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# Agro-industrial waste to biobutanol production: Eco-friendly biofuels for next generation

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ABSTRACT

Biobutanol offers several merits that make it as top-tier fuels to be discovered. Due to energy and environmental concern, traditional biobutanol production using Acetone-Butanol-Ethanol (ABE) fermentation have been revamped. An important facet for biobutanol production is selection of feedstock as a substrate. Currently, lignocellulosic biomass has attracted much interest globally due to its sustainable supply and non competitiveness with food. Cellulosic biobutanol production can be generated by using lignocellulosic residue such as agricultural crops and residue. Moreover, finding efficient pretreatment is another vital parameter in biobutanol production process. This review will briefly update the recent trends for lignocellulosic biomass as a substrate and feasible pretreatment that can be used for production of biobutanol.

## 1. Introduction

Rapid depletion of reserved fossil fuel and uncertain prices of crude oil have become of prime concern among society and this scenario has attracted many researchers and technologists to figure out biofuels as an alternative fuels. According to recent Energy Information Administration (EIA) reports, renewable energy contribute to 10% of energy consumption with 46% utilization of biomass as shown in Fig. 1 [1]. In the past 10 years, fuel obtained from renewable resources has become one of the primary energy consumption and it is expected to used more renewable energy in the future [2].

Bioethanol is primary biofuel that already being used in several countries such as United States of America (USA) and Brazil. However, among the renewable fuels, biobutanol is capable to replace gasoline and can be used as fuel in the vehicle without altering the internal combustion engine [3,4]. Traditionally, biobutanol is produced via Acetone-Butanol-Ethanol (ABE) fermentation while, Butanol can be produced through petrochemical route [5]. Biobutanol offers several advantages that make it superior to bioethanol. It has been reported that, Butanol has higher energy content than ethanol due to doubling of carbon atoms and higher boiling point that cause Butanol to spend more time to be burned in engines [6]. Table 1 shows physical and chemical properties of Butanol as compared to other hydrocarbon fuel sources.

Despite scarcity of fossil fuels in future, environmental issues such as global warming and emission of greenhouse gases (GHG) also make biobutanol purported as next generation of eco-friendly fuels. This is because biobutanol capable to reduce efflux of carbon to the atmosphere [11].

Biobutanol is a product from anaerobic biological process called ABE fermentation, which converts sugar by using genus Clostridia into Butanol, Acetone and Ethanol in a ratio of 6:3:1, respectively. In this process, genus Clostridia such as *Clostridium acetobutylicum, Clostridium beijerinckii, Clostridium saccaroperbutylacetonicum* and *Clostridium saccharoacetobutylicum* showed significant activity for synthesis of Butanol with higher yields [12].

Another pivotal features for biobutanol is the selection of carbon sources as a biomass. Biomass from the first generation are the food crops such as sugarcane, maize and cereal grains, while non-edible biomass is classified into second generation feedstock which are lignocellulosic materials that can be obtained from agricultural residues. Meanwhile, there are also several studies using algae as third

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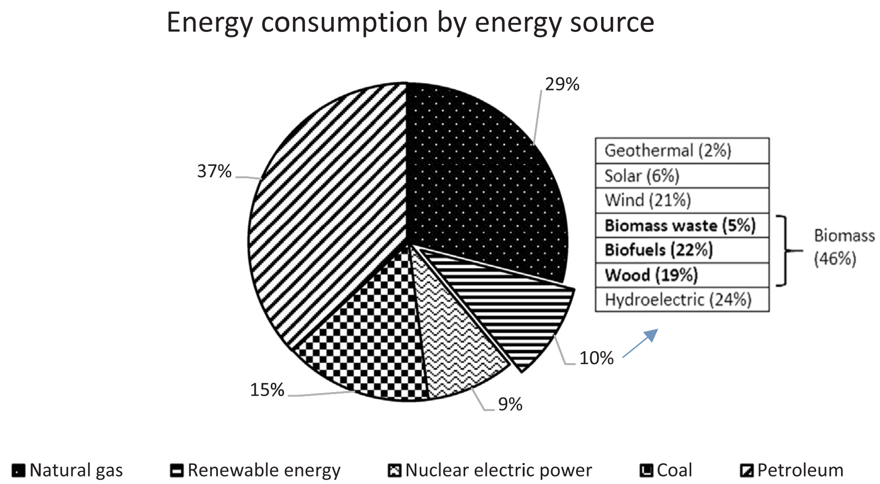


