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Production and evaluation of biodiesel and bioethanol from high oil corn using three processing routes

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HIGHLIGHTS

- Bioethanol and biodiesel were produced from six high oil corn (oil content: 4–21%).
- We compare three processing routes with the yield of ethanol and biodiesel.
- M–F–T and S–T|F route produce the highest ethanol and biodiesel yield, separately.
- M–F–T route is suitable for producing ethanol and biodiesel for corn with small germ.
- S–T|F route is suitable for producing ethanol and biodiesel for corn with large germ.

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ABSTRACT

Six Korea high oil (KHO) corn varieties varying in germ and endosperm size and oil content (4–21%, wet basis) were subjected to three sequential combinations of milling (M), germ separation (S), fermentation (F), and in situ transesterification (T) to produce bioethanol and biodiesel. Production parameters including saccharification, bioethanol yield, biodiesel yield and composition, and conversion rate were evaluated. The effects of the contents of germ, endosperm size, oil, and non-oil solid mass on the production parameters strongly depended on the processing routes, namely M–F–T, M–T–F, and S–T|F. The M–F–T route produced the highest bioethanol yield while the S–T|F route produced the highest biodiesel yield. The in situ transesterification reaction, if proceeded before fermentation, reduced the bioethanol yield while fermentation and/or presence of endosperm reduced the biodiesel yield.

1. Introduction

The world must seek alternative liquid fuels to replace fossil fuels in the near future because of the rapid depletion and eventual end of fossil energy sources (Pimentel and Patzek, 2005). Ethanol (ethyl alcohol, bioethanol) and biodiesel (fatty acid methyl ester or FAME) are two most commonly available commercial renewable liquid transportation fuels. Ethanol may be used as a fuel or as a gasoline enhancer (Sánchez and Cardona, 2008). Many countries have implemented or implementing programs for addition of ethanol to gasoline (Sánchez and Cardona, 2008). The fuel ethanol can be produced from energy crops such as corn (Pimentel and Patzek, 2005) and lignocellulosic biomass such as wood using fermentation (Hamelinck et al., 2005).

Biodiesel, also named as fatty acid methyl ester (FAME), is another kind of clean fuel and is safe for use in conventional diesel engines. It offers the same performance and engine durability as petroleum diesel fuel. In the United States, biodiesel is produced mainly from oil extracted from soybeans (Chisti, 2007) via transesterification (Van Gerpen, 2005). Other sources of commercial biodiesel include canola oil (Dizge and Keskinler, 2008), animal fat, palm oil, corn oil, waste cooking oil (Ma and Hanna, 1999) and jatropha oil (Barnwal and Sharma, 2005).

Corn has been traditionally regarded as the main ethanol feedstock in US (Baker and Zahniser, 2006). Corn is not considered a viable source of lipids for biodiesl production because of its low oil or lipid content, in the range of 2–4%, in typical corn kernel (Duckett et al., 2002), which is much lower than soybean (15–20%). Corn oil

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is used more in food and feed industry than other fields (Tolman, 2007).

A corn variety containing more than 19% oil in the kernel was found in North Korea by researchers from the University of Minnesota. The breeding research and development programs at the University of Minnesota produced six new varieties from the initial Korean high oil (KHO) corn seeds over the years. These new varieties contain 4–21% of oil. The high oil content of these corn seeds will enable them to compete with soybean (15–20% oil content) (Lu et al., 2005) as a major biodiesel feedstock (Noureddini et al., 2004). Combined with the ethanol production, the Korea high oil corn will become an excellent energy crop.

In KHO corn seeds, the germ contains almost 80% of total oil or lipid while starch is mainly conserved in endosperm (Taylor et al., 2001), it is likely that the most efficient way is to produce ethanol from endosperm and to produce biodiesel from germ. However, the traditional fermentation using yeast also needs the nutrients in germ such as protein and vitamin (Vidal et al., 2011; Murthy et al., 2006) while the oil transesterification is just a chemical process and is only related to the corn oil (Meher et al., 2006). Therefore it is necessary to adjust the processing method to optimize the ethanol and biodiesel yields.

In the conventional processing of normal corn for energy, corn seeds are first fermented to produce ethanol and a byproduct named as distillers dried grains with soluble (DDGS). The DDGS is used as animal feed or extracted for oil (Singh and Cheryan, 1998) which is then converted to biodiesel through the transesterification. There is also another method that corn is milled for oil extraction and then the residual is used for fermentation to produce the ethanol (Taylor et al., 2001). The oil extraction usually consumes a large amount of solvent (Kwiatkowski and Cheryan, 2002), which is inefficient for the normal corn which contains just 2–4% oil. New technique that combines oil extraction with transesterification emerges (Lewis et al., 2000). This new technique involves separation of germ and endosperm, in situ transesterification of the germ, pooling together the endosperm and in situ transesterification residue for fermentation producing ethanol.

