Glycerol Tert-Butyl Ether (GTBE): A Bio-Fuel Additive for Today

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MILESTONES: The most remarkable milestones to date are as follows:

- California CleanTech Open – finalist - 2006/2007
- Received start-up grant from NC IDEA - $37K award - March 2008
- Process to manufacture first GTBE quantities developed successfully with >90% yield; Manufactured first 5 liters of GTBE – November 2008
- Tested first GTBE and received outstanding test results from accredited laboratory with octane rating > 120 – December 2008
- The Rice Alliance Recipient for "Most Promising Energy and Clean Technology Company" - 2009
- Successful pilot plant operation completed – December 2010 – January 2011
- First Commercial sale – January 2011
- CleanTech Open – semifinalist - September 2011
- First CPS Biofuels, Inc. patent granted – November 2011
- All IP pending for both US and International rights ongoing and costs fully maintained – thru 2012
  We have recently completed our first manufacturing trials and testing of GTBE. The test results were outstanding and confirmed that our octane numbers are > 120 and testing in an engine illustrated extremely efficient and essentially emission free combustion.

SMALL BUSINESS STATEMENT: CPS Biofuels, Inc. claims the status of a small business entity per definition of annual sales of less than $40 million, including all domestic and foreign sales by the company, its subsidiaries, and its parent company.

EPA AWARD FOCUS AREA(S): The EPA award focus areas that fit the technology of CPS Biofuels, Inc are: 1. Use of greener synthetic pathways, 2. Use of greener reaction conditions, and 3. Use of greener chemicals.

U.S. COMPONENT: CPS Biofuels Inc., a Raleigh, North Carolina (USA) based biofuel company that owns patent-pending products and processes for improving the efficiency of biofuel production, has been in existence since 2005 and was fully incorporated in 2006. CPS in cooperation with Synthonix of Wake Forest, NC has demonstrated the manufacturing capabilities needed to produce the GTBE fuel oxygenate additives, thus housing all phases of research and development within the United States.

ABSTRACT: CPS Biofuels has developed a unique process for converting glycerol, a low-value by-product of biodiesel production, into glycerol ethers (GIPE/GTBE) which can then be used as a high-value bio-based fuel additive in petroleum and bio-based fuels to improve combustion and efficiency, as well as a fuel system icing inhibitor (FSII) in jet fuel. The result of this effort is the product glycerol tert-butyl ether (GTBE), commercially available as CPS PowerShot™ (www.cpspowershot.com), an environmentally friendly biofuel additive fuel oxygenate that acts as an octane booster improving both engine performance and gas mileage. GTBE is a "green" technology that utilizes waste glycerine from biodiesel production (approximately 200 million gallons waste per year), providing an excellent bio-based alternative fuel oxygenate and octane booster that helps fuel combust more completely and improves fuel efficiency with cleaner resulting emissions reducing greenhouse gas emissions (GHGE) and up to 35% particulate reduction with petroleum diesel fuels.

The historically common fuel additive MTBE has been phased out in many states and no obvious replacement has been identified. A combustion-boosting fuel oxygenate, glycerol ethers reduce toxic

hydrocarbon tailpipe emissions. Additionally, glycerol ethers can be added to military (JP-8) and commercial (Jet A) kerosene-type jet fuel as a fuel system icing inhibitor (FSII). Glycerol ethers are a non-toxic, biodegradable replacement for the existing jet fuel FSII compound, sold under the trademark name PRIST ®, known to have severe detrimental health risks to humans. CPS's technology provides fuel additives for the existing U.S. energy infrastructure, thus providing tremendous advantage over any alternative fuels requiring new facilities for production or the use of new vehicles. The core business is focused on improving efficiency of biofuel, most specifically E10 and E15 blends for the ***existing*** transportation infrastructure. CPS's Biofuels' GTBE fuel additive can be used in today's combustion engines without any modification.

There are no known existing biofuel based additives for octane boosting. Current petroleum based additives claim but do not significantly improve mpg for vehicles. This product will significantly improve mpg and reduce greenhouse gas emissions. In addition the product is completely non toxic and therefore safe (GRAS) for all consumers.

THE CHEMISTRY AND PROCESSING OF GTBE: Glycerol ethers are defined as compounds in which one, two or three of the hydroxy groups (OH) in glycerol has been etherified (O-alkyl). The synthesis of glycerol ethers has been described, for example, in U.S. Patent Nos. 5,308,365, US 1,968,033 and US 5,578,090.

