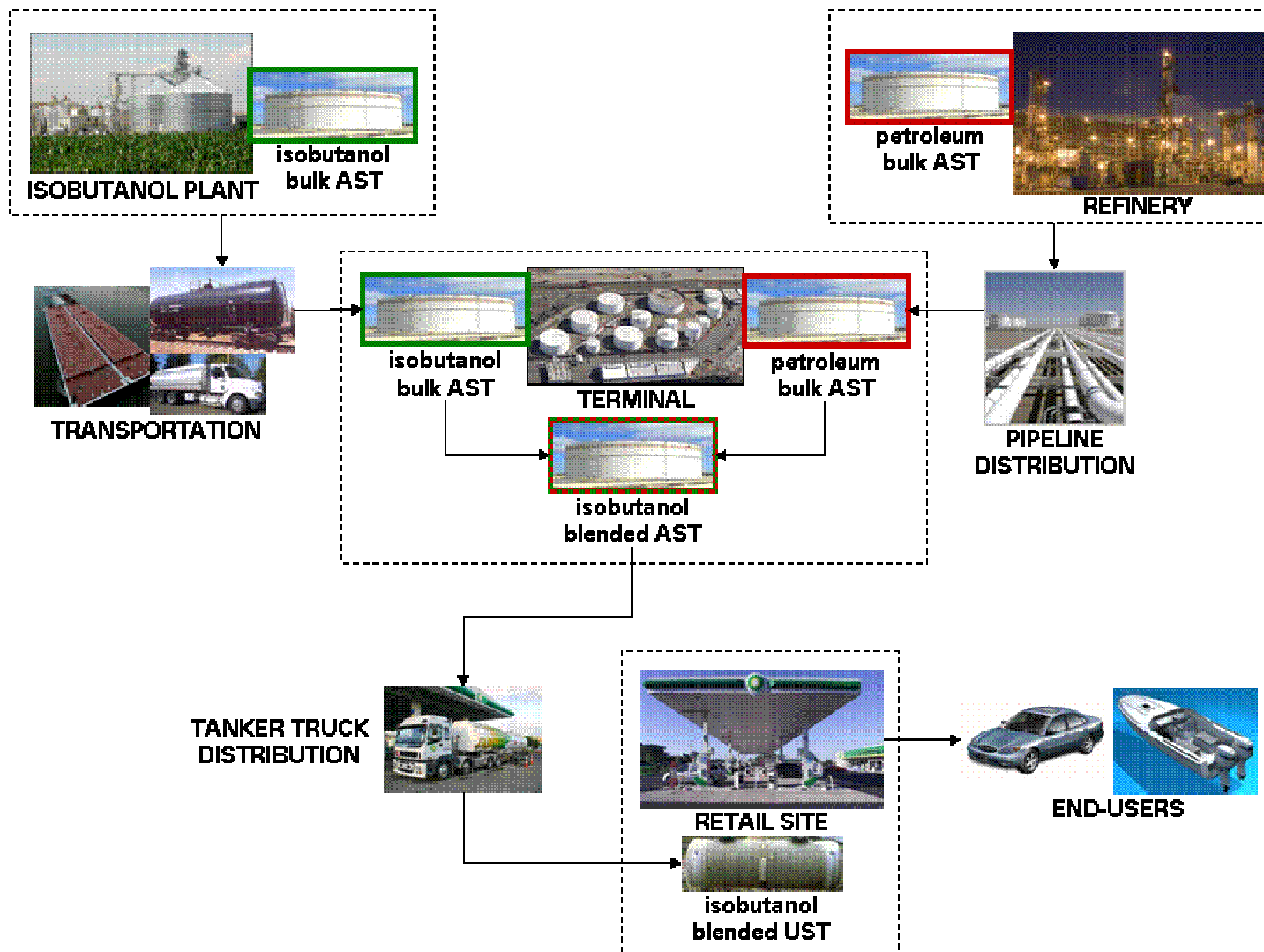


Figure 6-2. Life-cycle use of butanol - terminal blending

Table 6-1. Lifecycle Assessment of Iso-butanol Releases

Scenarios	Release Assumptions	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options	Similarity to Ethanol
Production						
Release of bulk iso-butanol from an AST at a production plant.	Large volume (>30,000 gal) iso-butanol releases to soils and groundwater from an AST or associated piping at an iso-butanol production plant.	Assumes bulk iso-butanol release into relatively pristine subsurface conditions. Petroleum hydrocarbons are assumed to be historically absent.	Small likelihood of occurrence. California currently has few biofuel production facilities. This scenario represents a release that could occur only once biomass iso-butanol production facilities are constructed in the state in the future.	Toxicity to ecological receptors in direct contact with the release. Any iso-butanol that infiltrates to groundwater will act as a source of groundwater contamination. Existing biological characteristics data indicate that iso-butanol may be relatively rapidly attenuated in the subsurface environment.	Engineered containment to control potential release, such as AST leak detection system. Spill prevention and containment contingency (SPCC) plans typically in place.	Release scenario identical to fuel ethanol. Attenuation similar. Toxicity may vary.
Storage, Transportation, and Distribution						
Release during bulk iso-butanol transport by rail or highway (from production plant to refinery or distribution terminal)	Assumes that a rupture of a rail tank car or tanker truck releases a large volume of bulk iso-butanol (10,000 – 30,000 gal) to soil and groundwater or surface water. While iso-butanol is highly soluble, it will tend to distribute near the water surface because it is less dense than water.	Assumes bulk iso-butanol release into relatively pristine conditions. Petroleum hydrocarbons are assumed to be historically absent.	Moderate likelihood of occurrence. Because California may have few iso-butanol production facilities, most iso-butanol used will initially be imported into the state.	Toxicity to ecological receptors in direct contact with the release. Any iso-butanol that infiltrates to groundwater will act as a source of groundwater contamination. Potential to impact surface aquatic ecosystem. It is likely that volatilization as well as biodegradation will be important mechanisms in the rapid attenuation of the bulk iso-butanol.	Rail car and truck tanker releases are typically treated as an emergency response action and generally require no long-term monitoring.	Release scenario identical to fuel ethanol. Attenuation similar but reduced in surface water compared to ethanol (lower solubility). Toxicity may vary.

Table 6-1. Lifecycle Assessment of Iso-butanol Releases (Cont.)

Scenarios	Release Assumptions	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options	Similarity to Ethanol
Storage, Transportation, and Distribution (Cont.)						
Release during bulk iso-butanol transport by marine cargo tanker (from production plant to refinery or distribution terminal)	Assumes that a rupture of a marine tanker ship releases a large volume of bulk iso-butanol (>100,000 gal) into marine surface waters. While iso-butanol is highly soluble, it will tend to distribute near the water surface because it is less dense than water.	Assumes a bulk iso-butanol release into the near-shore coastal marine environment.	Low likelihood of occurrence. However, the shipment of iso-butanol as marine cargo will increase because refineries and distribution hubs will prefer receiving larger quantities to minimize handling rail cars and tanker trucks.	Toxicity to ecological receptors in direct contact with the release. Potential to impact surface aquatic ecosystem. It is likely that volatilization, dispersion, and dilution as well as biodegradation will be important mechanisms in the rapid attenuation of the bulk iso-butanol.	Requires bulk iso-butanol to be shipped in marine tankers with release prevention constructions.	Release scenario identical to fuel ethanol. Attenuation similar but reduced compared to ethanol (lower solubility). Toxicity may vary.
Release of bulk or blended iso-butanol from an AST (or associated piping) at a refinery	Large volume (> 20,000 gal) bulk iso-butanol or blended fuel release from an AST or associated piping to soil and groundwater at a petroleum refinery site.	Fuel hydrocarbons are assumed to be historically present and may be present as free product trapped in the subsurface.	Moderate likelihood of occurrence.	Toxicity to ecological receptors in direct contact with the release. The iso-butanol is assumed to interact with soils impacted with existing fuel hydrocarbons (ongoing environmental fate testing to examine - see Appendix E). Previously immobile hydrocarbons may now be mobilized to groundwater. An existing fuel hydrocarbon groundwater plume may be expanded.	Engineered containment to control potential release, such as AST leak detection system. Spill prevention and containment contingency (SPCC) plans typically in place. Manage the location of iso-butanol ASTs to avoid known areas of petroleum hydrocarbon releases. Remediate the fuel hydrocarbon releases.	Similar to ethanol release scenario at distribution terminals. Attenuation similar. Toxicity may vary.

