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Biodiesel production from castor plant integrating ethanol production via a biorefinery approach

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ABSTRACT

Biodiesel, a promising alternative fuel, is not a completely renewable fuel, as it currently uses oil-based methanol for its industrial production. Integrated biodiesel and bioethanol production in a biorefinery unit can overcome this challenge together with an improved economy. In this study, castor plant was applied to an integrated biodiesel and ethanol production. The extracted oil was transesterified with ethanol produced through simultaneous saccharification and fermentation of the castor plant residue. An alkaline pretreatment using 8% w/v sodium hydroxide at 100 °C for 60 min was applied to improve the ethanol production yield from 27.2 to 71.0%. An experimental design using response surface methodology (RSM) was used to optimize the biodiesel production yield. The optimum biodiesel yield was 85.0 ± 1.0%, obtained at 62.5 °C using an ethanol to oil mass ratio of 0.29:1 for 3.46 h, which was in agreement with the predicted yield (84.4%). Accordingly, 1 kg of castor plant resulted in production of 149.6 g biodiesel and at least 30.1 g ethanol as the final products with no extra alcohol feedstock requirement.

1. Introduction

Biodiesel has attracted a great deal of attention over the last few decades due to its environmental compatibility and biodegradability (Aarthy et al., 2014; Reyero et al., 2014). Transesterification of triglycerides using methanol in the presence of an alkaline catalyst is the most common process for biodiesel production (Haigh et al., 2014; Perdomo et al., 2014). Ethanol can be used as a harmless substitute for methanol in transesterification reaction besides its individual application as a renewable alternative fuel. Furthermore, ethanol is produced through the fermentation of renewable biomass while methanol is industrially produced from fossil fuel sources. However, the production of methanol from biomass with an integrated biorefinery prospective has been widely studied (Ng and Sadhukhan, 2011; Martinez-Hernandez et al., 2014). Therefore, biodiesel production using bioethanol results in a completely renewable biofuel (Lam and Lee, 2011). Global biodiesel and ethanol production were about 25 and 87 billion liters in 2010, respectively, predicted to correspondingly increase to over 58 and 161 billion liters by 2020 (Pinto, 2011). According to the U.S. Department of Energy, ethanol, biodiesel, and regular diesel prices were around $0.42, $1.06, and $0.82 per liter at the beginning of 2015, demonstrating that biodiesel still cannot compete with diesel in the market (U.S. Department of Energy, 2015). Over 70% of biodiesel cost is correlated to oil feedstock which can be vegetable oil (edible or non-edible), waste cooking oil, or animal fat (Dias et al., 2013). The use of inexpensive non-edible oil, as a second generation feedstock, not only is economically more

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Nomenclature

ANOVA	analysis of variance
CCD	central composite design
GC	gas chromatograph
HPLC	high performance liquid chromatograph
RSM	response surface methodology
SEM	scanning electron microscopy
SSF	simultaneous saccharification and fermentation

favorable but also can reduce food versus fuel conflict (Bateni et al., 2014). However, precise planning and management are needed to identify and minimize further challenges toward sustainable development of biodiesel production (Sukkasi et al., 2010). In fact, it should be considered that cultivation of non-edible oil crop may be associated with using arable land and consequently increasing load on soil, water and biodiversity (Antizar-Ladislao and Turrion-Gomez, 2008). However, some of the non-edible plants, e.g., castor oil plant, can be cultivated in the wastelands irrigated by wastewater which can suppress the aforementioned challenges (Chakrabarti and Ahmad, 2008; Tsoutsos et al., 2013).

Ethanol is industrially produced from sugar and starch based materials; however, it can be produced from inexpensive and abundant lignocellulosic substrates such as agricultural residue, forest residue, and municipal solid wastes (Du et al., 2009; Karimi et al., 2013; Misailidis et al., 2009). Lignocelluloses are dominantly composed of cellulose, along with hemicellulose and lignin in a highly compact structure (Karimi and Chisti, 2015; Karimi and Pandey, 2014; Karimi et al., 2013). Therefore, a pretreatment process is required to remove lignin and hemicellulose and increase the accessibility of the enzyme to cellulose prior to the hydrolysis and fermentation processes (Asgher et al., 2014; Bateni et al., 2014). Alkaline pretreatment is one of the most promising chemical processes which can effectively facilitate further processes. Alkaline pretreatment using sodium hydroxide was frequently applied for softwoods, hardwoods, and agricultural residues to improve ethanol yield and showed promising results (Goshadrou et al., 2011; Mirahmadi et al., 2010; Mohsenzadeh et al., 2011; Nieves et al., 2011; Salehi et al., 2012; Salehian and Karimi, 2013). Sodium hydroxide pretreatment resulted in lignin removal, biomass swelling, more surface reactive functional groups like hydroxyl groups, and surface roughness improvement in the pretreated substrate (Islam et al., 2012; Teghammar et al., 2010). Although alkaline pretreatment, e.g., NaOH pretreatment, is associated with high alkali loading and a large volume of waste water for washing, it received great interest since it does not need complicated reactors (Wan et al., 2011). Sodium hydroxide pretreatment are classified into dilute and concentrated treatments. High concentration of sodium hydroxide is applied at moderate conditions, i.e., ambient pressure and relatively low temperatures. Dissolution of cellulose at these conditions is the main phenomenon, resulting in changing cellulose I (crystalline cellulose) to amorphous cellulose with low degree of polymerization amenable to enzymatic hydrolysis (Karimi et al., 2013). Moreover, high concentration sodium hydroxide provides an opportunity to recover and reuse the pretreatment solution, resulting in lower chemical waste disposal and consequently less environmental concerns (Karimi et al., 2013; Mirahmadi et al., 2010; Wan et al., 2011).