The ethers can be formed, for example, by reacting olefins or an alcohol with glycerol in the presence of an acid catalyst. Preferably, at least a portion of the glycerol ethers includes one or two hydroxyl groups. This is a preferred etherification because of the potential for hydrogen bonding between the glycerol ethers and most alcohols, such as methanol, ethanol, and butanol, which might be present. GTBE helps lower the vapor pressure of the alcohol in alternative fuel compositions. Glycerol ethers can also be prepared by reacting glycerol with an alkyl halide in the presence of a base. The glycerol referred to herein is obtained from the waste products of biodiesel production.

Olefins suitable for the etherification reaction include C_{2-10} straight, branched, or cyclic olefins. The olefins contain only hydrogen and carbon. The olefins are typically C_{2-6} olefins, ideally C_{3-4} olefins, and preferably, are either isobutylene or propylene. Propylene and isobutylene are preferred olefins due to their relatively low cost. Highly substituted olefins are preferred because they can stabilize a carbocation intermediate more readily than unsubstituted olefins, thus facilitating the etherification reaction. However, olefins can rearrange under acidic conditions, so even alpha olefins can be used and still form branched ethers. Since virtually any olefin will form a combustible product (in this case, an ether), it is unnecessary to form fatty acid esters or glycerol ethers from pure olefins. The mole ratio of olefin to glycerol ranges between 1/1 and 3/1, but is ideally in the range of about 2/1. That is, it is believed that di-ethers are preferable to mono-ethers and tri-ethers, although mixtures of mono-, di- and/or tri-ethers are within the scope of the invention. The di-ether is non-water soluble and can be obtained in high yield (>95%) and high purity (>98%). It is preferred that at least a portion of the glycerol ethers include one or two hydroxyl groups, so that the product has the ability to hydrogen bond with ethanol, and thus help lower the vapor pressure of the ethanol.

Any acid catalyst that is suitable for performing etherifications can be used, in any effective amount and in any effective concentration. Examples of suitable acids include, but are not limited to, hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, and solid catalysts such as Dowex 50™. Strong acids are preferred catalysts. The most preferred acid catalyst is sulfuric acid.

The production of glycerol ethers, particularly glycerol tert-butyl ether (GTBE) (Figure 1), comes from the conversion of glycerol and isobutylene or other appropriate olefins. In other words, glycerol, or purified glycerin, reacts with C_{2-8} olefins to form glycerol ethers. The olefins can be purchased offsite or produced from the Fischer-Tropsch synthesis process within a moderate size biodiesel production facility.

The GTBE process (Figure 2) is similar to that of MTBE production (Figure 3) and can in fact be performed at existing MTBE production sites. Because the liquid-gas reaction (glycerol plus isobutylene) to produce GTBE requires a higher temperature (100-150° C higher) the existing equipment may need to be retrofitted. It is also known that for an existing refinery, it is desirable that GTBE production should be at least 50,000 tons/year. In MTBE production, hydrocarbons and methanol are fed into a reactor. The resultant is cooled and distilled, and the product is the ether (the raffinate goes to methanol recovery). In the GTBE process, no alcohol is needed to replace the methanol - glycerol is used instead. The product is produced via catalytic conversion and fractional distillation. The GTBE produced can have as few as one or as many as three ether linkages. Salt by-products produced need to be removed, through a filtering and flushing process along with neutralization using brine and/or NaOH or other suitable bases.

CPS has developed a method of economically extracting these components from the byproduct mixture. In general the methanol can be extracted and reused in the biodiesel production or sold on the open market. The fatty acids can be mixed in bunker oils / marine diesel and sold at the market level price of this fuel. The fatty acids will improve the marine diesel by reducing emissions and reducing viscosity so the preheating can be reduced. The salts can be disposed of without regulation or sold. The remaining product is pure glycerol. Pure glycerol has many uses from pharmaceuticals and agricultural products to soaps. The glycerol purification process mentioned above is followed by extraction of the methanol, fatty acids, and salts. The purified glycerol is then used to make Glycerol t-Butyl Ether (GTBE). GTBE is an excellent fuel additive, which has a market price higher than purified glycerol. This GTBE can be added to virtually any fuel in order to improve performance and emissions.

