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Biobutanol production: Challenges and prospects

Shelly Rana and Parul

Abstract

The potential of renewable biomass as a source of liquid and gaseous biofuels is the current topic of interest among scientists and researchers, but as yet there is no commercial system for the economical production of biofuel. However, the mainstream research has only focused on the production of fuels from microalgae rather than from macroalgae. This article briefly reviews about the history of butanol production from various different biomasses and microorganisms employed for its generation via fermentation. The techniques and processes through which energy may be extracted from macroalgal biomass have been discussed. The review ponders upon the feasibility analysis of butanol when used as a fuel and explores the various aspects which hinder its production.

Keywords: biofuel, butanol, fermentation, macroalgae, renewable

Introduction

The principle energy requirement of a developing country like India to achieve its objectives with a huge population of over a billion, are electricity and transport fuels like diesel and petrol. The energy demands in various fields such as agriculture, industry and transport are increasing day by day. According to the statistics published in BP Statistical Review 2016, the growth in global primary consumption of energy remained low in 2015; and the fuel mix has gone from coal towards lower-carbon fuels. The growing demand of petroleum products and growing burden on the economy of the country for fuel has necessitated the need for searching alternatives sources of fuel. Another issue is the GHG (Green House Gas) emissions due to increasing consumption of diesel and petrol in India. India ranks amongst the top 5 contributors to carbon dioxide gas emissions according to EIA Statistics.

Figure 1.1 shows the different routes for the production of butanol.

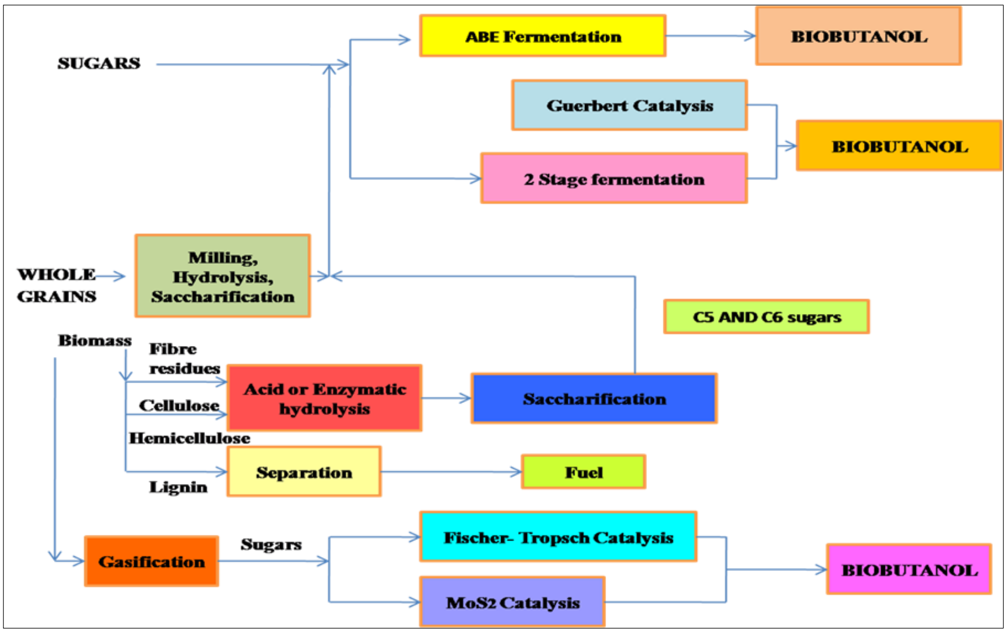

Fig 1.1: Routes for biobutanol production

Recently the attention has been shifted towards the use of Biofuels as an alternative source of energy production due to their several advantages. The growing demand for the use of renewable resources as raw materials in addition with advancements in biotechnology through genetic and metabolic engineering is creating curiosity in butanol production through fermentation. This article reviews the various aspects involved in the generation of butanol by clostridia and the utilization of biobutanol as a fuel for internal combustion (IC) engine.

Bio-butanol as a fuel offers several attractive characteristics as a transportation fuel over its counterparts. The ABE fermentation process has been discovered for the generation of butanol although the process had several limitations in comparison to other processes like Aldol condensation. To tackle these constraints researchers are carrying out several studies in developing butanol fermentation by genetic manipulation of microorganisms. The review also throws light about biobutanol as a fuel, its properties and its various advantages. The fermentation techniques for the production of biobutanol are being discussed along with the various substrates and microorganisms which have been used for its generation.

