

Biobutanol – production and application in diesel engines

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Introduction

The European Union recognized the energy derived from renewable sources as a key element in future low carbon energy sector. All Member States obtained 10-percent share of renewable energy in transport in 2020 is one of the sector objectives. The policy of the EU and other countries in the world has the influence on an intensive expansion of the biofuel market observed in recent years. On a large scale, as a substitute for fossil fuels, bioethanol and fatty acid methyl esters (FAME) are currently being used. It is estimated that first-generation biofuels will dominate the market by 2020. At the same time new products are being searched, that can be obtained from cheap and available feedstock (including waste), with simple and cost effective technology applied. Extensive research into alternative fuels, including the second generation biofuels, is performed in both research centers and fuel industry companies. Among the potential successors of ethanol, due to its specific properties, butanol is concerned. Butanol can be produced both in petrochemical processes and the fermentation of biomass and, therefore, from renewable sources (biobutanol). Gradually increasing interest is aroused due to new prospects opening up for the industrial production of butanol in biochemical processes. This article aims to discuss issues related to the biobutanol production and subsequent use as a potential component of fuels used in diesel engines.

Butanol properties

Butanol exists as four different isomers: n-butanol, sec-butanol, isobutanol and tert-butanol, based of the location of the hydroxyl group and the carbon chain structure (straight or branched). Due to differences in structure, these isomers show some differences in physicochemical properties (e.g. boiling point or flash point). Isobutanol, due to the relatively high value of the octane number, is a component of gasoline (quality standards allowing its content in gasoline up to 10% v/v). Tert-butanol is the octane number improver used as an additive to gasoline. N-butanol is used as an intermediate for organic syntheses, an oil additive, the feedstock for solvents and co-solvents production. The isomer also is mainly used for studies on the application in diesel engines.

Butanol is a good solvent for the petroleum-based fuels, being poorly soluble in water and exhibits a much less hygroscopic than ethanol. This entails blends stability, and long-term stability in storage (butanol is less prone to separate from the gasoline or diesel in the presence of water). Additionally, its use as a blend with petroleum fuels does not require any modification to existing vehicle engines up to 40% of alcohol content [1, 2] It can also be transported and stored within the existing infrastructure. N-butanol is less corrosive, has a higher calorific value than ethanol (33 MJ/kg), higher cetane number, and low heat of vaporization (which provides better ignition at low temperatures).

The oxygen content in butanol is 21.6%. The presence of oxygenates in diesel fuel improves combustion, reduces particulates emissions, carbon monoxide (CO) and nitrogen oxides (NO_x) emissions.

By virtue of oxygen content air-fuel ratio changes – mixture must be richer in fuel than in the case of hydrocarbon fuels.

Potential drawbacks of butanol refer to the increased toxicity relative to ethanol and the characteristic odour. Like other alcohols, butanol

has the property of fuel system ‘cleaning’ by deposits dissolution and detachment. The use of butanol containing mixture in cars previously fuelled by conventional fuels may result in filter clogging.

As being a solvent butanol, can be not indifferent to some fuel system components (e.g. seals elastomers) and cause their softening or dissolution. Research in terms of the influence of butanol and its diesel fuel blends on elastomers is conducted by e.g. DuPont Performance Elastomers [3].

Biobutanol production

The vast majority of butanol is currently produced from petroleum in petrochemical processes. However the changes in the fossil fuels markets area (rising prices, dwindling resources) and the emphasis put on developing of the fuel production technologies from renewable sources, caused the intense research on butanol fermentation processes led by increasing number of companies that merge biotechnology and fuel industries. One of the leaders in the market for conventional fuels, the company British Petroleum (BP), together with DuPont launched a partnership Butamax, dedicated to the development of new biobutanol fermentation technologies, including the use of lignocellulosic materials. Butamax estimates that a demonstration plant in Hull, in the United Kingdom should be commercialized in 2012 or 2013 [4].

