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Bioconversion technologies of crude glycerol to value added industrial products

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ABSTRACT

Crude glycerol that is produced as the by-product from biodiesel, has to be effectively utilized to contribute to the viability of biodiesel. Crude glycerol in large amounts can pose a threat to the environment. Therefore, there is a need to convert this crude glycerol into valued added products using biotechnological processes, which brings new revenue to biodiesel producers. Crude glycerol can serve as a feedstock for biopolymers, poly unsaturated fatty acids, ethanol, hydrogen and *n*-butanol production and as a raw material for different value added industrial products. Hence, in this review we have presented different bioconversion technologies of glycerol to value added industrial products.

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1. Introduction

Nowadays, people are busy in inventing new machines and instruments which need a lot of energy for running their application, these energies that are supplied naturally, biologically, chemically, electrochemically or physically. One of these is petroleum and its products like petrol, diesel, gasoline, etc. These have certain drawbacks like they have created global ecological disturbance [1]. So this has resulted in the emergence of eco-friendly, alternative fuel biodiesel. There are many types of feedstock for its production of oils and fats [2]. Biodiesel can be defined as long chains of alkyl esters, which are formed by transesterification of triglycerides with alcohol that results in glycerol as a waste product [3]. It is estimated that the biodiesel market will reach to 37 billion gallons by 2016 with an annual

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growth of 42% which is indirectly producing 4 billion gallons of crude glycerol as a byproduct 10 kg of glycerol (crude) will be produced from for 100 kg of biodiesel [4]. The scheme of events for biodiesel production through transesetrification reaction is depicted in Fig. 1 [5].

The up gradation of biofuel byproduct facilitates the added value of the economy of the process; moreover it falls under 4th generation biofuel strategy of minimum waste production in the process. Crude glycerol up gradation to value added products impinges a substantial effect on the economy of the biodiesel sector. Purification of crude glycerol is a cumbersome and hence utilization of crude glycerol as intact as source for any industrial product is a value added approach. The abundant surplus of glycerol from biodiesel production, makes the utilization of glucose more expensive while compared with crude glycerol. Furthermore, glucose competes directly with food and feed production, which is not the case for glycerol [6]. Glycerol has a greater degree of reduction than does sugars, and it is also cheaper and more readily available. In comparison with glucose fermentation, the almost exclusive synthesis of reduced products during glycerol fermentation reflects the highly reducible state of glycerol. Conversion of glycerol to phosphoenolpyruvate, or pyruvate, generates twice the amount of reducing equivalents than does producing pyruvate from glucose or xylose. As an example, glycerol fermentation produced ethanol and formic acid (or ethanol and hydrogen) with overall a yield of twice that of glucose fermentation since half of the glucose lost as carbon dioxide during bioconversion of glucose. Moreover, utilization of crude glycerol also alleviates the carbon catabolic repression/glucose effect present in case of glucose utilization. In case of carbon catabolite repression, the presence of a rapidly metabolizable carbon source such as glucose inhibits the expression of genes encoding proteins required for the utilization of alternative carbon sources such as glycerol and lactose etc. [7]. Glycerol has many uses in the different type of industries like pharmaceutical, soaps, food, paint, cosmetics, toothpaste [8]. There are many microbes that can metabolize glycerol aerobically and few microbes are able to metabolise it anaerobically, so none of them is used at industrial scale. *Escherichia coli*,*Klebsiella*, *Enterobacter*, *Glucanobacter*, *Clostridium*, *Candida, Aspergillus* can convert crude glycerol into value added products [9]. About 10 kg of biodiesel produces glycerol equivalent to 1 kg. The production cost of biodiesel increases by $0.021/L for every $0.22/kg reduction in glycerol selling price [10].

2. Bioconversion technologies of glycerol to value added products

The left unattended crude glycerol from the biodiesel industry is also a threat to environment. Hence conversion to other value added products through biological routes with the aid of microbes is a viable resource and which subsequently enhances the economy of the process. Different value added products from crude glycerol have been summarized as follows.

2.1. 1,3-Propanediol [$CH_2(CH_2OH)_2$]

This three carbon diol is a colorless viscous liquid used to produce polymers such as polytrimethylene terephthalate (PTT). It is used widely to produce aliphatic polyesters, co-polyesters, adhesives, composites, coatings, moldings, laminates, wood paints, and antifreeze [11]. 1,3-PDO have been reported to be produced by a recombinant strain of *E. coli* which was constructed by transferring DhaB1 (B12-independent glycerol dehydratase) and its activating factor DhaB2 from the species *Clostridium butyrium*. The overall yield, concentration and overall productivity of 1,3-PDO was 1.09 mol/mol, 104.4 g/L and 2.61 g/L/h respectively [12]. Bacteria *Citrobacter freundii* (DSM 15979) is another potential candidate for 1,3-PDO production through fed-batch fermentation [13]. *Klebsiella oxytoca* converts biodiesel derived crude-glycerol into 1,3-PDO by creating a lactate deficient mutant (LDH3) under batch and fed-batch fermentation conditions, the yield and productivity increased to 0.53 g/mol from 0.41 and 0.83 g/L/h from 0.63 respectively. In fed-batch fermentation, ethanol is formed along with 1,3-PDO with an initial glycerol concentration of 126 g/L [14].

2.2. Hydrogen [H_2]

Hydrogen, the only fuel to produce water as a by-product is seen as an ideal fuel for the future that can be produced in an eco-friendly manner. Crude glycerol serves as a raw material for

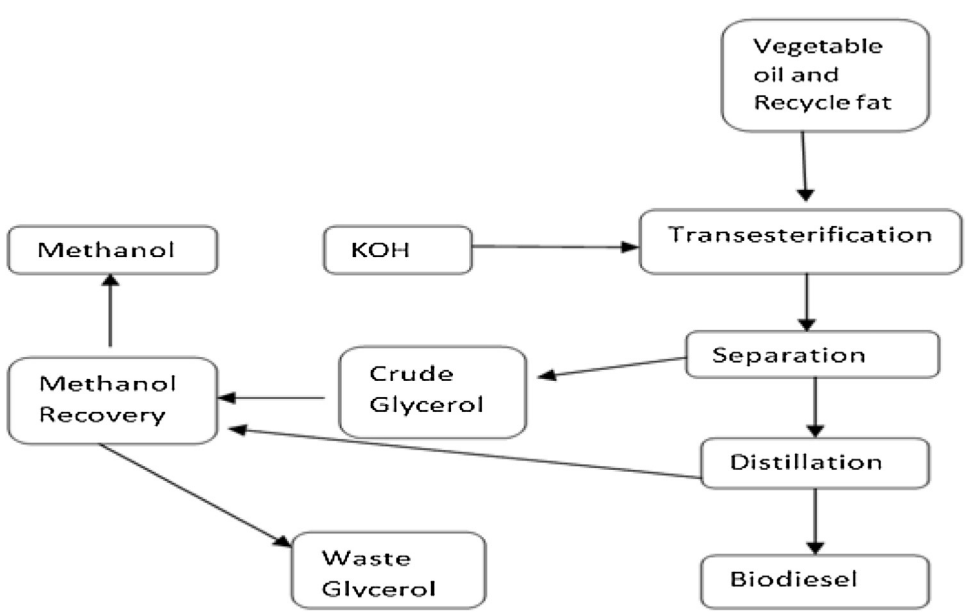

Fig. 1. Biodiesel production through transesterification reaction.