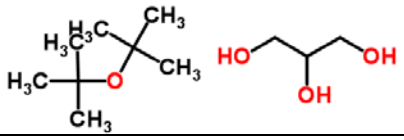


Figure 1: Chemical Structure of GTBE
1,2,3-Propanetriol - 2-methyl-2-[(2-methyl-2-propanyl)oxy]propane (1:1)
$C_{11}H_{26}O_4$

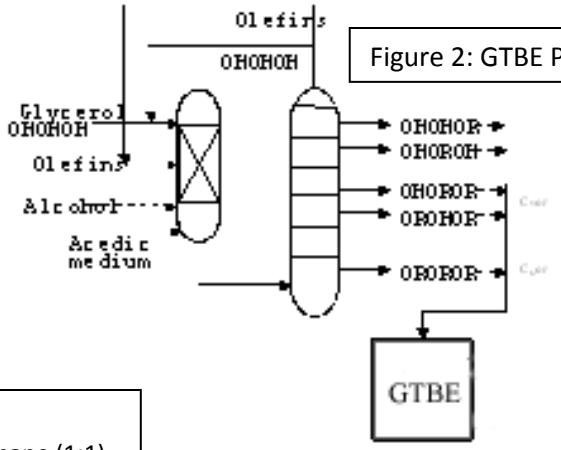


Figure 2: GTBE Production

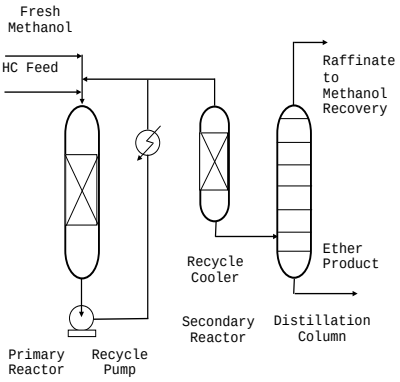
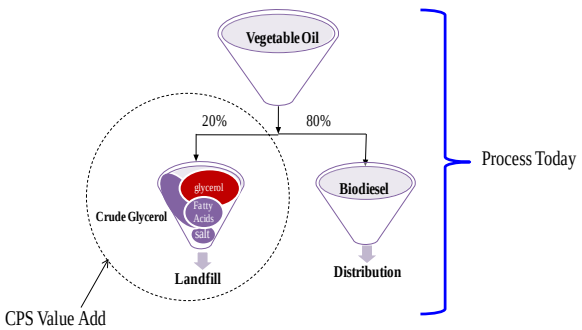


Figure 3: MTBE Production

Figure 4: Waste Products of Biodiesel Production



GTBE TECHNOLOGY - PROBLEMS ADDRESSED, IMPORTANCE, AND SOLUTION: For many years, fuel oxygenates, and in particular MTBE (methyl tert-butyl ether) have been required as additives to gasoline. Oxygenates raise the oxygen content of hydrocarbon fuel and allow it to burn more completely, thus reducing harmful tailpipe emissions from motor vehicles. MTBE in particular has been used in U.S. gasoline at low levels since 1979 to replace tetra-ethyl lead as an octane enhancer and to help prevent engine knocking. However, health, environmental toxicity, and other factors led to an increased unpopularity and eventually the outright banning (by the EPA) of MTBE in over 20 states.

Several alternatives to the use of MTBE have been proposed. One would be simply to use no equivalent additive. The obvious downside of this, however, is less efficient fuel. It is impossible for such fuel to achieve the same high octane /cetane ratings previously possible with MTBE. A second alternative would be to use similar compounds ETBE (ethyl tert-butyl ether) or TAME (tert-amyl methyl ether). But while ETBE and TAME shares many of the advantageous properties of MTBE, they also share the same or similar toxicity effects. It is likely that widespread use of ETBE or TAME would soon face opposition for the same reason that MTBE currently experiences (toxicity and carcinogenicity).

Glycerol tertiary butyl ether, or GTBE, produced from a biomass (glycerol-based) source, possesses none of the toxicity issues associated with the previously described additives, and has even been found to be useful for medicinal purposes. In addition, it is a more efficient fuel additive than is MTBE. With three -O-groups instead of one, GTBE is a better fuel oxygenate, and because there are two ether linkages, it also provides more energy per gallon.