Efforts are underway to obtain an effective modification of the oldest acetone-butanol fermentation process, so-called ABE fermentation (acetone, n-butanol and ethanol as main products, obtained in a ratio of 3:6:1). The process of ABE, known since the beginning of the twentieth century, is performed by anaerobic gram-positive bacteria of the genus clostridia (mainly *Clostridium acetobutylicum*, but also *C. Beijerinckii*, *C. butylicum* and others [5, 6]), is not profitable because of low productivity (due to the high sensitivity of bacteria clostridia to butanol, inhibiting the process even at low concentrations, approximately 20g/dm³) and poor selectivity (high cost of products separation) [7, 8]. In order to improve the process and its economics multidirectional research are conducted.

One of the courses covers metabolic engineering issues, i.e. modification of metabolic pathways to increase the resistance of clostridia bacteria to higher concentrations of fermentation products, and improve the efficiency and selectivity of the process [9]. However, how the metabolic fluxes of clostridia are regulated is still unclear [8]. It is also possible to obtain the synthetic pathways of butanol-specific synthesis in microorganisms that do not naturally possess pathways in this direction. They are selected in terms of increased possibilities of genetic modification, the growth rate and expected resistance to the toxic influence of butanol. Fermentation strains such as *Escherichia coli* [10], *Saccharomyces cerevisiae* (yeast responsible for fermentation of ethanol) and *Ralstonia eutropha* [9, 11] are adapted through clostridia genes encoding enzymes responsible for butanol synthesis, expression into their cells. Modified micro-organisms produce the desired products with higher efficiency, unavailable for the unmodified organisms. Fermentation strains selection also affects the isomers gained, e.g., *E. coli* produces n-butanol as the main product and isobutanol as a byproduct [1].

Low yield of the fermentation of butanol synthesis requires research on butanol recovery techniques. Many separation techniques of

fermentation products are described, e.g. product liquid-liquid extraction or perstraction [12÷15], pervaporation (membrane separation with gaseous permeate discharge) combined with the immobilization of bacterial cells [16÷18], adsorption [19] or reversed osmosis [20]. It is estimated that effective solutions development can help profitability increase up to 40-50% [9].

The authors of [21] described the use of FAME as butanol extractant in the process of ABE and subsequent use the received blend as fuel. FAME selectively extracted 40 - 50% of butanol received in fermentation and slightly increased its efficiency in the process. High cetane number and low ignition temperature characterizes the obtained fuel.

The feedstock used in fermentation determines the selection of strains and process conditions. It also affects process costs. In addition to well known technology using starch-based feedstock (grains, potatoes, corn) and sucrose (sugar cane, sugar beets), processes using cellulosic and lignocellulosic materials, including the dedicated energy crops or waste from agricultural production and industry (second-generation biofuels) are developed.

This involves, among others the development of multi-step processes using the appropriate microorganisms, as the currently used bacteria are not able to use lignocellulose directly as a feedstock.

One of the innovative processes for managing and utilizing the crude glycerol by-product from FAME (biodiesel) production has been developed [22] is anaerobic fermentation process. The company Green Biologics is developing biobutanol production from glycerol and other wastes from industry and agriculture, using genetically modified thermophilic bacteria of the genus *geobacillus* and sells derived fuel named Butafuel [23].

Biobutanol can be obtained in the fermentation processes of the same feedstock as ethanol, and in installations for the production of ethanol after conversion. This solution reduces the cost of new installation investment. It has been applied by the Gevo Company that launched the factory in Luverne, USA, and currently produces biobutanol from sucrose feedstock, and planning use of cellulose feedstock in the future. Gevo provides isobutanol for Total oil company [24]. There are also other companies planning to convert existing ethanol facilities for biobutanol production and some intending to place biobutanol production facilities nearby the chosen plants to use the wastes as a feedstock for production.

Currently, efficient biobutanol production in fermentation processes is carried out only in a pilot scale.

N-butanol as a component of fuel used in diesel engines

Numbers of important factors determine the interest in using the n-butanol as a component in blends with diesel or other fuels in compression ignition engines. The development of biobutanol production via biomass fermentation technology in the coming years can be expected as well as its increased availability and more favorable prices. Production of butanol coming from renewable resources, qualifies that alcohol as a 'bio' component, particularly desirable in the era of stringent international and EU requirements for increasing the share of biofuels in the energy market. Stringent environmental regulations impact on quest for new solutions both in the field of engine construction and fuel composition to reduce harmful emissions.