2. ABE fermentation

2.2. Microbial Cultures for ABE Fermentation

There are several number of clostridial cultures found to be producing solvents acetone, butanol and ethanol, with altering proportions through ABE fermentation process. The clostridial strains majorly have four species namely *Clostridium acetobutylicum, Clostridium saccharobutylicum, Clostridium beijerinckii,* and *Clostridium sachharoper butylacetonicum* (Keiss *et al*., 1995, Jones *et al.*, 2001) [27, 25]. Table 2.1 culminates the various clostridial strains producing butanol.

Table 2.1: Butanol yield from different clostridial strains

Species	Substrate	Yield (g/L)	Reference
C. beijerinckii DSM 6423	Wood	10.3	Survase *et al*., 2013 [57]
C. beijerinckii DSM 6423	Sugarcane bagasse	9.5	Survase *et al*., 2013 [57]
C. beijerinckii DSM 6423	Wood pulp	10.3	Survase *et al*., 2013 [57]
C. acetobutylicum	Lactose	4.59	Napoli *et al*., 2010 [42]
C. acetobutylicum	Cotton towel	12.3	Chen *et al*., 2013 [8]
C. beijerinckii BA101	Soy molasses	8	Qureshi *et al*., 2008 [46]
C. acetobutylicum IFP904	Jerusalem antichoke	14.8	Marshal *et al*., 1985
C. acetobutylicum P262	Sago starch	16	M.S. Madiha *et al*., 2001 [38]
C. beijerinckii P260	Wheat straw	12	Naseeb Qureshi *et al*., 2007 [47]
C. beijerinckii P260	Barley straw	18	Naseeb *et al*., 2010
C. acetobutylicum	Xylose	6.81	Chen *et al*., 2013 [8]
C. beijerinckii ATCC 55025	Hydrolysate of wheat bran	8.8	Liu *et al*., 2010 [35]
C. beijerinckii NCIMB 8052	Maize stock juice	0.27	Wang *et al.*, 2011 [59]
C. sporogenes BE01	Rice straw	3.49	Gottumukkala *et al*., 2013 [16]
C. saccharoperbutylacetonicum N1-4	Rice straw	6.6	Chen *et al.*, 2013 [8]
C. pasteurianum	Glycerol	8.8	Khanna *et al*., 2013 [29]
C beijerinckii NCIMB 8052	Corn cob	8.2	Zhang *et al*., 2012 [61]
C. acetobutylicum CICC 8008	Corn straw	6.2	Lin *et al*., 2011 [34]

2.3. Substrates for ABE Fermentation

The ABE is not a commercially viable process without a cheap and easily available substrate (Kheyrandish *et al*., 2015) [30]. The most widely available substrates for ABE fermentation are lignocelluloses because sources like agricultural wastes (rice straw, bagasse, molasses, etc) (Amiri and Karimi *et al*., 2015) [3]. However, the major limitation of using lignocellulosic substrates is the difficulty to produce fermentable sugar from them, as it is difficult to breakdown their structures and the enzymes used to hydrolyse their structure are very costly (Shafiei *et al.*, 2013) [54]. Thus it is imperative to introduce strategies to bring down the cost of the pretreatment process (Boonsombuti *et al*., 2015) [6]. Table 2.2 shows the different biomasses for the production of butanol. Thus, special care should be taken in selection and optimization of the pretreatment processes (Ding *et al*., 2015) [11].

Table 3.2: Production of butanol from various types of different biomass.

Biomass	Microbes	Butanol conc. (g/L)	Reference
Corn fiber	*C. beijerinckii*	13	Qureshi *et al*., 2007 [47]
Barley straw	*C. beijerinckii*	13.62	Qureshi *et al*., 2010 [48]
Potato starch	*C. acetobutylicum*	0.17	Yen *et al*., 2011
Whey	*C. acetobutylicum*	12.0	Stoeberi *et al*., 2011
Algae	*C. sachharoperbutylacetonicum*	5.61	Ellis *et al.*, 2012
Seaweed	*C. acetobutylicum*	10.4	Huesemann *et al*., 2012 [21]
Datepalm fruit	*C. acetobutylicum*	7.90	Abd-Alla *et al*., 2012 [1]
Palm Kernel Cake	*C. sachharoperbutylacetonicum* N1- 4	3.05	Hafiza *et al*., 2014 [17]
Cassava flour	*C. beijerinckii*	23.98	Tinggang Li *et al*., 2015 [58]
Corn starch	*C. beijerinckii BA101*	18.6	Ezeji *et al*., 2007 [14]
Food waste	*Clostridium beijerinckii P260*	9.2	Haibo Huang *et al*., 2015 [18]