Table 6-1. Lifecycle Assessment of Iso-butanol Releases (Cont.)

Scenarios	Release Assumptions	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options	Similarity to Ethanol
<i>Storage, Transportation, and Distribution (Cont.)</i>						
Release of bulk or blended iso-butanol from an AST (or associated piping) at a distribution terminal	Large volume (> 20,000 gal) bulk iso-butanol or blended fuel release from an AST or associated piping to soil and groundwater at a distribution terminal.	Fuel hydrocarbons are assumed to be historically present and may be present as free product trapped in the subsurface.	Moderate likelihood of occurrence.	Toxicity to ecological receptors in direct contact with the release. The iso-butanol is assumed to interact with soils impacted with existing fuel hydrocarbons (ongoing environmental fate testing to examine - see Appendix E). Previously immobile hydrocarbons may now be mobilized to groundwater. An existing fuel hydrocarbon groundwater plume may be expanded.	Engineered containment to control potential release, such as AST leak detection system. Spill prevention and containment contingency (SPCC) plans typically in place. Manage the location of iso-butanol ASTs to avoid known areas of petroleum hydrocarbon releases. Remediate the fuel hydrocarbon releases.	Release scenario identical to fuel ethanol. Attenuation similar. Toxicity may vary.
Release of blended iso-butanol during transportation through a pipeline (from refinery to distribution terminal)	Assumes a rupture of a pipeline releases a medium volume (>10,000 gal) of blended iso-butanol fuel to soil and groundwater.	Assumes blended iso-butanol fuel release into relatively pristine subsurface conditions. Petroleum hydrocarbons are assumed to be historically absent.	Moderate likelihood of occurrence because blended iso-butanol can be transported through pipeline in California.	Toxicity to ecological receptors in direct contact with the release. Any blended iso-butanol fuel that infiltrates to groundwater will act as a source of groundwater contamination. Existing biological characteristics data indicate that iso-butanol may be relatively rapidly attenuated in the subsurface environment.	Engineered containment to control potential release, such as pipeline leak detection system.	Release scenario unique to blended iso-butanol fuel. Attenuation similar to similar ethanol releases. Toxicity may vary.

Table 6-1. Lifecycle Assessment of Iso-butanol Releases (Cont.)

Scenarios	Release Assumptions	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options	Similarity to Ethanol
<i>Storage, Transportation, and Distribution (Cont.)</i>						
Release of blended iso-butanol during tanker truck transport (from a distribution terminal to retail sites)	Assumes that blended iso-butanol is transported by tanker truck to a retail site. Assumes a large volume (~5,000 gal) is released to soil and groundwater or surface water bodies. Potential for a release to streets and urban storm drains.	Assumes release occurs onto roadside environments where fuel hydrocarbons are historically absent.	Moderate likelihood of occurrence.	Toxicity to ecological receptors in direct contact with the release. Any blended iso-butanol fuel that infiltrates to groundwater will act as a source of groundwater contamination. Concentrations of BTEX in groundwater may initially be somewhat higher than for standard gasoline spill (cosolvency examined in ongoing environmental fate testing - see Appendix E).	Truck tanker releases are typically treated as an emergency response action and generally require no long-term monitoring.	Release scenario identical to fuel ethanol. Attenuation similar. Toxicity may vary.
Release of blended iso-butanol at a retail site during UST filling	Assumes that blended iso-butanol fuel is spilled during UST filling at a gas station. A low-volume (< 50 gal) is released to soil and groundwater. Potential for a release to streets and urban storm drains.	Assumes a small mass of petroleum hydrocarbons historically present in the subsurface and may be present as free product trapped in the subsurface.	A likely and common release scenario.	Toxicity to ecological receptors in direct contact with the release. The iso-butanol is assumed to interact with soils contaminated with existing petroleum hydrocarbons (ongoing environmental fate testing to examine - see Appendix E). Previously immobile hydrocarbons may now be mobilized to groundwater. An existing fuel hydrocarbon groundwater plume may be expanded.	UST over-fill buckets associated with upgraded USTs should minimize these releases.	Release scenario identical to fuel ethanol. Attenuation similar. Toxicity may vary.

Table 6-1. Lifecycle Assessment of Iso-butanol Releases (Cont.)

Scenarios	Release Assumptions	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options	Similarity to Ethanol
<i>Storage, Transportation, and Distribution (Cont.)</i>						
Release of blended iso-butanol at a retail site from a small UST puncture	Assumes a small puncture of the UST or associated piping resulting in a low volume release of blended iso-butanol fuel (<3 gal per day).	Assumes release may occur into subsurface environments with or without historic hydrocarbon fuel contamination.	A likely and common release scenario. Evaluation will be important to estimate potential impacts to groundwater resources.	Potential to release a large cumulative mass of blended iso-butanol fuel due to the large number of USTs in operation and the potential for small leaks to go undetected. The iso-butanol is assumed to interact with soils contaminated with existing petroleum hydrocarbons (ongoing environmental fate testing to examine - see Appendix E).	Current requirement for USTs to use double-walled containment reduce the likelihood of this scenario.	Release scenario identical to fuel ethanol. Attenuation similar.
Release of blended iso-butanol at a retail site from large UST puncture	Assumes a large puncture of the UST or associated piping resulting in a high volume release of blended iso-butanol fuel (~<10 gal per day).	Assumes release may occur into subsurface environments with or without historic fuel hydrocarbon contamination.	Moderate likelihood of occurrence.	Typically, larger UST leaks are rapidly detected, and corrective action is initiated. The iso-butanol is assumed to interact with soils contaminated with existing petroleum hydrocarbons (ongoing environmental fate testing to examine - see Appendix E). Previously immobile hydrocarbons may now be mobilized to groundwater. An existing fuel hydrocarbon groundwater plume may be expanded.	Current requirement for USTs to use double-walled containment reduce the likelihood of this scenario.	Release scenario identical to fuel ethanol. Attenuation similar.

Table 6-1. Lifecycle Assessment of Iso-butanol Releases (Cont.)

