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Green deep eutectic solvent assisted enzymatic preparation of biodiesel from yellow horn seed oil with microwave irradiation

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ABSTRACT

In this study, biodiesel was produced from yellow horn seed oil through transesterification using immobilized enzyme Novozym 435 in green deep eutectic solvents (DESs) medium with microwave irradiation method. Eleven DESs were prepared, DES-2 (molar ratio chloride/glycerol 1:2) was proved to be the most effective solvents. Under the optimum conditions, 8% dosage of Novozym 435, methanol/oil ratio 6:1, microwave power 400 W, temperature 50 °C, and reaction time 120 min, 95% conversion yield was achieved. Furthermore, recovered enzymes were used for four successive reaction cycles without any significant loss of enzyme activity. The usage of DES could greatly retain the enzyme activity, increase conversion yield, and make it easy to separate the product. In general, preparation of biodiesel with enzyme in green DESs would be an alternative for traditional transesterification method.

1. Introduction

Nowdays, biodiesel has become more attractive as a perfect alternative for conventional fossil fuel because biodiesel is environmentally friendly and is made from renewable resources [1]. Biodiesel is composed of fatty acid methyl esters (FAMEs) and usually prepared through the transesterification of vegetable oils or animal fats. The most commonly used oils are rapeseed, soybean, sunflower, palm, cotton seed and *Jatropha*. However, the high-cost feedstock and increasingly aggravating tension between energy crisis and food security became great challenges for biodiesel production [2]. The use of non-edible seed oils can not only increase supply at relative lower cost but also avoid the food versus fuel problem. Seed oil from yellow horn (*Xanthoceras sorbifolia* Bunge.) contains 85–93% unsaturated fatty acids and is of low acid value, also yellow horn is not major food crop, therefore it has great potential to be used in biodiesel industry [3]. In the present, transesterification of yellow horn seed oil to biodiesel is mainly catalyzed by homogeneous catalysts, including strong bases like alkali hydroxides, methoxides or homogeneous acids like sulfuric acid, phosphoric acid [4,5]. Although the conversion yield is superior, the process is commonly time-consuming and energy-wasting [6]. In addition, the separation process of aforementioned catalysts from biodiesel products is complicated and often disturbed by saponification of triglycerides [7,8]. Therefore, a new method for transesterification of yellow horn seed oil to biodiesel, which is more efficient, more economical and easier to separate catalysts from products, should be brought out for the wider application in industry.

Recently, the enzymatic transesterification manifests more advantages, such as mild reaction conditions, low energy cost, simple purification process, the reusability of enzymes, selectivity in enzymes for different substrates, as well as allowing a small amount of water in substrates, etc. [9–11]. On the basis of this, enzymes is successfully combined with ionic liquids (ILs) to catalyze the transesterification of vegetable oil [12,13]. In recent years, to overcome the weakness of ILs, like expensive cost and potential toxicity, deep eutectic solvents (DESs) attract much attention to be an alternative solvents [14,15]. DES is formed by mixing a solid organic salt (such as choline chloride) and a hydrogen bond donor (HBD, such as glycerol and urea) which form a eutectic with a melting point much lower than that of the individual components. It is mainly

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due to the generation of intermolecular hydrogen bonds between the components. DESs have properties similar to those of ILs, such as high thermal and chemical stabilities, low vapor pressure, low flammability, and high solvation capacity. In addition, they have many advantages over ILs such as low price, high biodegradability and low toxicity [16–18]. In enzymatic production of biodiesel: (1) DESs can be perfectly compatible with both methanol and oil, a pseudo-homogeneous can formed in the reaction; (2) DESs have excellent enzymes compatibilities, they can stabilize the active structure and function of enzymes; (3) DESs have temperate viscosity, mass transfer are enhanced so as to easier access of substrates to the enzymes [19,20]. DESs was reported to exhibit considerable effect on the enzymatic production of biodiesel from soybean oil [21], however tree born oil with relative low acid value like yellow horn seed oil has not been studied yet.

Transesterification of plant oils should be performed at heating condition, however by conventional heating methods whether catalyzed by homogeneous or heterogeneous catalysts, it takes much longer reaction times and requires a high reaction temperature [22,23]. Recently, microwave irradiation is a new technology which is widely used in green chemistry field [24]. Compared with the conventional heating method, microwave irradiation is clean, fast, convenient and energy-saving [25,26]. It was even reported that microwave irradiation could be 1000 times faster than conventional method [27]. Enzymatic transesterification in ILs under microwave irradiation has been already proved to be of high conversion yield, because ILs have excellent microwave absorbing ability, which enhances the reaction rate mostly [28,29]. Therefore, DESs are also expected to have apparent effect for the transesterification under microwave irradiation because of their similar properties and molecular components with ILs. Up to our knowledge, the combination of the microwave irradiation technology and enzymatic transesterification in DESs together to produce biodiesel from yellow horn seed oil has not been reported yet.