The objectives of the present study were to examine the effects of corn feedstock composition and processing conditions on fermentation and in situ transesterification and hence ethanol and biodiesel yields in order to develop an optimal refining plan to maximize the energy production from the high oil corn seeds.

2. Methods

2.1. Materials

Six KHO corn varieties (LH 119 × LH59, LH119× (LH59 × AHO-1), LH59 × AHO-1, AHO-1× (LH59 × KHO), open-pollinated KHO, AHO-1) were provided by the plant pathology in University of Minnesota. Methanol, sodium chloride, sodium hydroxide, phosphoric acid, sulfuric acid and chloroform were purchased from Fisher Scientific Inc. (Pittsburgh, PA, USA). α-Amylase, glucoamylase, and dried yeast (*Saccharomyces cerevisiae*) from Sigma–Aldrich Inc. (St. Luis, MO, USA). All chemical reagents were of analytical grade and used without further purification. Deionized (DI) water was used throughout the work.

2.2. General description of the processes

Following processes were used alone, in combination, or in different sequence in the study as described in Section 2.3.

2.2.1. Drying

Harvested corn kernels were oven dried by at 50 °C and kept at room temperature and RH (Relative Humidity) 15%.

2.2.2. Milling

A disk crusher (Model 4E, Straub, Hatboro, PA) was used to grind the corn kernels. For each grinding, 10–50 g of corn kernels were added into the hopper, and allowed to drop to the moving disks. Preliminary tests were conducted to adjust the distance between the disks to obtain homogeneous powders.

2.2.3. Separation of germs from endosperms

Hundred grams of corn kernels were steeped in water containing 3% of lactic acid and 10,000 ppm of $Na_2S_2O_3$ for 3 h at room temperature (25 °C) to soften the pericarp. The steeped corn kernels were carefully cut with a blade and the germ was separated from endosperm with a pair of tweezers. Then the proportion of germ and endosperm was weighted using a forced air oven at 103 °C for 72 h according the standard method 44-15A (AACC, 1983).

2.2.4. Yeast fermentation

The fermentation procedure was modified from the literatures (Lin and Tanaka, 2006). Briefly, 5 g of dried sample and 100 ml DI water were added to a serum bottle. The mixture was gelatinized by autoclaving at 121 °C for 10 min, followed by liquefaction with 0.04 ml α-amylase (500 units/mg) at pH of 6.0–6.5 (adjusted using 3N sodium hydroxide or 3N phosphoric acid) at 85–90 °C for 2 h. The liquefied sample was mixed with 0.04 ml glucoamylase (5000 units/ml), adjusted to pH 4.2–4.4, and held at 55 °C with continuous stirring for 12 h to facilitate saccharification.

Dry yeast was activated 5 days prior to fermentation by cultivating 3 g dry yeast on 100 ml of potato dextrose (PD) culture medium at 35 °C for 2 days. 10 ml of this culture broth was transferred to a fresh PD culture medium and cultured at 35 °C for another 2 days, resulting in second generation yeasts.

10 ml of the second generation yeast was added to the fermentation bottle containing 100 ml of the saccharified liquid whose pH was adjusted to 4.5 ± 0.1 using 3N sodium hydroxide or 3N phosphoric acid. After filling nitrogen, sealing the bottleneck using aluminum cover and connecting an empty gas bag, the bottle was maintained at 35 °C for 72 h.

The fermentation liquor was centrifuged and supernatant was filtrated using 40 μm millipore filter for further tests. If the fermentation was followed by transesterification, the centrifuge residue was gathered and dried in the oven at 105 °C for 24 h, and used for transesterification.

2.2.5. In situ transesterification

5 g of dried sample residue was mixed with 28 ml methanol for oil extraction with stirring at room temperature for 2 h. Additional 2 ml methanol and 0.3 ml 98% H_2SO_4 as catalyst were added into the mixed liquor. The overall ratio of methanol to solid was 30 ml to 5 g. The acid catalyzed transesterification reactions took place in a sealed bottle at 65 °C for 12 h (Leung et al., 2010). The mixture was centrifuged and supernatant (biodiesel) was used for the composition analysis. If the transesterification was followed by fermentation, the centrifuge residue was washed with DI water twice to remove methanol, dried at 50 °C for 24 h, and used for fermentation.

2.3. Processing routes

Three processing routes differing in sequence of the processes described in Section 2.3 were investigated for ethanol and biodiesel yields and economic performance. In the first route dubbed M–F–T, whole corn kernels were milled (M), fermented (F) for ethanol, and then subjected to in situ transesterification (T) for biodesiel production. In the second route dubbed M–T–F, whole corn kernels were milled (M) followed by transesterification