Scenarios	Release Assumptions	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options	Similarity to Ethanol
<i>Storage, Transportation, and Distribution (Cont.)</i>						
Use						
Release of blended iso-butanol from watercraft emissions into surface water bodies.	Assumes very small volume of fuel released through exhaust as uncombusted free product.	Assumes pristine freshwater lakes and rivers	A likely and common release scenario	The biodegradation and volatilization of iso-butanol in surface waters is expected to be rapid. Small increases in nutrient loading and decreases in dissolved oxygen concentrations may occur.	Increase engine combustion efficiency.	Release scenario identical to fuel ethanol. Attenuation similar.
Tailpipe emissions from vehicle or watercraft (using blended iso-butanol) to surface soils and waters.	Assumes iso-butanol vapors and combustion products will partition into atmospheric moisture.	Assumes widespread non-point source deposition with various amounts of recharge to groundwater and runoff to surface water bodies.	A likely and common release scenario.	Iso-butanol emissions preferentially partition into water and will be expected to rainout. The biodegradation of iso-butanol in surface waters is expected to be rapid.		Release scenario identical to fuel ethanol. Attenuation similar.

7. Environmental Transport and Fate of Iso-butanol

According to the risk assessment report (included in **Appendix B: US EPA Profiler Estimation**) published under the framework of Screening Information Data Set (SIDS) program by Organization for Economic Cooperation and Development (OECD), iso-butanol is manufactured at 16 plant sites in the United States of America (all using chemical-based processes) and is considered a high production volume chemical. This report included the current state of knowledge of iso-butanol from an extensive literature review sponsored by the US EPA, Risk Assessment Division. The SIDS data can be used to "screen" the chemicals and set priorities for further testing or risk assessment/management activities. The US EPA considers the OECD/SIDS testing program to be an integral part of the U.S. domestic chemical testing program under TSCA.

The OECD SIDS report concluded that *iso-butanol is currently of low priority for further [environmental] work due to its low hazard profile* and that *these [human health] hazards do not warrant further work as they are related to reversible, transient effects that may become evident only at high exposure levels.*

In addition, the US EPA PBT Profiler is used to predict the potential of iso-butanol to persist or bioaccumulate in the environment, and its toxicity to human health and the environment. The PBT Profiler is a research tool to identify chemicals that may need further evaluation for potential persistence, bioaccumulation, and toxicity. The details of the PBT Profiler estimation for iso-butanol are also included in **Appendix B: US EPA Profiler Estimation**

The EPA PBT profiler estimation verified that *iso-butanol is estimated not to be persistent in the environment, iso-butanol is not expected to bioaccumulate, and iso-butanol is not chronically toxic to fish.*

The data from the OECD SIDS report and the PBT profiler are presented in this section to discuss the iso-butanol environmental fate, transport, and exposure.

7.1. A Multimedia Framework for Fate, Transport and Exposure

Iso-butanol may be present in the environment through releases from waste streams during manufacturing and processing, through spills during bulk liquid storage and transportation, as well as through leaks during the distribution and use of gasoline-iso-butanol fuel blends. Iso-butanol is also a naturally occurring substance associated with the natural fermentation of carbohydrates, fruits, animal wastes, and microbes, and as a plant volatile.

The primary routes of environmental releases are from surface spills and subsurface leaks. In the case of surface spills, iso-butanol can be volatilized into the atmosphere, adsorbed onto soil, and dissolved in water. When released into the subsurface, iso-butanol can be absorbed onto soil and potentially dissolved in groundwater. Once exposed in the atmosphere, iso-butanol can be degraded through photochemical reactions and aerobic biodegradation. Iso-butanol can also be biodegraded in the unsaturated soil (aerobically), surface water (aerobically or anaerobically), and groundwater (typically, anaerobically but aerobically as well).

Human exposure to iso-butanol may occur in the work environment, while using iso-butanol fuel, or by contact with soil or water impacted with iso-butanol. Workplace exposure during manufacture, storage, transportation, and handling of iso-butanol is limited based on those processes being enclosed and mitigated through design of equipment, process control equipment, administrative controls, or personal protective equipment. The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for iso-butanol is 100 ppm (300 mg/m³) as an 8-hour time-weighted average (TWA) concentration²⁴. The OSHA PEL for ethanol is 1,000 ppm as an 8-hour TWA. Since iso-butanol is flammable at a concentration range of 1.7% to 10.6%, precautions are taken to limit open vapor concentrations in the workplace.

Consumer exposure to iso-butanol as a fuel component during the dispensing and use is also limited and is similar to the exposure posed by ethanol fuel or gasoline. Current dispensing equipment should mitigate any liquid exposures to the consumer in manners identical to ethanol-based fuels or gasoline. Fuel dispenser vapor recovery units should likewise mitigate emission exposures while dispensing.

Iso-butanol and other gasoline-iso-butanol fuel components can impact soil and groundwater from fuel releases. While immediate exposures to the impacted soil should be limited in frequency and duration, long-term exposure may be possible if the gasoline-iso-butanol fuel components impact and dissolve in groundwater. People who use the contaminated groundwater may thus be exposed.

7.2. Data Needs for Multimedia Transport

A series of physical, chemical, and biological processes control the fate and transport of iso-butanol in the environment. The major physical processes include partitioning between water and fuel, volatilization from water and fuel, as well as sorption to soil. A multimedia transport study requires physical-chemical properties, photo-oxidation rates, and biodegradation data to calculate the distribution of the iso-butanol mass in air, water, soil, and sediment media and its persistence in the environment if a fuel release occurs. Table 7-1 lists the physical-chemical properties of iso-butanol and ethanol for comparison. The environmental behavior of iso-butanol may also impact the fate of other fuel hydrocarbons in a gasoline-iso-butanol fuel blend. The effects of iso-butanol on the partitioning and biodegradation of petroleum hydrocarbons are also being evaluated and are discussed in this report.

Iso-butanol may be rapidly photodegraded (oxidized) in the atmosphere, but is more stable in soil and water. Biodegradation is the dominating process of mass reduction in the environment for petroleum hydrocarbons and ethanol. The susceptibility of iso-butanol to biodegradation is an important characteristic in estimating the fate and transport of iso-butanol in the environment. Field measurement of iso-butanol in fuel impacted aquifers appears not available yet. The only field data related to iso-butanol is a citation is the Hazardous Substances Data Bank (HSDB) that iso-butanol has been observed at levels ranging between 142 and 652 ppm in the Hyashida River, which contained effluents from the

²⁴ 29 CFR 1910.1000, Table Z-1

leather industry²⁵. The evaluation of the fate and transport of iso-butanol fuel in the environment is limited to model estimation and laboratory research. Currently, environmental fate studies examining the biodegradability, mechanistic pathways, and sorption and partitioning characteristics are being conducted by Butamax™ Advanced Biofuels (see **Appendix E**).

Table 7-1. Physical-Chemical Properties of Iso-butanol and Ethanol

Property	Iso-butanol ^a	Ethanol ^b
Molecular weight	74	46
Melting point (°C)	-108	-114.1 ^c
Boiling point (°C)	108	78.5
Relative density	0.806 at 15°C	0.79
Vapor pressure (hPa) 25°C	13.9	65 to 75.3
Water solubility (g/L) at 25°C	85	miscible
Partition coefficient n-octanol/water (log K _{ow})	0.79	-0.31 ^c
Henry's law constant (atm m ³ /mol)	1.19 x10 ⁻⁵	5.13 to 8.77 x10 ⁻⁶ ^{b, d}

^a Iso-butanol data obtained from OECD SIDS report

^b Ethanol data obtained from Glenn Ulrich, 1999

^c Data obtained from California EPA

^d Data obtained from Ueberfeld, 2001

7.3. Abiotic Properties Influencing Iso-butanol Migration in Environmental Media

7.3.1. Volatilization of Iso-butanol

According to the US EPA 2004 User's Guide for Evaluating Subsurface Vapor Intrusion into Buildings, chemicals with a Henry's Law constant greater than 1.0×10^{-5} atm-m³/mol are categorized as volatile. The Henry's Law constant for iso-butanol is calculated to be 1.19×10^{-5} atm-m³/mol and is therefore considered slightly to moderately volatile based on this definition. Ethanol has a Henry's Law constant of 5.13 to 8.77×10^{-6} atm-m³/mol, and is considered not volatile. By comparison, many gasoline components are considered volatile, including benzene which has a Henry's Law constant of 5.56×10^{-3} atm-m³/mol. Similar to ethanol, iso-butanol is less likely to volatilize from water into the atmosphere. The atmospheric partial pressure of iso-butanol (13.9 hPa at 25°C) is five times lower than ethanol (65 to 75.3 hPa), thus the evaporative emissions of iso-butanol from non-aqueous liquid fuel in direct contact with air should be much less significant than those of ethanol. The OECD SIDS report included a model estimation of iso-butanol volatilization from a surface water bodies and concluded that *volatilization is a minor transport and removal process of iso-butanol from surface waters*.