Alcohols, due to its oxidative nature, contribute to the reduction of emissions particularly dangerous particulates in blends with diesel fuel, and to a lesser extent, other exhaust components. Hence the interest and attempts to apply bioethanol, the common biofuel, in blends with diesel. However, the properties of ethanol (high polarity and poor miscibility with hydrocarbon fuels related with high affinity for water, a very low cetane number - about 8, the high heat of vaporization, low viscosity and poor lubricity, corrosivity, very low flash

point) significantly differ from diesel properties which takes effect in many application problems. In this regard biobutanol as a higher alcohol shows much better performance.

Selected physical and chemical properties of n-butanol and diesel are shown in Table I.

Table I
Physical and chemical properties of n-butanol and diesel fuel [2]

	Boiling point °C	Flash point °C	Density at 20°C kg/m ³	Kinematic viscosity at 40°C mm ² /s	Cetane number	Oxygen content % m/m	Heating value MJ/kg
n-butanol	116 ÷ 118	34	811	3.6*	~25	21.6	33
diesel	180 ÷ 360	>55	837	2 ÷ 4.5	50	0	43

* measured at 20 °C

Due to the presence of longer carbon chain in butanol molecule, and its reduced polarity, n-butanol shows low solubility in water (77g/l) and a much better miscibility with hydrocarbons. This feature has direct impact on basic parameter for a motor fuel - stability.

Preliminary studies show good miscibility and stability of mixtures of n-butanol with diesel fuel at room temperature in tested range (up to 40% v/v alcohol content); no phase separation in long term is observed [2]. However, comprehensive study of mixtures stability, at low temperatures also, is necessary.

Butanol addition to oil causes a drop in density, flash point, kinematic viscosity and cetane number of resulting fuel. Viscosity affects the atomization of the fuel during injection, and its reduction may cause injectors and pump leakage. Ignition temperature determines the lowest temperature of ignition under the influence of external sources and is an indicator of refueling, transport and storage safety. The cetane number affects the engine start and the parameters of its performance.

In Drive Cycle Test carried out using 20% and 40% mixtures of n-butanol with diesel, the use of n-butanol in an amount up to 20% in the mixture did not result in interference with the engine during test performance [25]. Similar results were obtained in [2] for blends up to 24% of n-butanol. For the 40 % butanol blend drivability of the vehicle decreased noticeably, especially for the cold-start urban drive cycle [25] and a general deterioration of engine operating parameters. Although attempts are being made use of 100 % biobutanol as fuel in spark ignition engines, increasing the percentage of biobutanol (up to 40% or more) in fuel for diesel engines requires significant modification in engine construction.

Tests carried out at different compression ignition engines [2, 24, 26], for various fuels (diesel and diesel - n-butanol blend in different ratio), under different loads and at different speeds, enabled to calculate the parameters for define and compare the engine performance (brake specific fuel consumption and brake thermal efficiency). The tests also provided emissions information (including particulates content, nitrogen oxides content, carbon monoxide content and total hydrocarbon content - THC).

Brake specific fuel consumption for n-butanol mixtures with diesel slightly increases (a few percent) in comparison with neat diesel fuel and the increase with increasing n-butanol content in the fuel. This effect is expected due to reduction of the blend calorific value as well as blend incomplete combustion at low loads [2].

Brake thermal efficiency (dependant on brake specific fuel consumption and blend calorific value) is slightly higher in the presence of butanol in the mixture. A similar effect is observed in mixtures containing other fuel oxygenates (e.g. bioethanol).

Butanol has the appropriate properties to reduce emissions of particulates (PM), considered as the most hazardous components of the exhaust along with nitrogen oxides. Significant reduction in PM is observed as a positive result of the combustion being assisted by the presence of fuel-bound oxygen in evaporated fuel. It is observed especially

at high engine loads. The effect of particulates emissions reduction is significantly higher the higher the percentage of butanol in the blend.