Cassava	*C. beijerincki, C. tyrobutyricum*	6.6	Li *et al.*, 2013 [32]
Oil palm sap	*C. acetobutylicum DSM 1731*	14.4	Komonkiat *et al.*, 2013
Barley liquor	*C. acetobutylicum DSM 1731*	9.0	Yang *et al.*, 2014 [37]
Glycerol	*C. acetobutylicum KF 158795*	13.57	Yadav *et al.*, 2014 [52]
Rice straw	*C. sporogenes BE01*	5.52	Gottumukkala *et al.*, 2013 [16]
Spoilage palm fruits	*C. acetobutylicum ATCC 824*	21.56	M.H. Abd- Ala *et al.*, 2012 [1]
Oil palm trunk fibre	*C. beijerinckii TISTR 1461*	10	Komonkiat *et al.*, 2013
Seep weed	*C. acetobutylicum ATCC824*	3.5	Wang *et al.*, 2013 [60]
Crystalline cellulose	*C. thermocellum+ C. saccharoperbutylacetonicum N1-4*	7.9	Qureshi *et al.*, 2008 [46]
Corn cob	*C. beijerinckii NCIMB8052*	5.6	Hipolito *et al.*, 2007 [19]
Wheat straw	*C. acetobutylicum ATCC824*	7.05	Qureshi *et al.*, 2008 [46]

2.3.1. Macroalgae as substrate

Macroalgae are multicellular marine algae which cultivates near-shore plantations all over the world. The interest in macroalgae cultivation and its use for the generation of fuels in the past few years was reinitiated by the European countries, Japan and Korea. *Sargassum* is another free floating species found in the ocean and thus can be used for the generation of biofuel. In Japan the investigation of the cultivation of *Sargassum fulvellum* and the production of ethanol from it was initiated by the Ocean Sunrise Project. The Central Salt and Marine Chemicals Research Institute had researched on the generation of ethanol from *Kappaphycus alvarezii*. Another ethanol conversion technology has been developed in Denmark, from *Ulva lactuca* found abundantly in Denmark (Huesemann *et al.*, 2010) [20]. The Marine Biomass (BioMara) Project in Ireland and the United Kingdom investigated the feasibility of using macroalgae for ethanol production. Figure 2.1 shows the processes used for the production of Biobutanol from macroalgae.