²⁵ U.S. EPA, 1986

7.3.2. Partitioning of Iso-butanol between Water and Fuel

The solubility of iso-butanol is 85 g/L and its n-octanol/water partition coefficient is 0.79 (log value). Ethanol is miscible in water and has an n-octanol/water partition coefficient of -0.31 (log value). Therefore, iso-butanol is an order of magnitude less soluble in water than ethanol. If a bulk iso-butanol spill enters water, high dissolved iso-butanol concentrations can be expected, but it should only be a fraction of the concentration of ethanol which would be observed from a bulk ethanol release. Ethanol concentrations exceeding 10,000 ppm (1 vol%) were observed after a bulk fuel-grade ethanol release at a terminal (Buscheck 2003). If this scenario had been a bulk iso-butanol release instead of ethanol, the expected iso-butanol concentration would have been expected to be an order of magnitude lower given the lower solubility (partial vs. complete miscibility) and n-octanol/water partition coefficient (order of magnitude difference) between iso-butanol and ethanol, respectively.

Because the gasoline-iso-butanol fuel mixture may contain 16% by volume, relatively high iso-butanol concentrations are also likely to be observed in groundwater from a fuel blend release. In a static system, where the fuel blend is allowed to equilibrate with water, the concentration of a soluble compound can be calculated using a partitioning mass balance model, such as the Rixey model developed at the University of Houston. The Rixey model is used to estimate the dissolved iso-butanol and ethanol concentrations from releases of a 16% v/v iso-butanol fuel and a 10% v/v ethanol fuel, respectively. Figure 7-1 shows the predicted equilibrium alcohol concentrations as functions of the total hydrocarbon concentration in soil. The details of the simulation are in **Appendix C: Equilibrium Dissolved Iso-butanol/Ethanol Concentration Estimation**. The dissolved iso-butanol concentration is slightly greater than ethanol when the total soil hydrocarbon concentration is less than 15 g/kg. As the total soil hydrocarbon concentration increases, the iso-butanol concentration starts to reach an asymptotic value at its selective solubility while the ethanol concentration continues increasing.

A typical UST release of a blended fuel may result in a total soil hydrocarbon concentration of less than 10 g/kg. The calculated equilibrium iso-butanol and ethanol concentrations in water are around 8,000 mg/L. Experience indicates that the theoretical aqueous concentrations could be an order of magnitude higher than those that would actually be observed in the field measurement due to water dilution by natural groundwater flow (non-static conditions). The rate of alcohol diffusion from gasoline may also limit its dissolution into water. Therefore, the dissolved iso-butanol concentration from a gasoline-iso-butanol blend is unlikely to exceed 1,000 mg/L.

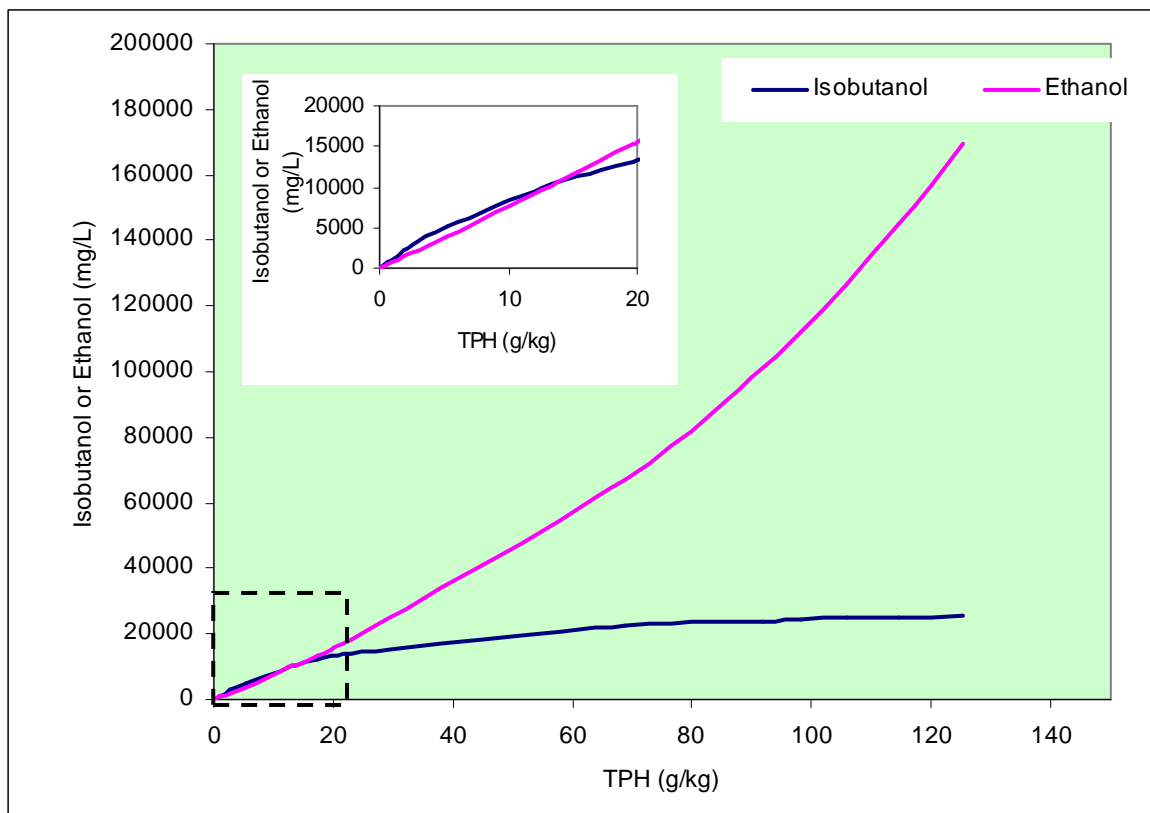


Figure 7-1 Equilibrium dissolved alcohol concentration in subsurface water

7.3.3. Cosolvency

The presence of ethanol in water can significantly increase the solubility of petroleum hydrocarbons. The phenomenon is referred as ethanol cosolvency. Laboratory batch equilibrium experiments on this topic concluded the following.