The development of biofuels production is still limited due to lack of economic proficiency (Zhu and Zhuang, 2012; Karimi and Pandey, 2014). Biorefinery, which is a facility with integrated, efficient and flexible biomass processing to various value-added products and energy, can suppress the economic barriers and lead to the proficient biofuel production (Sadhukhan et al., 2014; Luo et al., 2010; Zhu et al., 2014). The concept of biorefinery was developed analogous to the current complex crude oil refineries leading to multiple fuels and value-added chemicals (Sadhukhan et al., 2014).

Castor plant is an important non-edible oilseed crop which can tolerate various climate conditions (humid tropic to dry subtropic) and has a wide range industrial applications (Ramanjaneyulu et al., 2013). Currently, the average global castor seed production yield is about 1.1 t/ha (Scholz and da Silva, 2008) with a productivity of 470 kg oil/ha considering seed oil contents in a range of 45–55% (Santana et al., 2010). Castor plant cultivation under favorable conditions can boost the seed yield to 4–5 t/ha, leading to promising oil productivity (Scholz and da Silva, 2008).

Castor oil consists mainly of ricinoleic acid (12-hydroxy-cis-octadec-9-enoic acid), an hydroxylated fatty acid with one double bond. The presence of ricinoleic acid in castor oil results in some unique properties, e.g., very high solubility in alcohol (Perdomo et al., 2013). Therefore castor oil can be converted to biodiesel (Kılıç et al., 2013; Perdomo et al., 2013) even at low temperature (Bateni et al., 2014). Castor biodiesel has a high calorific value and high cetane number (Scholz and da Silva, 2008). However, some properties of the final biodiesel, e.g., high kinematic viscosity, may complicate its engine performance (Berman et al., 2011; Scholz and da Silva, 2008). Castor biodiesel can be diluted or blended with conventional diesel to produce an appropriate fuel for diesel motors (Scholz and da Silva, 2008).

The presence of ricinoleic acid in the castor seed cake results in a more limited application compared to the other seed cakes. Castor seed cake can be used for production of organic nitrogenous fertilizer due to their nitrogen, phosphorous and potassium content (Ramachandran et al., 2007). However, it cannot be directly used for animal feed due to the poisenous and allergic properties (Ogunniyi, 2006; Adedeji et al., 2006). Previous study (Bateni et al., 2014) showed the great potential of castor seed cake for biogas production.

Previous studies have investigated the influence of reaction parameters including temperature, reaction time, catalyst concentration, and alcohol content on transesterification of castor oil (Cavalcante et al., 2010; Da Silva et al., 2006; De Oliveira et al., 2005; Jeong and Park, 2009; Ramezani et al., 2010). De Oliveira et al. (2005) used the Taguchi experimental design to evaluate the effect of reaction conditions on "commercial refined" castor oil. They (De Oliveira et al., 2005) deduced that increasing reaction temperature (30–70 °C) and time (1–3 h) positively affected the reaction conversion, whereas increasing catalyst concentration (0.5–1.5 w/w%) yielded a negative effect. In addition, it was concluded that increasing the alcohol concentration had no significant effect on the conversion (De Oliveira et al., 2005). Da Silva et al. (2006) used response surface methodology to optimize the transestrification parameters of a "commercial" castor oil. Optimum results were achieved with the lowest temperature and the highest alcohol concentration in the presence of 0.8–1.3 w/w% sodium methoxide as a catalyst (Da Silva et al., 2006). Ramezani et al. (2010) evaluated the potential of different basic catalysts ($NaOCH_3$, $KOCH_3$, NaOH, KOH) together

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