A noticeable increase of unburned hydrocarbons emissions (THC) is observed with the use of n-butanol –diesel blends, proportional to the percentage of butanol in the blend. The same effect is observed for ethanol-diesel blends. The mechanisms of these effects are not thoroughly investigated yet. The highest THC emissions occur on idling, and decrease with increasing load up to 50÷75% [27].

The absence of sulfur in butanol reduces its percentage in a blend with diesel fuel, causing a decrease of sulfur dioxide emissions proportional to the lower sulfur content.

Changes in emissions of nitrogen oxides (NO_x) and carbon monoxide CO are slight, and the emissions influencing factors are complex and not fully understood.

In the Drive Cycle Test [25] conducted using 20% and 40% blends of butanol with diesel, CO and THC increased in the urban cycle, while nitrogen oxide emissions decreased with the increase of butanol in the blend. For the highway drive cycle the butanol blends did not show any particular effect on the THC and CO emissions, but caused an increase in emissions of oxides of nitrogen.

To neutralize the negative effects of n-butanol in diesel blends on some parameters, it is proposed to introduce a new component to a n-butanol – diesel blend. The component is fatty acid esters (FAE). The presence of FAE in the mixture and the appropriate quantitative ratio of components regulate such properties as density, viscosity, calorific value and cetane number, to levels similar to those of neat diesel fuel [28]. However, the impact of FAE on the ignition temperature is minimal. Both mixtures, n-butanol – diesel, as well as mixtures of n-butanol – diesel – FAE show the dominant influence of n-butanol on this parameter. Its presence in the mixture lowers the ignition temperature below 55°C (as determined by the PN-EN 590), which results a change in classification of class of flammability: from the third (> 55°C to 100°C) to the second class (>21°C to 55°C) and increased requirements for security measures.

Low pour point of n-butanol did not significantly improve low-temperature properties neither of mixtures with diesel nor with the fatty acid methyl esters (FAME) [29]. In study of phase stability of n-butanol - diesel - FAME mixture, and the long-term stability (90 days), in a wide range of concentrations it was found one liquid phase, which at low temperature (10°C) demonstrated a tendency to cloud, probably due to crystallization of mono and diglycerides [28].

Research is also conducted for the ternary system: diesel – n-butanol – vegetable oil. N-butanol is added as an agent increasing the blend stability, lowering the viscosity, and improving the combustion characteristics as well as reducing emissions of soot [27, 30].

Few, till today, results of research of biobutanol use as a component of fuels used in diesel engines, confirm its advantages. The authors of paper [2] assess n-butanol as a safe component of the fuel for diesel engines, both in terms of energy efficiency and emissions reduction and consider the use of cetane improver or emulsifier not necessary.

However, the final assessment of the potential and safety of biobutanol use in diesel engines requires comprehensive research to be conducted. These should include the physical and chemical properties of received blends and the possible use of additives, the engine performance and emissions, materials compatibility as well as issues related to storage and transportation.

Summary

Implementation of biobutanol in transportation as an alternative fuel or component requires time, further researches conducting and widespread market acceptance. Certainly, significant advantages of this alcohol are fairly high energy value, good miscibility with hydrocarbon fuels and reduced corrosiveness, as well as the possibility of use as a component of both gasoline and diesel.

The demand for transport fuels derived in a sustainable way will continue to grow. Biobutanol can be produced both from currently available resources and with the cultivation of energy crops and agricultural waste in the future. Biobutanol also offers the ethanol producers the transformation opportunity to a higher added value product.

The International Energy Agency estimates that demand for biofuels will grow from 60 million tons in 2008 to 690 million tons in 2050. The world market for butanol is estimated at around 2.8 million tones per year. Development of this market is expected 3.2% per year until 2025 [31]. With the improvement of the economics of biobutanol production process one can expect a significant acceleration of growth. For this to happen the developed technologies based on fermentation processes are necessary to commercialize.

Translation into English by the Author

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