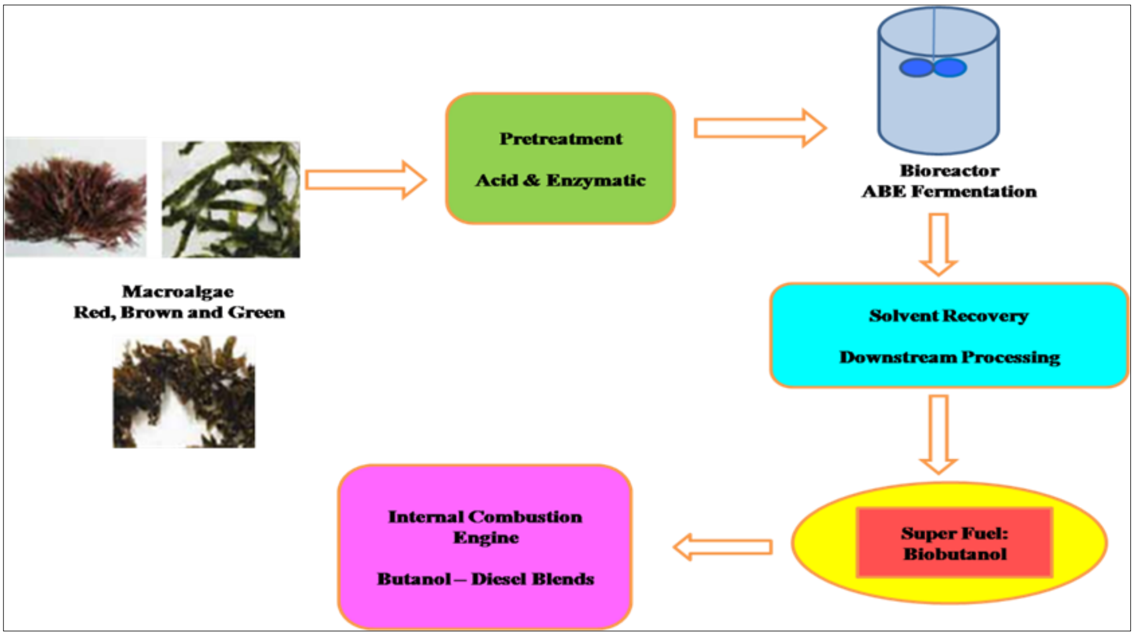

Fig 2.1: Scheme for production of Biobutanol from macroalgae

Macroalgae has the following advantages when used for biofuel synthesis:

1. Macroalgae is found to have higher product yields in comparison to traditionally used biomasses.
2. Macroalgae has higher carbohydrates and lower lipid and protein content which form potential feedstock for the production of liquid biofuels (DuPont *et al.*, 2009) [12].
3. Macroalgae do not compete with food crops for the availability of land.
4. Macroalgae helps in the reduction of CO_2 emission having a positive environmental effect.

3. N-Butanol: A super biofuel

Alcohols are being used as fuel for internal combustion (IC) engines since a very long time. For example alcohols like butanol, methanol and ethanol are used as alternative liquid fuel and can be derived from chemical and biological sources (Pradeep Dey *et al.*, 2013) [45]. A highly demanded entrant alcohol for employment as a fuel in a diesel engine is n-butanol which is an aliphatic alcohol with a straight-chain structure with a carbon terminal having a –OH group (Jin C *et al.*, 2010) [24]. N-butanol has several properties which makes it a superior choice to be used as a renewable biofuel. It has higher energy content, is less hydrophilic, has higher viscosity, high cetane number, and has higher miscibility and lower vapour pressure than other liquid alcohols, making it additionally favourable for usage as a fuel with blends of diesel. In the year 2007, BP and DuPont started up a collaboration to restart the production of butanol as a biofuel. In 2009, both these companies started up a joint enterprise, called Butamax TM, in Delware, USA (Butamax Advanced Biofuels LLC.). In 2012, a few more companies like Gevo and Green Biologics also went ahead to produce butanol by biological means. With further research an increasing number of new strains were isolated and efficient methods developed for the production of butanol.

Frassoldati *et al.*, 2012 [15] discussed the importance of butanol as a prospective substitute for other fuels in the industry. The research then throws light on the detailed directions involving the chemistry of butanol combustion (Sang Yup Lee *et al.* 2008) [53]. Studies carried out by Mahdi Shahbakhti *et al.*, 2010 [39] reached to a conclusion that butanol is a potential fuel used as a substitute for traditional fuels like petrol and diesel. Kenneth R. Szulczyk *et al.*, 2010 [28] examined ethanol and butanol as fuels for engines powered on gasoline.

3.1. Challenges in biobutanol production and possible solutions

The ABE fermentation process primarily involved in butanol production has various disadvantages which presently make the production of butanol at commercial scale unfavourable. The several factors contributing to making the biological production of butanol expensive include high costs of feedstock, high costs of separation methods (gButanol/gSugar consumed) (Ezeji *et al*., 2007, Aresta *et al.*, 2003) [14, 4].

There are various factors affecting the use of agricultural residues like corn stover, bagasse, rice straw and wheat straw such as the seasonal availability, deviation in the cultivation yield, land-use alteration as well as the transportation costs (Qureshi *et al*., 2008, Qureshi *et al*., 2010) [46, 48]. Among the key factors influencing the productivity of a butanol plant, feedstock cost has the most prevalent impact on the overall cost (Pfromm *et al*., 2010) [44]. Thus, the shift towards cheaper, non-edible feedstock is obligatory when we yearn to commercialize the production of butanol.