The use of GTBE can make E85 a popular alternative by increasing its fuel efficiency to levels comparable to traditional gasoline. Ethanol is more expensive than gasoline: on average E85 currently sells at a 30% premium over traditional 87 octane unleaded (measured on a BTU basis by the Alternative Fuel Index). Gasoline/ethanol blends suffer from relatively low energy content per unit volume. For example, E85, a mixture of about 85% ethanol and about 15% gasoline by volume tends to provide roughly 20% fewer miles per gallon than gasoline (one gallon of E85 contains less energy than does one gallon of gasoline). In flexible-fuel vehicles (FFVs) produced before 2003, fuel economy is reduced about 30% when using E85. In those produced since then, it is reduced by about half as much (15%). Thus, unless new vehicles are made with larger gas tanks, drivers will be forced to fill their car's fuel tank more often when using E85. Blends of glycerol ethers with gasoline/ethanol blends can improve their gasoline mileage. The glycerol ethers lower the vapor pressure of the ethanol in gasoline/ethanol blends, thus improving their performance. The glycerol ethers also increase the cetane value of diesel/ethanol blends, which improves their performance as well.

Most importantly, GTBE can be used in currently existing engines without modification as an additive to both traditional gasoline and E85 and virtually any fuel from bunker oils for ships to jet fuels. The glycerol ethers, when combined with conventional diesel fuel, biodiesel fuel, or conventional gasoline products, provide advantageous properties similar to those provided by methyl t-butyl ether (MTBE). The glyceryl ethers lower the viscosity of the fuel, and hydroxy groups on partially etherified glycerol may help to incorporate a small amount of water into the fuel, which can lower SO_x and NO_x emissions. Particulate emissions can be reduced as much as 35% from petroleum based diesel fuels.

GTBE also has great potential in the jet fuels industry, as they are currently using a product known as PRIST® to remove moisture from their fuel systems. PRIST® is toxic, thus GTBE can suit these needs while providing an environmentally friendly alternative. When used as a PRIST replacement or as aviation fuel, GTBE has an affinity for water molecules and "removes" water from the fuel line as well as lowering the freezing point depression. This is extremely important, because it helps ensure that water does not stop the flow of the fuel to the engines.

GTBE can also be used as Avgas (Aviation Gasoline) because it meets the energy requirements by boosting octane levels and can replace the use of tetraethyl lead based kerosene currently being used.

A fourth potential application and market for GTBE is marine diesel, currently known as an extreme environmental pollutant because barges currently are burning large amounts of marine diesel which release pollutants in excess of the total pollutants released by all land vehicles world-wide. Each of these markets could be well served with the use of our GTBE technology.

Aviation Gasoline, Avgas, is a high-octane fuel used to power aircrafts that currently uses tetraethyl lead to boost octane levels. This lead based gasoline, is extremely detrimental to the environment and has been shown to impair brain development in children. GTBE would be an environmentally superior solution that would also work to boost octane level in aviation gasoline. This market will be hard to enter because the Federal Aviation Association (FAA) has strict regulation standards.

Barges currently use marine diesel (i.e. bunker oil) for operation, which is extremely hazardous to the environment. GTBE can help reduce the emissions form diesel fuel that burns poorly and creates pollution. For Marine Diesel, the main issue is solely emissions, and the emission reduction by adding only slight amounts of GTBE (1-3%) to the marine diesel will reduce emissions by as much as 30%. Pollution and particle emissions from world-wide barge transportation is greater than all pollution from all land based vehicles worldwide, so small, in fact that a 1-2% decrease in marine diesel emissions will have an immediate impact on the earth's environment. GTBE fills a clear market need for marine diesel as improvements in efficiencies and reduction in pollutants are being mandated by governments. This market has the strongest entry barriers because regulations are set by the EPA and the Department of Transportation.

GTBE can comprise approximately 2-5% by volume of vehicle fuels. The United States consumes approximately 350 million gallons of on and off-road diesels per day. If GTBE eventually comprises only a small percentage of the total market, the value proposition is tremendous.

The production of biodiesel from vegetable oils results in a 22% by volume waste byproduct called crude glycerol. This byproduct is typically disposed of at the local landfill. This is the single biggest headache in biodiesel production. In fact, about 200 million gallons of this byproduct disposed of in the United States in 2009 alone. CPS has developed a method of improving biodiesel production efficiencies by converting these waste byproducts into high-energy and safe oxygenates and fuel additives that improve vehicle performance and reduce particulate emissions. The process can virtually eliminate all the waste from biodiesel production.