“Benzene, Toluene, Xylenes and other hydrocarbon concentrations can be significantly enhanced when ethanol concentrations in the aqueous phase are greater than 10% by volume. Benzene is enhanced by a factor of 1.2 at 10% v/v ethanol. Enhancements increase in proportion to ethanol concentration and are much greater for lower solubility compounds (e.g., enhancement for 1,2,4-trimethylbenzene >> benzene). These results are also consistent with previous studies (Heerman and Powers, 1998).”²⁶

Because of the high dissolved ethanol concentration threshold for noticeable cosolvency effects to occur, BTEX solubility may be enhanced only under the scenario of a bulk fuel ethanol release onto existing liquid non-aqueous phase hydrocarbons in soil. Spills of ethanol fuel blends (containing 10% v/v ethanol) are unlikely to produce sufficiently high dissolved ethanol concentrations to generate an obvious increase of petroleum hydrocarbon concentrations in water.

²⁶ Rixey 2005

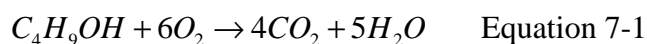
The solubility of iso-butanol is 85 g/L (10.5% by volume using a relative density of 0.806 g/cm³) and, therefore, the expected dissolved iso-butanol concentration may be orders of magnitude less than this theoretical maximum of 10.5% v/v, even from a bulk iso-butanol release. Based on comparison to the threshold level for ethanol (Rixey, 2005), the lower expected dissolved iso-butanol concentration is unlikely to materially enhance petroleum hydrocarbon solubility. Therefore, cosolvency appears not to be a concern for iso-butanol. However, a laboratory batch equilibrium test will be conducted to verify this speculation (see **Appendix E**).

7.4. Aerobic and Anaerobic Biodegradation of Iso-butanol

It is well documented that the biodegradation of hydrocarbons by natural microorganism is the primary mechanism for the natural attenuation of fuel spills in aquifers. The majority of the hydrocarbons, such as BTEX and alcohols, can be readily biodegraded under various oxidative-reductive (redox) conditions. This includes aerobic (oxygenated) environments as well as reductive environments (nitrate reducing, iron reducing, sulfate reducing, methanogenic, etc. conditions).

The aerobic iso-butanol biodegradation has been reported in several tests that were conducted following specific US or OECD test guidelines. The aerobic biodegradability of iso-butanol is calculated from either the consumption of oxygen (biochemical oxygen demand decrease) or the mass reduction of test substrate during a standard time frame. The stoichiometric biochemical equation of iso-butanol aerobic biodegradation is shown in

$C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$ **Equation 7-1.** The theoretical oxygen demand of iso-butanol is 2.59 mg O₂ per mg iso-butanol.



For reference, the corresponding aerobic biodegradation equation is given as

$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ **Equation 7-2.** The theoretical oxygen demand of ethanol is 2.09 mg O₂ per mg ethanol.

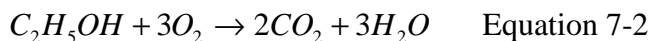


Table 7-2 summarizes the aerobic iso-butanol biodegradation tests that are presented in the OECD SIDS report. The OECD SIDS report concluded based on those published data *that these data indicate that iso-butanol is readily biodegradable*” (with the presence of oxygen).

Table 7-2. Summary of Iso-butanol Aerobic Biodegradation Studies ^a

Biodegradation percentage					Reference
5 days	10 days	15 days	20 days	30 days	
64%	73%	76%	72%		20-day BOD test, (Price et al.,1974)
14%		74%		74% (day 28)	OECD 301D Closed Bottle test (Waggy et al. 1994)
61%	75%			55%	30-day BOD test at 30°C(Dias and Alexander ,1971)
55%		73%		75%	OECD 301D Closed Bottle (Huels AG, 1978)

^a The table is compiled using data adopted from the OECD SIDS report.

Currently, ongoing studies conducted by Butamax™ Advanced Biofuels are evaluating the aerobic and anaerobic biodegradability of iso-butanol under various redox conditions. Furthermore, the biodegradation pathways, kinetics, identification of breakdown products, and microbial characteristics are being elucidated in these studies as well (see **Appendix E**).

7.5. The Estimation of Iso-butanol Transport in Environmental Media

The PBT profiler estimation (see Appendix B) concluded that ***“If released to the environment, iso-butanol is expected to be found predominantly in soil. It is also expected to be found in water, but not in sediment.”*** Also, ***“iso-butanol is estimated not to be persistent in environment.”*** A similar evaluation of ethanol concluded that “If released to the environment, ethanol is expected to be found predominantly in soil. It is also expected to be found in water, but not in sediment.” Also, “Ethanol is estimated not to be persistent in the environment.”

The OECD SIDS assessment conducted a fugacity modeling (Level III) estimation using the EPA EPIWIN (v.3.10) tool. Input parameters are summarized in Table 7-3. Equal releases to air, water, and soil were assumed. Media-specific half-lives were selected or calculated by the model. The model used a half-life of 37.3 hours for atmospheric photo-oxidation, while biodegradation half-lives in water, soil, and sediment were 360 h, 360 h, and 1440 h, respectively. Biodegradation half-lives were selected by the model based on the biodegradation sub-models within EPIWIN (v.3.10). All other parameters used were the model default values. The results support the above conclusions regarding the movement of iso-butanol in the environment with 4.85% distributing to air, 51.6% to water, 43.4% to soil and 0.091% to sediment.

The OECD SIDS assessment of ethanol using fugacity modeling (Level III) showed ethanol movement in the environment with 57% distributing to air, 34% to water, and 9% to soil (sediment was not evaluated). However, the release assumptions used a ratio of 1000:100:10 air:water:soil based on usage patterns and expected release scenarios as opposed to equal releases for iso-butanol.

Table 7-3. Fugacity Modeling Input Parameters For Iso-Butanol And Ethanol

Property	Iso-butanol	Ethanol ^a
Molecular Weight	74.12	46.07
Melting Point	-108°C	-114°C
Boiling Point	108°C	78.3°C
Water Solubility	85,000 mg/L	Fully miscible
Log K _{ow}	0.79	-0.31
Henry's Law Constant	1.19e-5 atm-m ³ /mol	2.52e-4 atm-m ³ /mol
Atmospheric Photo-Oxidation Half-Life	37.3 hours	203 hours
Biodegradation Half-Life in Water	360 hours	182 hours
Biodegradation Half-Life in Soil	360 hours	Not given
Biodegradation Half-Life in Sediment	1440 hours	210 hours

^a Data taken from Mackay et al, 1996 in OECD SIDS.

7.6. Impacts of Iso-butanol Biodegradation on Petroleum Hydrocarbon in Groundwater

Ethanol fuel release studies reported that the presence of ethanol in water could affect the environmental fate of petroleum hydrocarbons. Ethanol is more prone to biodegradation than petroleum hydrocarbons. Microorganisms may preferentially degrade ethanol relative to petroleum hydrocarbons in the subsurface. The rapid biodegradation of ethanol in groundwater may also consume electron acceptors which otherwise are used for the biodegradation of petroleum hydrocarbons. This secondary impact of ethanol on petroleum hydrocarbons was reported in several laboratory studies and field tests²⁷. Mathematical modeling estimated that the ethanol biodegradation can slow down BTEX biodegradation and, therefore, prolong the groundwater contamination plume from an ethanol fuel release²⁸.

Iso-butanol is also readily biodegradable in the subsurface, and may retard the biodegradation of petroleum hydrocarbons in groundwater. Very limited data are available to evaluate the impacts of iso-butanol biodegradation on the petroleum hydrocarbons fate and transport in the subsurface. However, ongoing environmental fate studies conducted by ButamaxTM Advanced Biofuels are evaluating the potential impacts of iso-butanol on the rates of petroleum hydrocarbon degradation (see **Appendix E**).

