Renewable and Sustainable Energy Reviews 91 (2018) 531–548

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Biodiesel production from corn oil: A review

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ARTICLE INFO

Keywords:
Biodiesel
Corn
Germs
Oil extraction
Transesterification
Zea mays L.

ABSTRACT

This paper deals with biodiesel production from corn oil as a feedstock via the transesterification and esterification reactions. To date, corn oil has not been considered a viable biodiesel feedstock because of its high edible value and relatively high price, but some industrial corn processing co-products, such as corn germ and dried distillers grains with solubles (DDGS), have potential for this application after the extraction of corn distillers oil (CDO). Here, after brief discussion of the issues related to corn botany, cultivation, and use, as well as the corn germ and oil composition, properties and use, the methods of corn processing for germ and DDGS recovery are presented. In addition, the mechanical and solvent extraction techniques for oil recovery from whole ground corn kernels, germs, and DDGS are considered. Furthermore, biodiesel production from corn oil, waste frying corn oil, and CDO is critically analyzed. It is expected that further investigation will be directed toward developing simpler, more effective and energy-saving technologies for biodiesel production from corn oil-based feedstocks, especially from CDO. The integration of biodiesel production directly into corn-based ethanol production will advance the overall economy of industrial plants. Furthermore, the fuel properties, performances and exhaust gas emissions of corn-based biodiesel and its blends with diesel fuel are discussed, taking into account the biodiesel quality standards. Finally, issues related to the environmental and socio-economic impacts of corn-based biodiesel production and use are also tackled.

1. Introduction

Biorenewable energy resources have attracted attention of governments, businesses and scientists globally because of rapid technological developments, obvious economic benefits and increased global warming and environmental pollution [1]. Among them, biodiesel is a very prospective alternative to mineral diesel fuel. Biodiesel is defined as a mixture of long chain fatty acid alkyl esters that meet the specified standards. Biodiesel is commonly produced by the esterification of free fatty acids (FFAs) or the transesterification (alcoholysis) of triacylglycerols (TAGs) from different biological renewable recourses, with an excess of methanol or ethanol, in the presence of an acid, base or enzyme catalyst, although non-catalytic processes are also possible. Global biodiesel production is expected to continue to expand in the upcoming years, rising from $29.7{\cdot}10^6$ m^3 in 2014–$39{\cdot}10^6$ m^3 in 2024, a 27% increase [2]. This expansion is supported by the expectation that the global biodiesel price will remain almost unchanged until 2024 because of the projected decrease in vegetable oil prices. High production prices, caused by the high contribution (70–95%) of currently used oily feedstocks to the total production costs, is considered to be the primary barrier to the commercial use of biodiesel [3]. Therefore, other oil crops should be examined, especially those that could grow on marginal lands and produce non-edible oils. With the goal of biodiesel price reduction in mind, oil-containing co-products and waste from the existing production processes are also preferred as biodiesel feedstocks. Such co-products include corn germ (the portion of corn kernel that contains oil) from starch production and distillers dry grains with solubles (DDGS) from ethanol production [4,5].

Corn or maize (*Zea mays* L.) is an interesting oil crop that is produced in large quantities globally. In 2014, 1,060,107,470 and 3,189,137 t of corn crop and corn oil, respectively, were produced globally [6]. Large amounts of corn are used in starch and ethanol production, and corn oil is a by-product. The proposed ethanol production could generate $1.5.10^6$ m^3 of corn distillers oil (CDO, i.e., whole

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https://doi.org/10.1016/j.rser.2018.04.024
Received 20 April 2017; Received in revised form 12 April 2018; Accepted 12 April 2018
1364-0321/

stillage-extracted corn oil) from $56.8.10^6$ m^3 of corn if the extraction degree is only 8.9 kg of oil per metric ton of corn [7]. Historically, corn oil has not been viable biodiesel feedstock because of its high value as an edible oil and relatively high price. However, there is a trend in the United States of America for the increasing use of CDO for biodiesel synthesis, representing the fastest expanding oily feedstock for biodiesel production in 2013 [8]. About 479,000 t CDO was used to produce biodiesel in 2015, compared with 51,000 t in 2010 [9]. Approximately 85% of dry grind ethanol plants in the United States of America extracted corn oil in 2015, producing about 1.22 10^6 t CDO [10]. This offers the possibility for the integrated production of ethanol and biodiesel. Another positive effect of corn oil extraction is the reduction of induced land use emissions because of the integrated ethanol/biodiesel production, which is based on the same or smaller land area [11]. Aside from innovative technologies, a realistic way of increasing the quantity of corn oil is the use of corn varieties that produce a higher oil content compared to the currently grown varieties. The negative side of corn-based biodiesel might be the impact on food prices because greater demand for corn is expected to increase the prices of other crops competing for the same land. However, corn-based ethanol expansion of $3.8{\cdot}10^6$ m^3 (one billion gallons) increased the corn price by 3–4% in 2015, with even smaller projected changes in the future [12].

This paper provides a general overview of the usage of corn oil as oily feedstock for biodiesel production. First, corn cultivation, corn germ composition, and use, as well as corn oil composition, properties and use are briefly described. Then, the corn processing methods to recover corn germs and DDGS are presented. Furthermore, the techniques of oil recovery from whole ground corn kernels, corn germs, and corn DDGS are reviewed. Subsequently, biodiesel production from corn oil, waste frying con oil (WFCO) and CDO by catalytic and non-catalytic transesterification reactions is critically considered. Afterward, fuel properties, performances and exhaust gas emissions of corn-based biodiesel and its blends with diesel fuel are discussed, taking into account biodiesel quality standards. Finally, issues related to the environmental impact of corn-based biodiesel production and usage are tackled.

