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Bioengineering strategies on catalysis for the effective production of renewable and sustainable energy

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ABSTRACT

The ever increasing energy demand put forth biofuels a favorable choice over fossil fuels due to their renewability, biodegradability and generating exhaust gases of acceptable quality. Biofuels can be solid, liquid or gaseous in nature and are mainly produced from the biomass that includes biochar, bioethanol, biobutanol, biodiesel, biohydrogen and biomethane. These fuels can be produced by processing and hydrolyzing the lignocellulosic biomass derived from agricultural and forestry waste. Pretreatment and hydrolysis of these waste materials involves either thermochemical processes or biological processes. The traditional thermochemical approach involves harsh environmental conditions and the usage of strong chemicals. This may lead to the equipment corrosion, large volume of waste streams and additional problem in disposal or treatment of chemicals. So it is preferred to have low energy required enzymatic process to every possible step in the biofuel production. The steps chosen for the biofuel production and the enzymes used depend on the type of biofuel produces and the feedstock used. This review provides a complete overview of diversified sources for biofuel production and highlights the criteria for enzymes involved in various processes of biofuels. Further, the bioengineering strategies like recombinant technology and metabolic engineering for improving the efficiency of these enzymes at each possible step were discussed. Perspectives and future directions to enhance the biomass conversion to biofuels were also described.

Contents

Abbreviations: %, Percentage; °C, degree celsius; ABE, acetone–butanol–ethanol; ASTM, American Society for Testing and Materials; atm, standard atmosphere (unit); ATP, adenosine triphosphate; AXE, acetyl xylan esterase; C, carbon;
CBM, carbohydrate binding modules; CH_3OK, potassium methoxide; CH_3ONa, sodium methoxide; CMCase, carbomethyl cellulose hydrolyzing enzyme; CO, carbonmonoxide; CO_2, carbondioxide; Cu, copper; DMAPP, dimethylallyl
pyrophosphate; DMF, 2,5-dimethyl furan; DNA, deoxyribo nucleic acid; DyPs, decolourising peroxidases; EN, European standards; FAEEs, fatty acid ethyl esters; FAMEs, fatty acid methyl esters; FFAs, free fatty acids; g/l, gram per litre; g, gram; H^+, hydrogen ion; H_2, hydrogen; HBT, 1-hydroxy benzotrizole; HMF, 5-hydroxy methyl furan; h, hour; HTPs, heme thiolate peroxidases; IPP, isopentenyl pyrophosphate; IR, infrared; KOH, potassium hydroxide; l, litre; lcc, laccase gene; LiPs, lignin peroxidases; LPMO, lytic polysaccharide monooxygenase; m mol, milli mole; mM, millimolar; Mn, manganese; MnPs, manganese peroxidases; mol, mole; NADP, nicotinamide adenine dinucleotide phosphate; NADPH, nicotinamide adenine dinucleotide phosphate (reduced); NaOH, sodium hydroxide; O, oxygen; r-FHL, *Fusarium heterosporum* lipase; SO_2, sulphur dioxide; VPs, versatile peroxidases; WCCs, whole cell catalysts

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1. Introduction

Biofuels are very often described as solid, liquid or gaseous fuels from biological feedstocks and they can be used as a substitute for petroleum derived fuels [1,2]. For a decade biofuels emerged as one of the most significant alternative renewable and sustainable energy source to meet the three intertwined policies of developing world-energy security, economic development and environmental protection [3]. Especially in recent years an unprecedented increase in the production and usage of biofuel was observed [4]. According to a statistical review of world energy, a 6 fold increase was observed in the biofuel production within a decade from 2002 to 2012. Around 60.2 million tonnes oil equivalent of biofuel was produced from all over the world. 90% of the world wide biofuel is produced in North America, South America, Europe and Eurasia. India produced only around 2.94 lakh tonnes oil equivalents of biofuel production which is a mere 0.5% of the total biofuel production. Thus there is lot of scope to implement various strategies that enhance the biofuel production.