²⁷ Power 2001

²⁸ Mackay 2006

8. iso-Butanol Toxicity

8.1. Human/Ecological Risk

Human Health: A robust battery of mammalian toxicity studies indicates that iso-butanol has a very low hazard profile (OECD SIDS dossier). Test data indicate that human exposure to iso-butanol in neat or concentrated form may produce skin and eye irritation, and CNS depression. These potential health effects, typical of small-chain alcohols, are transient, reversible, and occur only at very high exposures. Ethanol produces the same profile of transient health effects, also at very high exposures.

Ecological: Iso-butanol has a low order of toxicity to fish, amphibians, aquatic invertebrates, plants, algae, bacteria and protozoa. Iso-butanol is classified as “readily biodegradable” under aerobic conditions (according to OECD criteria). The octanol:water partitioning coefficient ($\log K_{ow}$) for iso-butanol and its calculated bioconcentration factor indicate that bioaccumulation in food webs is not expected. Based on Level III distribution modeling it is estimated that the majority of iso-butanol released to the environment will partition into water and soil. After soil exposure, iso-butanol is expected to migrate readily through soil to groundwater and can - dependant on degradation - transported to deeper soil areas with larger water loads; groundwater contamination is possible. Given its limited water solubility and relatively low molecular weight, a Henry's law constant of slightly $> 1 \text{ Pa m}^3 / \text{mol}$ was calculated, indicating that iso-butanol will only slowly evaporate from water surfaces into the atmosphere. The photochemical removal of iso-butanol as mediated by hydroxyl radicals occurs relatively slowly ($T_{1/2} > 24\text{h}$).

The human health and ecological risks posed by the use of iso-butanol as a biofuel is expected to be minimal.

8.2. Acute Oral and Acute Dermal Toxicity

Iso-butanol has a low order of acute toxicity by all routes (OECD SIDS dossier). The oral and dermal LD_{50} values are $> 2,000 \text{ mg/kg}$ (rat). The oral and dermal LD_{50} values for ethanol are reported to be in the range of $7,000$ to $9,000 \text{ mg/kg}$ (rat) and $13,000 \text{ mg/kg}$ (rabbit), respectively.

8.3. Toxic Air Pollutants and Human Health

Effects of iso-butanol on toxic air pollutant levels and the resultant impact / benefit to human health – requires information from **Section 5**.

8.4. Aquatic Toxicity

Endpoint	Effect concentration (i-Butanol ²⁹)	Effect concentration (Ethanol ³⁰)
Fish	<i>Pimephales promelas</i> 96-h LC ₅₀ > 1000 mg/L	(e.g. <i>Salmo gairdneri</i> , <i>Pimephales promelas</i>) 96-h LC ₅₀ > 1000 mg/L
Aquatic Invertebrate	(e.g. <i>Daphnia magna</i> Straus, <i>Daphnia Pulex</i> , <i>Ceriodaphnia reticulata</i>) 48-h LC ₅₀ > 1000 mg/L <i>Daphnia magna</i> 21-d NOEC > 20 mg/L	e.g. <i>Artemia salina</i> 24-h LC ₅₀ = 1000 mg/L Artemia Salina with a 24hr LC50 of 1833 mg/l. <i>Cerodaphnia sp</i> 10-d NOEC = 9.6 mg/l (10 day reproduction)
Green Algae	<i>Scenedesmus subspicatus</i> 48-h EC ₁₀ / EC ₅₀ > 100 / 1000 mg/L <i>Scenedesmus quadricauda</i> EC ₃ > 100 mg/L	<i>Chlorella vulgaris</i> 96-h EC ₁₀ = 1000 mg/L <i>Lemna gibba</i> 7-d NOEC = 280 mg/l

Table 8-1. Comparison of Ecotoxicity data for i-Butanol (CAS# 78-83-1) and Ethanol (CAS# 64-17-5)

Acute aquatic fish, aquatic invertebrate, and algae toxicity data are available for iso-butanol. An acute test with fathead minnows reported a 96-hour LC₅₀ of > 1000 mg/L. Forty-eight hour EC₅₀ values of > 1000 mg/L were reported for different water column-dwelling invertebrate species. In conclusion, the results, reported show that iso-butanol is, with high probability, not acutely harmful to aquatic organisms.

A chronic test (evaluation parameters: mortality of the parent animals, reproduction rates and appearance of the first offspring during the test period) resulted in a NOEC > 20 mg/L for *Daphnia magna*.

Table 8-1 also shows the reprehensive ecotoxicity endpoints for ethanol for comparison (from the OECD SIDS document). This illustrates the low aquatic hazard potential for both of these two alcohols.

We were not able to find literature, which is available to the general public, demonstrating that ethanol-gasoline blends might be more toxic to aquatic organisms than either neat ethanol or 100% gasoline. We suggest a two tiered approach to investigate this possibility. In Tier 1, we would evaluate the results of the phase

²⁹ OECD. 2004. SIDS initial assessment report for SIAM 19 – isobutanol (CAS No: 78-83-1). Berlin, Germany

³⁰ OECD. 2004. SIDS initial assessment report for SIAM 19 – Ethanol (CAS No: 64-17-5). Berlin, Germany

partitioning/cosolvency study (study #3) which is already planned. This study evaluates if butanol- or ethanol- gasoline blends may increase aqueous concentrations of potentially toxic fuel constituents (e.g. enhancing solubilization, migration of the mono-aromatics benzene, toluene, ethyl-benzene and xylenes). We are predicting that the substantial lower butanol water-solubility (85 g/l at 25°C) relative to that of ethanol (100% miscible) will result in a much lower partitioning of potentially toxic fuel constituents into the aqueous phase. If the test results support this prediction, we do not believe that additional aquatic toxicity testing on Bu16 are needed and that the existing data base on 100% iso-butanol and gasoline is sufficient for the purpose of conducting the risk assessment. However, if concentrations of these constituents are be found to be elevated in the aqueous phase of butanol-gasoline blends over E10, we would institute Tier 2) which would include conducting a series of aquatic toxicity tests on Bu16 and E10 with the appropriate internal controls. A test plan describing the methodology would be submitted to MMWG for review and comments prior to test initiation.

8.5. Toxicity in Aerated Soil

Although terrestrial ecotoxicological data on iso-butanol were not available, vetted read across data from 1-butanol were now identified in a report of the international program on chemical safety³¹. The IPCS report states the seed germination in lettuce (*Lactuca sativa*) and cucumber (*Cucumis sativus*) was inhibited by 50% at a concentration of 1-butanol of 390 mg/l and 2500 mg/l, respectively³². Furthermore, 1-Butanol had an antisenescence effect on the leaves of oat seedlings (*Avena sativa*). It both maintained chlorophyll levels and prevented proteolysis in the dark³³.

This terrestrial ecotoxicological data is not extensive and species studied are not routinely used in today's risk assessments. But the data follow the general trend of supporting – especially by including the existing aquatic toxicity data – that butanol and its isomers should not represent a significant risk. Given that spills and leaks to subsurface soil are the most important exposure scenarios, terrestrial plants are not likely receptors. In this respect, toxicity data for microorganisms are more important because microbial activities on biodegradability might be influenced. A very recent study, which elucidated aerobic biodegradation of butanol and gasoline blends, revealed that the addition of alcohols to gasoline resulted in positive synergic effects on fuels biodegradation in soil and water matrices, whereas results suggest that, in soil, butanol better enhanced the biodegradation of gasoline than ethanol³⁴. The IPCS report's read across data on 1-butanol clearly revealed that it would be highly unlikely that bacteria would be affected by butanol and its isomers in the field. Protozoan are more susceptible than bacteria, but only transitory effects on protozoan populations are likely from spills and effluent since the experimental

³¹ IPCS No. 65, World Health Organization, Geneva, 1987

³² Reynolds, 1977; Smith & Siegal, 1975

³³ Satler & Thimann, 1980

³⁴ Mariano et al., 2009

no-observed-adverse-effect levels are high (also see **Table 8-2** below): 1-Butanol at a concentration of 20 mg/l in water reduced nitrification; a concentration of 5 mg/l was the no-observed-adverse-effect level for nitrification³⁵. 1-Butanol does not bioaccumulate³⁶.