COMPARISON TO OTHER TECHNOLOGIES ADDRESSING THE SAME PROBLEM: Several alternatives to the use of MTBE have been proposed. One would be simply to use no equivalent additive or ethanol (which is being used but significantly reduces MPG). The obvious downside of this, however, is less efficient fuel. It is impossible for such fuel to achieve the same high octane / cetane ratings previously possible with MTBE. A second alternative would be to use the similar compounds ETBE (ethyl tert-butyl ether) or TAME (tert-amyl methyl ether). But while ETBE and TAME shares many of the advantageous properties of MTBE, they also share the same or similar toxicity effects. It is likely that widespread use of ETBE or TAME would soon face opposition for the same reason that MTBE does currently. Ethanol is presently the best alternative fuel oxygenate for gasoline engines and is technically viable for future diesel engines. However, the energy per unit volume is 34% less than gasoline and 50% less than diesel. In addition, off road vehicles including marine vessels cannot readily use ethanol due to its inherent solvent properties, which can damage seals and fiberglass fuel tanks. New engines could be designed to utilize ethanol but there are still over 100 million vehicles with some having 30 more years of viable life in use today. There is an apparent need to develop an environmentally safe fuel oxygenate that has a significantly increased effective energy content. Biodiesel production leaves behind a significant amount of crude glycerol. This crude glycerol has a relatively low market value, but CPS Biofuels can recycle and reuse this waste stream to produce a higher value fuel oxygenate.

Glyceryl t-butyl ether (GTBE) is a green, renewable, sustainable non-toxic biofuel oxygenate and octane boosting additive alternative that increases octane by 5.5 points (using 2% with E10 87 rated octane as the standard), and improves vehicle performance. GTBE is the first renewable, sustainable, greenhouse gas and particulates emissions reducing, biofuel additive developed for commercial use. GTBE is an alternative non-toxic equivalent to MTBE (recently outlawed throughout the United States by the EPA). GTBE possesses none of the toxicity issues of the previously mentioned additives, and has even been found to be useful for some medicinal purposes

Existing fuel additives are petroleum based. There are no existing biofuel based additives for octane boosting. Currently petroleum based additives do not significantly improve mpg for vehicles. This product will significantly improve mpg and reduce greenhouse gas emissions. In addition the product is completely non toxic and therefore safe (GRAS) for all consumers.

GTBE also has great potential in the jet fuels industry, as they are currently using a product known as PRIST® to remove moisture from their fuel systems. PRIST® is toxic, thus GTBE can suit these needs while providing an environmentally friendly alternative. When used as a PRIST replacement or as aviation fuel, GTBE has an affinity for water molecules and "removes" water from the fuel line as well as lowering the freezing point depression. This is extremely important, because it helps ensure that water does not stop the flow of the fuel to the engines.

GTBE can also be used as Avgas (Aviation Gasoline) because it meets the energy requirements by boosting octane levels and can replace the use of tetraethyl lead based kerosene currently being used. A fourth potential application and market for GTBE is marine diesel, currently known as an extreme environmental pollutant because barges currently are burning large amounts of marine diesel which release pollutants in excess of the total pollutants released by all land vehicles world-wide. Each of these markets could be well served with the use of our GTBE technology.

REALIZED POTENTIAL BENEFIT & LIFECYCLE ANALYSIS: CPS is targeting the low risk high value market of refining glycerol from the biodiesel process which provides 95% yields and 98% purity with essentially no waste other than used brine solutions for neutralization. The GTBE manufacturing includes basically a 2-step process: 1.) The glycerol purification process which allows the biodiesel manufacturer to reuse the methanol and fatty acids and easily dispose of the salts, and 2.) take the pure glycerol from step 1 and create glycerol ethers. The glycerol ethers (GTBE) will then be mixed with diesels and bunker oils as an environmentally friendly oxygenates and performance enhancer.

Step 1 Glycerol Purification: The production of biodiesel from vegetable oils results in a 22% by volume waste byproduct called crude glycerol. This crude glycerol consists of methanol, salts, fatty acids and pure glycerol all mixed together. This byproduct is typically disposed of at the local landfill. This is the single biggest headache of the biodiesel production. There will be about 200 million gallons of this byproduct disposed of in the United States this year (2007).