Interestingly studies by Fontes and Gilbert have revealed that 1011 t of plant biomass was found to be hydrolyzed by microbes releasing an energy corresponds to 640 billion barrels of crude oil [5]. Moreover, the conversion of cellulosic biomass to fermentable sugars also represents a viable means for the production of ethanol [6,7]. It was found that the rate limiting step in the conversion of biomass is hydrolysis of biomass. Emerging trends have indicated the crucial and pivotal role of cellulosome to combat the problem of hydrolysis during biofuel generation [8–10].

In view of meeting the fuel demand, ease of production, productivity and green process, there is a surge in the industrial interest in commercializing biomass conversion into fuels and chemicals [11]. The major hindrances to the commercialization of biofuels are the production cost, availability of the feedstock and the type of conversion process. [12,13]. The tools and techniques of biotechnology can be utilized to improve the yield of cellulosic raw materials, hydrolysis and their conversion into energy and chemicals. These improvements include faster growing of crops that are more amenable to conversion, advanced pretreatments, better enzymes which are involved in the conversion, as well as improved organisms for the production of ethanol, butanol, other alcohols, alkanes and diesel fuel substitutes [11]. This will definitely lead to the cost reduction and greener process of biofuel production.

Production of biofuels from the plant-derived lignocellulosic biomass such as agricultural and forestry residues could serve the dual role of renewable energy production and waste reduction. But due to their complex chemical nature, these materials are resistant to enzymatic and hydrolytic conversion into biofuel. Hence a pretreatment is highly recommended before an actual fermentation. Physical (milling, homogenization etc.), thermochemical (utilizing inorganic salts or alkalies) and biochemical (enzymatic) methods have been used for the pretreatment of the feedstocks to breakdown the complex lignocellulosic raw materials to cellulose. The biochemical methods are more specific in its action and does not involve any toxic compounds. The biochemical pretreatment process utilizes free or immobilized enzymes such as laccases [EC 1.10.3.2] derived from fungi such as *Anthracophyllum discolor* [14], *Pycnoporus sanguineus* [15], *Trichoderma harzianum* [16] etc. and peroxidases derived from bacteria such as *Legionella pneumophila* [17].

Pretreatment is often followed by hydrolysis of lignin degraded biomass feedstock to fermentable sugars. The cellulosic biomass can be hydrolyzed by using acid [18], alkaline [19,20] or enzymatic [21] method. The harsh environmental conditions and the purification steps involved with the acid and alkaline treatments can be avoided by enzymatic hydrolysis. Enzymatic conversion relies on the sequential and synergistic action of several enzymes, such as endogluconase, exogluconase, β-glucosidase and xylanase. The obtained hydrolysate containing very large amounts of monomeric sugars, such as glucose and xylose can be used for the production of biohydrogen, biomethane, bioethanol and various other high valuable products [22,23].

Oil rich seeds, nuts, recovered waste vegetable and animal fats are also used as raw material for the biodiesel production [24]. Oil extracted from theses sources can be simply converted into biodiesel by several methods like blending, micro emulsification, pyrolysis and transesterification [25]. The most attractive and widely prevalent method is the transesterification of animal and vegetable fats from the most widely distributed feedstocks including rapeseed, soybean, sunflower seed, palm oil and Jatropha [3]. The conventional method of transesterification involves homogenous base catalysts (NaOH and KOH) and mild heating (50–60 °C). The modified process involves heterogeneous base catalysts as well as enzymatic protocols [25]. The hydrolysis, synthesis of ester and transesterification in the presence of lipases–glycerol ester hydrolases is the most promising processes in the biodiesel production [26]. Oil extracted from microalgae is another potential source of biomass for the production of biodiesel and is found to be less economic when compared with other sources. These algal feedstocks can be used directly to generate energy by combustion after drying or it can be processed to liquid and gaseous biofuels by biochemical and thermochemical conversions [27]. This review explains about various aspects on biofuel production with special emphasis on biofuels obtained from lignocellulosic trash and green process of biofuel production by considering biological catalysts at each possible step. Bioengineering strategies like metabolic engineering and recombinant technology that holds a promise for industrial applications have been discussed.

2. Classification of biofuels and their production strategies

Based on the nature, source, production techniques and development stages biofuels were classified into several ways [1,28,29].