Species	Concentration / Parameter	Reference
Protozoa		
Uronema parduczi (ciliate)	8 mg/l (20-h no-observed-adverse-effect level / total biomass)	Bringmann & Kuehn (1981)
Chilomonas paramecium (flagellate)	28 mg/l (48-h no-observed-adverse-effect level) / total biomass	Bringmann & Kuehn (1981)
Entosiphon sulcatum (flagellate)	55 mg/l (72-h no-observed-adverse-effect level)/ total biomass	Bringmann & Kuehn (1981)
Bacteria		
Pseudomonas putida	650 mg/l (16-h no-observed-adverse-effect level)/ total biomass	Bringmann & Kuehn (1976)
Bacillus subtilis	1258 mg/l (EC50) / spore germination	Yasuda-Yasaki et al. (1978)
Culture on acetate substrate	7400 mg/l / no degradation inhibition	Chou et al. (1978)

Table 8-2. Toxicity Data for Microorganisms

There are no relevant ecotoxicity data on terrestrial animals; however, as for terrestrial plants, significant exposure to butanol is unlikely. The butanol log K_{ow} of 0.79 indicates that terrestrial animals are exposed exclusively to the pore water of the soil. It is possible to generate effect data on soil animals, directly exposed via pore water and/or soil, based on the equilibrium partitioning method using existing aquatic toxicity data and the soil water partition coefficient ($K_{soil-water}$). Existing butanol aquatic toxicity data can be considered to calculate predicted no effect concentration of soil organisms because The $K_{soil-water}$ can be calculated once study #2 (soil sorption) is conducted and results are available.

The following formula will be used:

$$PNEC_{soil} = (K_{soil-water} / RHO_{soil}) \times (PNEC_{water} \times 1000^*)$$

* Assessment factor to address uncertainties

Explanation of Symbols

$PNEC_{water}$	Predicted No Effect Concentration in Water	[mg x l ⁻¹]
RHO_{soil}	Bulk density of wet soil	1700 kg x m ³
$K_{soil-water}$	Partition coefficient soil water	[m ³ x m ⁻³]
$PNEC_{soil}$	Predicted No Effect Concentration in Soil	[mg x kg ⁻¹]

³⁵ Nazarenko, 1969

³⁶ Chiou et al., 1977

9. iso-Butanol Life Cycle Impacts

9.1. Life Cycle Assessment

As indicated in Section 1.2, iso-butanol will initially be produced from the same feedstocks as ethanol through retro-fits of existing grain and sugarcane to ethanol assets. As with bio-ethanol, factors such as agricultural feedstock selection, co-product production and use, and the source of electricity and steam are the most significant contributors to the overall Life Cycle Assessment (LCA) results. In the case of a retrofit, these aspects of the biorefinery are likely to remain unchanged and so the LCA results are likely to be similar.

In addition, individual iso-butanol facilities, just like bioethanol facilities do today, will have their own site specific greenhouse gas (GHG) emission and energy use profile. Depending on the many factors listed above, there is a rather wide range in GHG emission results for bioethanol plants today. While the differences among various bioethanol processes can be significant, the difference between the GHG emission profile of an existing ethanol facility and this same facility retrofitted to produce iso-butanol are expected to be small. However, this assertion will be tested by conducting an LCA of the iso-butanol production system and comparing it to the existing production system for bioethanol.

➤ **Complete the LCA for retrofits of typical existing grain and sugarcane based ethanol plants to iso-butanol production.**

LCA is currently being used as an iso-butanol process development tool during the piloting phase. LCA is used alongside process development and economic evaluation to guide the research and development team to the most sustainable iso-butanol design. In this way, different iso-butanol process options are compared to each other from an engineering, economic, and environmental perspective. Iso-butanol process options can then be compared to external benchmarks like conventional gasoline and bioethanol in order to compare LCA results to other potential fuels and fuel additives on the market. This comparison is done on the basis of a unit of energy delivered by the fuel. Greenhouse gas emissions and non-renewable energy use are the environmental indicators of primary focus.

The current iso-butanol production process is similar to the dry grind corn grain ethanol process, as described in **Section 3.1**. Preliminary results based on generic process models indicate that iso-butanol will have comparable greenhouse gas emissions and non-renewable energy use to bioethanol based on the site and process specific considerations described below. More quantitative LCA results will be available in the final version of the Biobutanol Multimedia Evaluation Report. A detailed discussion of greenhouse gas emission results at each point in the value chain for iso-butanol compared to bioethanol will be included.

9.2. Emissions to Air

Production of volatile organics other than iso-butanol are also associated with the fermentation process. These will be characterized as part of the piloting process and appropriate abatement controls will be included in the commercial production design to meet local, State and Federal air quality emissions limits. Particulate and odor assessments will be included as part of process development and engineering controls will be provided in the final design to prevent any offsite impacts to the local communities in which these facilities are located. As the production processes for iso-butanol are largely identical to those for ethanol produced from the same feedstock, it is anticipated that VOC emissions, other than the substitution of iso-butanol for ethanol, from production of iso-butanol will be substantially unchanged.

Photochemical Ozone Creation Potential (POCP) is a measure of the relative potential of a chemical to form ozone in the atmosphere. POCP is not measured directly but rather is developed from atmospheric and chemical mechanistic models. As a result, reported POCP values for a single chemical may vary considerably with atmospheric conditions including meteorology, amount of sunlight, and the concentration of nitrogen oxides and other volatile organic compounds already in and being newly emitted to the air. POCP values for butanol ranging from around 25 to 60 can be found in the literature.

Representative values of 44.6 for ethanol and 59.1 for iso-butanol (both relative to ethane at 100) were published by R. G. Derwent, et al³⁷.

9.3. Solid Waste and Emissions to Water

Iso-butanol production facilities will be sited, constructed and operated in accordance with local, State and Federal environmental permit requirements. The iso-butanol process is currently in the piloting stage so the actual solid waste and wastewater emission data are not available at this time. However, water will be recycled and reused to the extent possible to reduce the amount of wastewater that needs to be treated. In addition, solid wastes steams will be minimized through the development of value adding co-products such as DDGS or burned for energy recovery. The design goal is to reduce to the extent possible the amount of solid wastes and wastewater that will require further treatment. The exact chemical and composition characteristics of these byproduct streams will depend on the agricultural feedstock used and final processing steps which can be influenced by local siting requirements and available markets for the value adding co-products. In general, the solid waste and water emissions from an iso-butanol production plant will be generally similar to those associated with the same plant when it was producing ethanol.

³⁷ R. G. Derwent, et al., Photochemical Ozone Creation Potentials for a Large Number of Reactive Hydrocarbons under European Conditions, *Atmospheric Environment*, Vol. 30, No. 2, 1996.