**Fig. 1.** Primary energy consumption [1].

**Table 1**
Chemical and physical properties of Butanol compared to other fuels [7–10].

| Properties | Butanol | Ethanol | Methanol | Gasoline |
|---|---|---|---|---|
| Molecular formula | $C_4H_9OH$ | $C_2H_5OH$ | $CH_3OH$ | $C_4$ - $C_{12}$ |
| Molecular weight | 74 | 46 | 32 | 95–120 |
| Mass composition of C, H,O (%) | 65,13.5, 21.5 | 52,13,35 | 37.5,12.5,50 | 86,14,0 |
| Boiling point (°C) | 118 | 78 | 65 | 200 |
| Freezing point (°C) | - 89 | - 114 | - 97 | - 40 |
| Density (kg/m$^3$) | 810 | 790 | 796 | 760 |
| Heat of vaporization (MJ/kg) | 0.43 | 0.92 | 1.20 | 0.36 |
| Energy density (MJ/L) | 30 | 19 | 16 | 32 |
| Air: fuel ratio | 12 | 9 | 7 | 15 |
| Cetane no | ~ 25 | 5–8 | 3.8 | 5–20 |
| Rating octane number (RON) | 96 | 107 | 106 | 95 |
| Motor octane number (MON) | 78 | 89 | 92 | 90 |
| Lubricity (μm) | 591 | 1057 | 1100 | – |
| Flash point (°C) | 35 | 13 | 12 | − 42 |
| Auto-ignition temperature (°C) | 397 | 423 | 463 | 257 |
| Oxygen content (%) | 22 | 46 | 50 | 95–120 |

generation feedstock to produce biobutanol [13,14]. In addition, current trend in biofuel production has also introduced fourth generation of biofuel by using photobiological solar fuels and electrofuels [15].

Among the substrates used, wastes derived from agriculture have been widely used for the past few years. Debate regarding the diversion of crops to produce biofuel increases the food price and may become major cause of food shortage crisis for several countries. From previous works, common agricultural waste from corn, rice and wheat are being utilized. The trend for selection of substrate used by researcher are shown in Table 2. The summary shows that the exploration of novel agricultural feedstock for biobutanol production will bloom in the future. Therefore, this review will provide information for all types of agricultural residue that are viable as a substrate together with the recent promising pretreatment processes used to enhance production of fermented sugar for biobutanol production.

## 2. Production process

### 2.1. Petrochemical and fermentation process

In petrochemical route, n-butanol or also known as butyl alcohol can be produced by using three industrial process which are propylene oxo synthesis, conversion of n-butanol from ethanol and the Reppe synthesis. Among these method, oxo synthesis is mostly being used by industry as the feed streams are propene, syngas and catalyst. This method involved hydroformylation of propylene followed by hydrogenation of the formed aldehydes with addition of catalysts such as cobalt (Co), Rhodium (Rh) or Ruthenium (Ru) [27]. This method has been discovered since 1938 by Otto Roelen and have been used for decades with improvements and modifications to ascertain the efficiency of the process. For example, traditional oxo-synthesis used high pressure with addition of Co-catalyst which yield 75% n-butanol and 25% isobutanol. Meanwhile, latest discovery shows that 95% n-butanol with 5% isobutanol can be achieved by using low pressure in the presence of Rh-catalyst [28].

Prior to the rise in petrochemical route, ABE fermentation was firstly discovered by Louis Pasteur on 1861. However, exploitation of this fermentation begin on 1916 when Chaim Weizzman successfully isolate *Clostridium acetobutylicum* that capable to produce large amount of acetone with butanol and ethanol. The substrate used in ABE fermentation were molasses and after World War II, this fermentation become non-profitable. As a results, many ABE fermentation pilot plants were closed due to cheap oil prices that favored the petrochemical production [5]. As the demand for energy together with environmental concern begin in the past few decades, ABE fermentation have been revamped as well recognition of biobutanol as a next generation of biofuels.

It has been reported that petrochemical process is much cheaper than ABE fermentation process where the cost of production were $1.52/kg and $1.87/kg n-butanol, respectively [29]. Other than that, study by Uyttebroek et al. [27] compare the material efficiency and energy input of both process. It was found that, material efficiency in oxo synthesis process was 92% and its energy input was 69 GJ/ton. Meanwhile, material efficiency in fermentation within range of 27–42% while the energy input increase to 116 GJ/ton. For petrochemical route, research on appropriate catalyst is required to produce high yields of n-butanol, while in fermentation process, selection and modification of bacterial strain is required to tolerate with high titer of biobutanol. Generally, both process are important for future generations as it is a precious resources available in the world.

### 2.2. Current status of biobutanol production from various countries

Currently, research on biobutanol production increase widely in terms of commercialization, research and developments (R&D) as well as production of biobutanol in pilot-scale study. Table 3 listed out the top company associated with biobutanol production from various countries. In Scotland, biobutanol derived from whiskey production has been test without any modification made on the car [30]. Meanwhile, Europe leading with mega project known as “The ButaNext Project” where this project aims to make biobutanol as renewable fuel alternatives for Europe with environmental benefits as well as bring the latest innovations an developments [31]. Besides, National University