CPS has a method of economically extracting these components from the byproduct mixture. In general the methanol can be extracted and reused in the biodiesel production or sold on the open market. The fatty acids can be mixed in bunker oils / marine diesel and sold at the market level price of this fuel. The fatty acids will improve the marine diesel by reducing emissions and reducing viscosity so the preheating can be reduced. The salts can be disposed of without regulation or sold. The remaining product is pure glycerol. Pure glycerol has many uses from pharmaceuticals and agricultural products to soaps. Supplies of pure glycerol are high resulting in low market prices of around $.50 per gallon. Even considering the low market price, purifying the glycerol by the economical CPS process can result in appreciable profits for the biodiesel producer and allow a significant reduction in landfill waste.

Step 2 Glycerol Ethers: The glycerol purification process mentioned above is followed to extract the methanol, fatty acids and salts. The purified glycerol is then used to make Glycerol t-Butyl Ether (GTBE).

GTBE is an excellent fuel additive, which has a market price higher than purified glycerol. This GTBE can be added to virtually any fuel in order to improve performance and emissions.

A Life Cycle Assessment (LCA) for the production and use of glycerol ethers illustrates the environmental benefits over petroleum products and even traditional biofuels like ethanol and biodiesel (Table 1). Much data exists for the LCA of biofuels over petroleum so we compared our analysis to other biofuels. First the glycerol ethers are created from waste generated by the biodiesel process or from soybean and other renewable plant matter then the use of isobutylene from existing gasoline refineries is used to complete the glycerol ether reaction. Additionally, the glycerol ethers can be transported within the existing pipeline and tanker infrastructure and will not outgas like ethanol when pumping into automobiles.

A full and comprehensive LCA has yet to be performed however CPS Biofuels, Inc anticipates doing so. A complete cradle-to-grave-to-cradle analysis of this technology can be performed using the software program application, LCAPIX (www.KMLtd.com). The principal in this company owns IP in this field (US Patent No. 6,490,569, "System for Combining Life Cycle Assessment with Activity Based Costing Using a Relational Database Software Application") for LCAPIX and is a recognized expert in LCA.

Table 1:

Glycerol Ethers (GTBE) LCA				
Categories				
Fuel:	Gasoline	Ethanol	Biodiesel	GTBE
Dispensing	2%	1%	0%	1%
Distribution / Storage	5%	5%	1%	5%
Production	61%	39%	29%	5%
Gas Leaks / Flares	2%	0%	0%	1%
Feedstock:	oil	cellulosics	soy	soy waste
Fertilizer Manufacturing	0%	23%	24%	0%
Feedstock Delivery	10%	8%	2%	2%
Feedstock Production / Recovery	20%	21%	26%	7%
Land-Use / Cultivation	0%	25%	81%	0%
Emissions Displaced	0%	-23%	-64%	-35%
Total CO2 equivalent (10-E6 BTU)	20,778	34,494	132,242	17,500

GTBE costs are directly related to volume production and feedstock availability. As volume of manufacturing increases and feedstock costs stabilize due to consolidation, GTBE will be cost competitive with MTBE and other fuel oxygfenates. As a retail octane booster and fuel injection cleaner, GTBE already competes in cost and pricing with $90/gallon kerosene. Eventually, GTBE should be produced for less than $5.00/gallon. GTBE, marketed as CPS Powershot™ (www.cpspowershot.com), can fill a bio-based niche in the fuel additive industry comparable to the existing market accessed by companies such as Gold Eagle (www.goldeagle.com). GTBE can also be used as a non-toxic alternative to paint thinner.

CPS Powershot ® - our fuel additive - has been registered with the EPA and approved on April 1, 2010, EPA No. 24722001. GTBE CPS Powershot® - has been applied for at the US Patent and Trademark office, which also has been issued a Notice of Allowance 77-871,904 on June 22, 2010. CPS Powershot® (www.cpspowershot.com) became commercially available in 2011.

CPS has a patent pending (US 12/152,845) on the use of GTBE as a fuel additive for E85 and either petroleum or bio-based gasoline and stand-alone additives for any fuel including off-road diesels. GTBE is compatible with any fuel, bio- or petroleum-based.

As this product is environmentally friendly and completely non-toxic, CPS Biofuels, Inc. is in compliance for reporting GTBE under appropriate laws such as TSCA, FIFRA, and FFDCA.