9.4. Management of Genetically-Modified Microorganisms

The proprietary microorganism to produce iso-butanol will be genetically engineered to enable the conversion of sugars into iso-butanol. The microorganism is currently under development and organism-specific health and environmental safety information is not available at this time. However, the recipient microorganism will be selected based on its history of safe use in industrial biotechnology and/or in other food and feed industries. All candidate host microorganisms are non-pathogenic and have histories of safe use and are listed as eligible for exemption under 40 CFR part 725.420

The engineered production organism will be regulated by U.S. EPA via the 40 CFR Parts 700, 720, 721, 723, and 725 (see **Table 9-1**). EPA has already conducted human health and environmental risk assessments on 10 recipient microorganisms and found them to represent a low potential risk³⁸. These microorganisms are classified as Tier 1 and

40 CFR Part(s)	Title
Parts 700-723:	Authority, Definitions, Scope and Applicability for Final Rule
Part 725:	Reporting Requirements and Review Processes for Microorganisms
Subpart A:	General Provisions and Applicability
Subpart B:	Administrative Procedures
Subpart C:	Confidentiality and Public Access to Information
Subpart D:	Microbial Commercial Activities Notification Requirements
Subpart E:	Exemptions for Research and Development
Subpart F:	Exemptions for Test Marketing
Subpart G:	General Exemptions for New Organisms
Subpart L:	Additional Procedures for Reporting on Significant New Uses of Microorganisms

qualify for an exemption under TSCA as long as certain microorganism and facility containment criteria are met. Non-exempt microorganisms will require that a human and environmental risk assessment be conducted and submitted to EPA for approval. In either case, a risk assessment for the production microorganism will be conducted.

Table 9-1. Microbial Products of Biotechnology; Final Regulation Under the Toxic Substance Control Act (40 CFR)

For Tier 1 microorganisms, US EPA requires that the microorganism and the production facility must meet specific criteria. For the microorganism, the genetic changes must be well characterized, limited in size, free of toxic sequences and poorly mobilizable. These changes must be well documented and records must be maintained in support of this documentation. For the facility, a contained structure is required which restricts release of the microorganism to the environment. This includes a deactivation step which is required to contain the microorganism. Records demonstrating the effectiveness of the deactivation and containment measures must be maintained. Access to the facility must be controlled and documented engineering controls and procedures must be in place to contain and prevent exposure to workers and the community.

³⁸ US EPA, Microbial Products of Biotechnology: Final Rule (62 FR 17910), http://www.epa.gov/biotech_rule/pubs/biorule.htm

A pilot facility is being built and operated to develop the basic design and operational information for the commercial production facilities. Although EPA has determined that Tier 1 microorganisms represent a very low risk to human health and the environment, additional environmental fate and worker safety studies will be conducted on the microorganism during the pilot stage and a product stewardship review will be undertaken prior to commercial plant operations to insure compliance with the EPA requirements.

10. Tier I Conclusions

The hazardous properties of the different butanol isomers have been widely studied and reported in the technical literature. These properties are intrinsic to the molecule and independent of the production pathway.

The Butamax™ Advanced Biofuels production process for iso-butanol will be identical in most respects to existing technology for bio-ethanol production, resulting in comparable carbon intensities for iso-butanol as for ethanol produced from the same feedstocks.

Limited data currently available indicate that 16vol% iso-butanol/gasoline blends will have vehicle emission characteristics similar to those of 10vol% ethanol/gasoline blends while displacing twice as much petroleum gasoline and providing consumers with comparable fuel economy.

Additional data needs focus on lifecycle aspects that are unique to the use of iso-butanol as a gasoline component —

- **Test representative elastomers for swell and hardness impacts due to exposure to mixtures of ethanol and iso-butanol blended CARB gasolines.**
- **Test for compatibility of California gasoline blended with iso-butanol with fiberglass tank resins and sealants.**
- **Determine the electrical conductivity of E10 and 16vol% iso-butanol/gasoline blends.**
- **BP will perform a review of applicable terminal vapor recovery requirements.**
- **Perform exhaust emissions testing for 16vol% iso-butanol blends in California reformulated gasoline versus 10vol% ethanol blends in California reformulated gasoline to determine whether any adjustments to the Predictive Model are required to model 16vol% iso-butanol blends. Determine impact on Ozone Reactivity and Potency-weighted Toxics emissions.**
- **Determine toxic air pollutants in automotive exhaust using EPA Section 211(b) methodology with California reformulated gasolines blended with 10vol% ethanol and with 16vol% iso-butanol.**

- **Determine the composition of the headspace of 10vol% ethanol and 16vol% iso-butanol blended California reformulated gasoline blends over a range of temperatures and calculate differences in potency-weighted toxics and reactivity. Headspace samples to be generated using the methodology attached as Appendix F.**
- **Determine permeation emissions of 16vol% iso-butanol relative to 10vol% ethanol in CARB gasoline per the program described in Appendix D.**
- **Complete environmental fate studies currently in progress (described in Appendix E).**
- **Complete the LCA for retrofits of typical existing grain and sugarcane based ethanol plants to iso-butanol production.**

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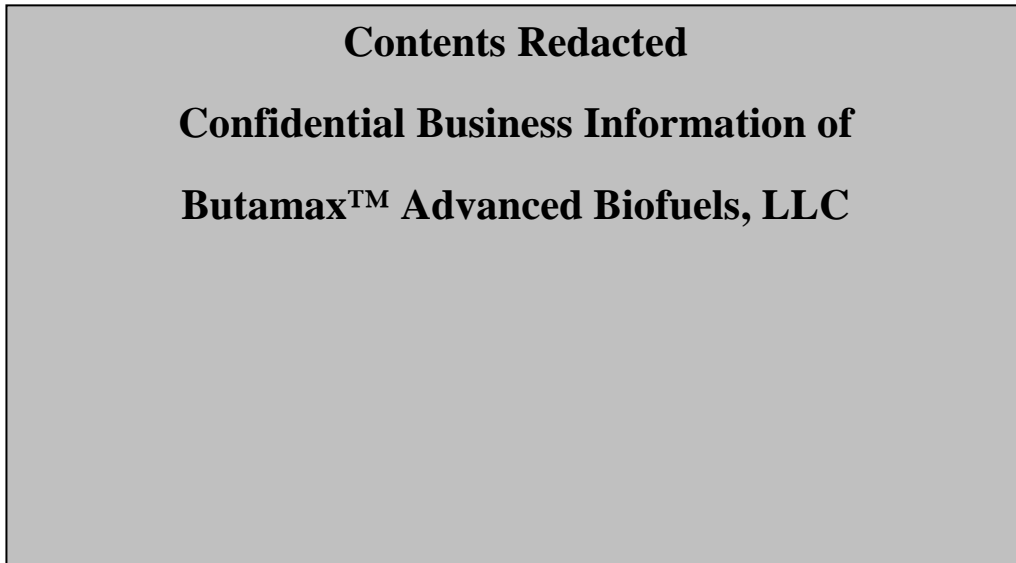
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12. Appendices



12.1. Appendix B: US EPA Profiler Estimation



Appendix B Butanol
PBT.pdf

12.2. Appendix C: Equilibrium Dissolved Iso-butanol/Ethanol Concentration Estimation



Appendix C Mod of
Rixey-Wilson.pdf

12.3. Appendix D: Iso-butanol Permeation Scope of Work



Butanol Permeation
Scope of Wo...

12.4. Appendix E: Environmental Fate Studies Scope of Work



Biodegradation
Study

12.5. Appendix F: Headspace Analysis of Ethanol and iso-Butanol blended Gasolines



CA headspace
App7.doc