Another significant factor affecting the economics of butanol production is butanol tolerance of the bacterium used for fermentation. Low butanol productivity increases the cost of product recovery from the fermentation broth (Ezeji *et al.*, 2010) [13]. During acidogenesis, the internal pH lowers with the reduction in external pH with the development of acetic and butyric acids. It is alleged that a least amount of 10 mM butyric or acetic acid are needed to encourage the solventogenesis process. The acidogenesis and solventogenesis phase products of the ABE fermentation, causes inhibition of the process of fermentation following the attainment of a specific concentration in the media. Borden and Papoutsakis *et al.* in 2007 studied 16 genes for improving the butanol tolerance with the help of genetic engineering. Improvements in separation of butanol can be made by pertaining to non-conventional recovery methods like gas stripping, pervaporation, etc. (Jang *et al.*, 2012) [23].

4. Diesel engine

Since the primary focus of this review is on the use of butanol as a biofuel from marine macroalgae it is imperative to also study its feasibility in an engine. The combustion and emission characteristics of diesel engine need to be studied for understanding the basics of conventional diesel combustion. Direct injection diesel engine is the most prevalently used technology in recent years. The diesel engine functions on either a two-stroke or four-stroke cycle (N. Lontis *et al.*, 2011) [41]. Another feature of a diesel engine is that it can run with a combination of conventional fuel and bio fuels. The most stupendous attribute of the diesel engine is its efficiency. The diesel engine is not restricted by the problems of pre-ignition that are persistent with the high-compression SI engines as it compresses air instead of employing an air-fuel mixture. Thus, with diesel engines we are able to achieve higher compression ratios, higher theoretical cycle efficiencies in comparison to CI engines. The principal shortcoming of diesel engine is its emission of air pollutants. Diesel engines release high levels of soot, nitrogen oxides (NOx) and carbon monoxide (CO).

4.1. Brake thermal efficiency

Brake thermal efficiency (BTE) is represented as the ratio of percentage of the output and input. Huang *et al*., 2009 [22] carried out studies on engine performance of a diesel engine using 10%, 20% and 30% diesel fuels blended with ethanol. According to their work it was concluded that the brake thermal efficiencies depreciate with increasing ethanol in the blended fuels. Rakopoulos *et al*., 2010 [49] considered the effects of 5 % and 10 % diesel-ethanol blends on the emission and performance characteristics of a diesel engine. It was observed that the greater the amount of ethanol the greater is the brake specific fuel consumption. Govindarajan *et al.*, 2010 found that the brake thermal efficiency increased while the fuel consumption was reduced when the engine ran on gasoline blended with 5% butanol and 10% ethanol. A common rail diesel engine is fuelled with blends of butanol/diesel blends of M10, E10 and B20 among tested fuel demonstrated superior results in terms of engine performance. M. Krishnamoorthi *et al.*, 2016 found that 70% diesel blended with 30% isopropyl alcohol gave the best results in terms of thermal efficiency.

4.2. Brake specific fuel consumption

Brake specific fuel consumption (BSFC) is to quantify the fuel efficiency of an engine that ignites fuel and generates shaft power. In other words it is the rate of consumption of fuel divided by the power generated. M. Al-Hassan *et al.*, 2012 [36] studied the engine performance of a four stroke diesel engine with 5%, 10% and 20% ethanol-blended diesel fuels. The study noticed that the brake specific fuel consumption (BSFC) of the blended fuel was elevated in comparison with only diesel (Rakopoulos *et al*., 2008) [10]. It was seen that the BSFC of blends were higher than that of plain diesel fuel, and rises with the increase of ethanol concentration. This is due to the lower heating value of ethanol and biodiesel in comparison to diesel fuel (M. Al-Hassan *et al*., 2012) [36].

4.3. Emission studies

In view of the fact that the gases from internal combustion (IC) engines is the primary factor causing air pollution, the regulations on exhaust gas emission levels have become more stern. The gaseous pollutants primarily include carbon monoxide (CO), nitrogen oxides (NOx) and unburnt hydrocarbon (UHC). In addition

CO_2 emissions are considered to contribute to the global warming. Among the diesel engine emissions, soot and NOx are the most crucial and thus are comprehensively studied.