Herein, in the present study we developed the approach for the immobilized enzyme Novozym 435 transesterification in DESs to produce biodiesel from yellow horn oil under microwave irradiation. The effects of several reaction variables, such as DESs types, methanol/oil molar ratio, enzyme dosage, microwave power, temperature and reaction time were examined. Besides those

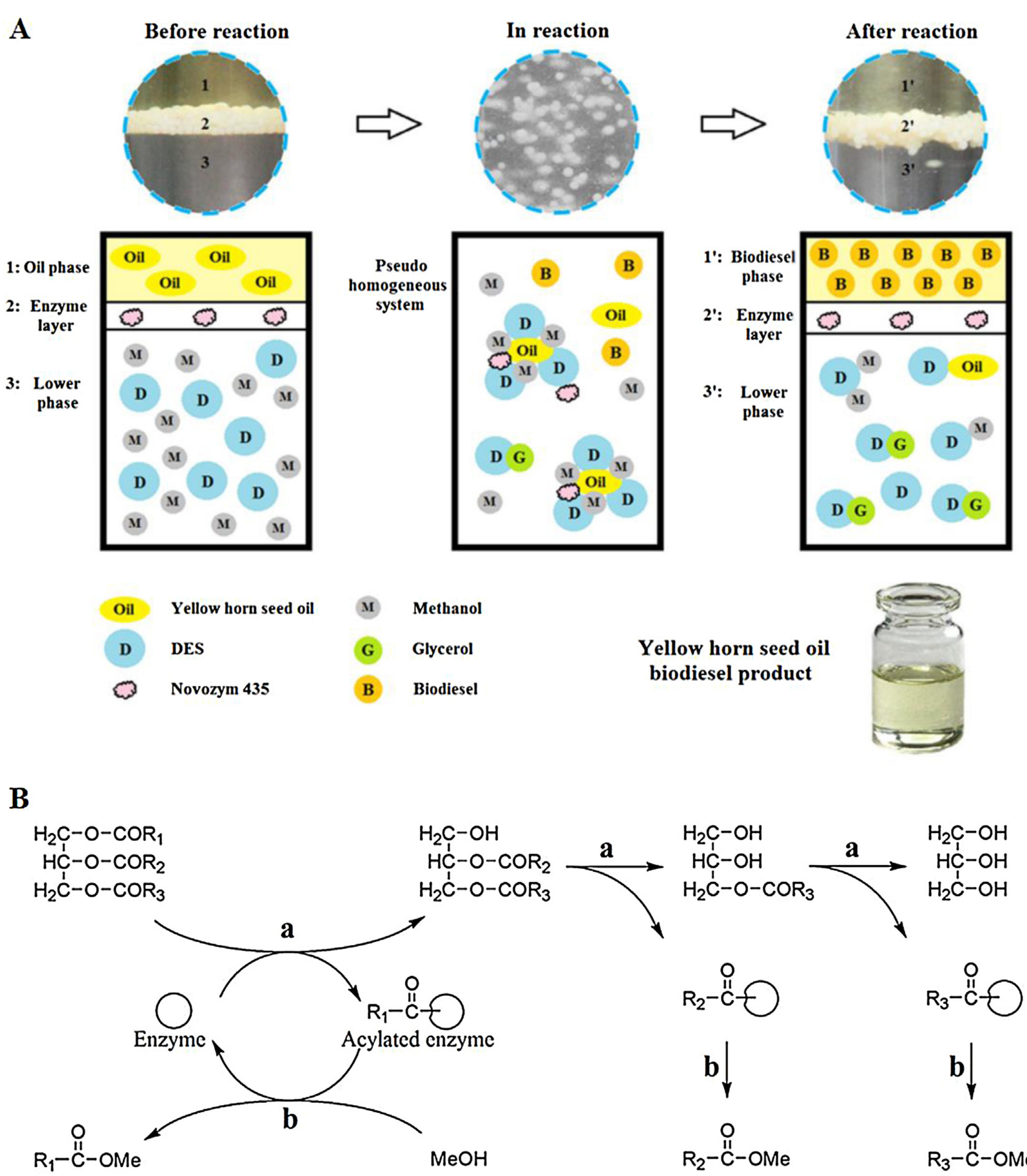

Fig. 1. Schematic illustration of biodiesel preparation process (A), and mechanism of enzymatic transesterification reaction (B).