2. Botany, cultivation, and uses of corn

Corn (*Z. mays* L.) is an annual plant of an average height of 2.5 m with yellow or white grainy fruit. It belongs to the genus *Zea*, the family Poaceae (grasses), and the order Cyperales. The genus *Zea* consists of four species of which *Z. mays* L. is economically important and has a number of hybrids that differ from one another with respect to the chemical composition and grain structure [13]. The other *Zea* species (teosintes) are wild grasses native to Central America and Mexico.

Corn is widely cultivated all over the world, and each year its production increases more than that of any other grain product [14]. Today, corn is mostly grown in the United States of America (about 40%) and China (about 20%); other top producers are Brazil, Argentina, Indonesia, Ukraine, India, Mexico, Indonesia, and France [15]. Corn is mainly used as animal feed, as a raw material in industry, and, to a lesser extent, as human food (especially in the developing countries). Because of growing world population and the increased need for food, it is predicted that the production of corn will have surpassed the production of wheat and rice by 2050 [16,17]. The volume of corn production in the world is mostly attributed to the development of technology and seed industry, increased agro-efficiency, innovative corn food, and technical corn products, and, principally, innovation and increased production of bioethanol and biodiesel [18]. In Serbia, corn is considered the most suitable crop for alternative fuels production because of its large oversupply [19].

As human food, corn is used in different products, such as grits, meal, starch, and syrups, while different crop parts (stalks, grain, and cob) are used in the pharmaceutical industry and for biofuel production. Nowadays, the lignocellulosic part of the corn plant is drawing interest as a raw material for the production of bioethanol, paper, packaging, plywood, cardboard, and many other technical products.

2.1. Composition and use of corn kernel

Corn kernel is composed of four main fractions: the kernel root (tip cap, 1–2%, mainly cellulose), pericarp (hull, 5.5–6%, mainly cellulose), germ (embryo, 10–14%, containing mostly oil, proteins and carbohydrates), and endosperm (82% containing mostly starch, proteins and fats) [20]. Because corn kernels are rich in starch (60–75%), industrial corn production is oriented toward obtaining starch, whereas the germ is treated as a by-product. About 80–84% of the total kernel oil is present in the germ followed by 12% in the aleurone and 5% in the endosperm [21]. The oil content in corn grains can be genetically controlled. After a long selection process, the kernel oil content can be increased by up to 20% [22]. Corn with an oil content level above 6% is designated 'high oil corn'. The corn germ is the most important part of the kernel for oil production. Corn germ contains 35–56% oil, linoleic acid being the most common fatty acid (49–61.9%) [23]. In addition, corn germ contains about 1–3% phosphatides, 1% sterols, and 1.5% FFAs. Nowadays, numerous corn grain products are used in the food, pharmaceutical, chemical, and textile industries; thus, after, processing, there is practically no loss. Corn germ oil is especially important because of its use in human foods and biodiesel production.

2.2. Composition, properties and uses of corn oil

In the corn plant, oil can be found in kernels (seeds), the germ (embryo, a portion of the kernel) and the fiber. Therefore, several terms can be found in the literature, such as 'corn kernel oil' [24], 'corn germ oil' [25] and 'corn fiber oil' [26]. Because of their low oil content, corn kernels and the fiber (about 3–5% and 2–3%, respectively) are used for obtaining the oil at the laboratory scale for research purposes [26]. Oil yields from wet-milled corn germ, dry-milled corn germ and corn fiber by *n*-hexane extraction are 40–50%, 20–25% and 2–3% (based on a dry weight) respectively, while oil yield from ground or flaked whole corn by ethanol extraction is 3–5% [27]. The corn kernel and fiber oils are richer in phytosterols (2–3% and 10–15%, respectively) compared to corn germ oil (about 1%) [28]. Corn oil is commercially obtained from the germ only. The main producers of corn oil are the United States of America, Mexico, Russia, Belgium, France, Italy, Germany, Spain and the United Kingdom [29].

Corn with high oil yield per unit area is behind rapeseed and sunflower [30]. Corn oil yield is about 172 L/ha [31]. The moisture at harvest and drying temperature are the most influential factors affecting the germ oil content and oil yield [32]. Generally, the germ weight and oil yield decrease as the kernel moisture at harvest and the temperature of the drying air increase. Edible oil is obtained from the corn germs from the wet-milling process. Because of its composition and favorable characteristics, corn oil belongs to the group of high-quality oils. Containing essential fatty acids and tocopherols, corn oil is of better quality than other edible oils [33]. The composition of corn oil includes both saturated and unsaturated fatty acids such as palmitoleic (11.67%), stearic (1.85%), oleic (25.16%), linoleic (60.60%), linolenic (0.48%), and arachidic (0.24%) [29]. In addition to those, corn oil contains caprylic, capric and myristic fatty acids [34]. It is also rich in vitamin E, which is a strong antioxidant. Corn oil is amongst the richest sources of tocopherols, having reported concentrations of α- and γ-tocopherol of 21.3 and 94.1 mg/100 g, respectively [35]. Corn oil is an important component of many foods and has a distinctive taste [36]. Because of its easy digestibility, corn oil has also found applications in medicine. Moreover, recently, corn oil has been used in biodiesel manufacture, especially in combination with ethanol production. Corn oil has an acid value of less than 0.5%, which is a desirable feature with respect to its use in biodiesel production [37].