4.3.1. NOx emissions

Nitric dioxide and nitrogen oxide are together known as NOx. Raouf Mobasheri *et al*., 2012 [51] observed that diesel engine working on ethanol-diesel blends had noteworthy reductions in CO and NO emissions (Mahdi *et al*., 2010) [39]. Cinzia Tornatore *et al*., 2011 [9] carried out two combustion tests for fuel combinations i.e., diesel and a mixture of butanol and diesel. Increasing NOx emissions were overcome by working at a former injection timing in which a controlled regime for combustion was followed. Rakopoulos conducted tests on a bus in order to explore the mechanisms of NOx emissions during hot start with different alternative blends of fuel. In comparison to the pure diesel fuel the biodiesel blended fuel resulted in descent of emissions, on the other hand the butanol blended showed augmented NO emission. (C.D. Rakopoulos *et al*., 2010) [49]. M. Krishnamoorthi *et al*., 2016 noted that when blends of 30% ethanol, 30% n-butanol, 30% isopropyl alcohol, the NOx emissions were reduced by 7.98%, 6.62%, 11.62% respectively. In the Drive Cycle Test (Rakopoulos *et al.*, 2011) [50] conducted using 20% and 40% blends of butanol with diesel, NOx emissions decreased with higher amounts of butanol in the blend (Joshi *et al.*, 2010) [26]. Alasfour *et al.*, 1998 [2] noted that the NOx levels were reduced by 9% at low temperature while preheating the inlet air resulted in knocks and misfires. M. Krishnamoorthi *et al.*, 2016 noted that when blends of 30% ethanol, 30% n-butanol, 30% isopropyl alcohol, the NOx emissions were reduced by 7.98%, 6.62%, 11. 62% respectively.

4.3.2. Carbon dioxide and carbon monoxide emissions

The butanol/diesel blends of 10, 20, 30 and 40% were studied for engine performance and emission. It was observed that the carbon monoxide and hydrocarbon emission reduces with increase in oxygen content when blends of methanol are considered. M. Krishnamoorthi *et al*., 2016 found that diesel and alcohol blends reduced pollution and also improved engine efficiency. While using blends of 25% Ethanol, 25% n-butanol, and 30% isopropyl alcohol the CO_2 emissions are depreciated by 5%, 1.6% and 25% respectively. A common rail diesel engine can be fuelled with butanol/diesel blends between 5 – 20% with no considerable drop in engine performances. It was observed that the CO and HC emission reduces with increase in oxygen content when we consider blends of methanol, the emission for CO and HC is least for M30 almost at all operating conditions.

4.3.3. Soot production

Rakopoulos *et al*., 2011 [50] experimentally investigated on a DI diesel engine, under steady-state conditions. These studies demonstrated the valuable effects of using various different blends of diesel and n-butanol on smoke and CO_2 emissions. Again, it is the high oxygen content of n-butanol that leads to superior soot oxidation, which finally decreases the harmful emissions. For the n-butanol and diesel blended fuel, the n-butanol lowers the production of soot owing to its property of having lower viscosity and higher volatility. Kozak *et al*., 2011 [31] studied the results from a 10% n-butanol blended with 90% diesel (Bu10) and used it in a European passenger car. It was found that the fuel blend was proficient in reducing particulate emissions. A turbocharged diesel engine was studied with neat diesel fuel, a blend of 30% biodiesel with 70% diesel (B30) and a blend of 25% n-butanol / 75% diesel fuel (Bu25). The emissions decline to a larger extent for n-butanol in comparison to biodiesel blend (Armas *et al*., 2012) [5].

Kozak *et al.*, 2011 [31] reported results from a 10% n-butanol blended with 90% diesel (Bu10) and used it in a European passenger car. It was found that the fuel blend was proficient in reducing particulate emissions. Studies on the effect of n-butanol on diesel engine emissions have been carried out (Rakopoulos *et al.*, 2010, Rakopoulos C D *et al*., 2011) [49, 50]. The research came to a conclusion that through all the accelerations tested; the n-butanol blended diesel fuel emitted less smoke in comparison to neat diesel fuel operation.

A six-cylinder, turbocharged diesel engine was studied while running on neat diesel fuel, a blend of 25% n-butanol / 75% diesel fuel (Bu25), and a blend of 30% biodiesel with 70% diesel (B30). Both biofuel blends were found to decrease the emissions. The peak soot value and the smoky period both increased for biodiesel blend whereas n-butanol shows a decrease in both of them (Armas *et al*., 2012) [5].

5. Conclusions

This review demonstrates that macroalgal biomass is advantageous over other raw materials for the production of biofuels, even though it is apparent that there are noteworthy obstacles to surmount before macroalgae can be used commercially for the generation of biofuel. Among a variety of liquid fuels in the market butanol is a superior choice keeping in view its various advantages. Butanol as a fuel has been found to have higher engine efficiency and fewer harmful gaseous emissions and thus is an environmentally safe fuel.

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