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Alkaline-catalyzed ethanolysis of soybean oil ethanolic miscella

Naiane Sangaletti-Gerhard *, Thais Maria Ferreira de Souza Vieira, Samuel Schievano Groppo, Joseanne Rodella Rodrigues, Marisa Aparecida Bismara Regitano-d'Arce

Laboratory of Oils and Fats, Department of Agri-food Industry, Food and Nutrition. College of Agriculture "Luiz de Queiroz", University of São Paulo. Avenida Pádua Dias, 11. P.O. Box 9, Piracicaba 13418-900, São Paulo, Brazil

HIGHLIGHTS

- Bioethanol used for both oil extraction and transesterification reaction.
- Direct transesterification of ethanolic miscella using alkaline catalyst.
- High yield of biodiesel from rich miscella ethanolysis.
- Advantageous process regarding to environmental and energy economic aspects.

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ABSTRACT

The rich-in-oil miscella obtained from the soybean oil extraction using ethanol shows chemical and physical characteristics that allow production of biodiesel by direct transesterification. It may be a promising raw material for skipping the oil refining process, thereby reducing the biodiesel production steps, as well as increasing the environmental sustainability of the process by replacing the hexane by ethanol from renewable source. The aim of this work was to perform alkaline-catalyzed (NaOH) ethanolysis of soybean oil ethanolic miscella and assess the biodiesel quality according to the Brazilian legislation. The molar ratio 1:12, NaOH 0.6% and temperature 30 °C were the best conditions which leads to 97.2% of ethyl esters yield. The meal resulting from ethanol oil extraction was suitable for animal feed due to the lower reduction of antinutritional compounds. The rich-in-oil miscella proved to be a technically viable feedstock for biodiesel production due to its high yield reaction under alkaline-based catalysis.

1. Introduction

Biodiesel production has aroused interest mainly because of the environmental benefits [1]. The replacement of fossil oil derivatives by biodiesel presents advantageous characteristics such as the absence of aromatics compounds and sulfur, high cetane number, high flash point, lower hydrocarbon emissions rate, lower CO and CO_2 emission, as well as easy storage and safe handling [2]. In some countries, like Brazil, blending biodiesel and diesel is required by law [3].

Transesterification reaction (alcoholysis) is commonly used for biodiesel production, where a molecule of triacylglycerol from vegetable oils or animal fats reacts with three molecules of alcohol (usually methanol and ethanol) in the presence of a catalyst, producing a mixture of fatty acid alkyl esters (biodiesel) and glycerol [4]. Catalysts used for biodiesel production may be homogeneous or heterogeneous, and include acids [5,6], alkalis [7], metal complexes [8], organometallic compounds [9] and enzymatic [10,11]. Alkaline catalysts are commonly applied because of their easy usage and low cost [12].

Methanol is the most used alcohol in biodiesel production due to its rapid conversion and high ester yields [7]. However, in Brazil it is derived from petroleum and it is highly toxic when compared to ethanol, which is easily manipulated and comes from sugarcane, a renewable source. Despite lower reactivity of ethanol compared to methanol during transesterification due to its longer carbon chain [13], ethyl esters have cloud and pour points lower than methyl esters, avoiding flow problems in pipes and filters in the diesel engine [14]. Alkaline-catalyzed ethanolysis has been studied with different feedstocks and ethyl ester yields are close to those obtained by methanolysis [15,16].

Vegetable oils such as soybean, sunflower, rapeseed, cottonseed, palm, and peanuts are most used in biodiesel production, and their choice depends of the availability and feedstock cost [17,18]. Use of refined vegetable oil causes an increase of around 80% in biodiesel production costs, turning the process quite unfeasible [19], hence the use of waste frying oil [20], microalgae [7],

* Corresponding author. Tel.: +55 19 3429 4150; fax: +55 19 3429 4228.
E-mail addresses: naisangaletti@yahoo.com.br (N. Sangaletti-Gerhard), tvieira@usp.br (Thais Maria Ferreira de Souza Vieira), samuel_groppo@hotmail.com (S.S. Groppo), joseanne.rodrigues@usp.br (J.R. Rodrigues), marisadarce@usp.br (M.A.B. Regitano-d'Arce).

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agro industry waste [6] and non-edible oils [16,21] emerges as a low cost alternative feedstock to petroleum diesel.

Oil extraction is usually performed with petroleum derived solvents such as hexane. This solvent presents some disadvantages such as flammability, explosivity, toxicity and variable costs according to the petroleum international market. In the soybean crushing plants, hexane emissions represent the bulk of the life cycle THC (total unburned hydrocarbons) emissions [22]. Furthermore, production of one kilo of hexane requires 48.6 MJ [23] while production of sugarcane bioethanol requires only 3.60 MJ [24]. Thus, its substitution by bioethanol results in direct energy economy linked to environmental friendly process, using only renewable resource inputs in production chain. Ethanol was used as solvent in oil extraction, for the first time, in1934 by Manchuria Soybean Industry Co., located in Dairen, today in China [25]. The hot oil extraction process produced miscella that once cooled, generated two phases: one heavier with 95% oils and a lighter phase with small amount of oil [25]. Years later, Rao and Arnold [26] and Abraham et al. [27] found that the rich-in-oil miscella (heavier phase) from cottonseed flakes presented 4% ethanol and up to 92.8% of oil.

Ethanol extraction promotes a partial refining of crude oil compared to hexane extraction process. Phospholipids and free fatty acids (FFA) are lowered in rich oil miscella from ethanolic extraction [28]. Therefore, possibility of transesterify directly the rich miscella may reduce the biodiesel production cost by skipping degumming, alkali-refining and clarification. Furthermore, those steps involve energy consumption and generate by-products whose destination must be determined. Soybean meal from oil extraction with ethanol presents more pleasant flavor and taste, lighter color, lower sugar (oligosaccharides) and lower solvent toxicity [28]. These advantages are highly valued by food industries.

Regardless of feedstock or technological route (methylic or ethylic), biodiesel quality must be ensured by regulations. The biofuel quality is affected by the presence of reactants that have not been converted into fatty esters such as glycerides, alcohol and residual catalysts. Small amounts of free fatty acid, water, glycerol and soap also are required because can cause operational problems in engine and environment, as well as, create a harder process of recovery and purification of biodiesel by emulsion formation [2,18,29].

Considering that soybean is one of the main commodities produced in Brazil and it is currently the major feedstock for biodiesel production [3], and based on Brazilian expertise in bioethanol production technology, there was strong interest in evaluate the potential of rich miscella for biodiesel production. The aim of this work was to achieve to a high ethyl esters yield by direct transesterification of soybean rich-in-oil miscella using the alkaline catalyst NaOH and ethanol as acyl acceptor and to evaluate quality parameters of biodiesel and meal.

2. Materials and methods

2.1. Materials

Soybean freshly flaked was produced by Cargill S/A (Uberlândia, MG, Brazil) and ADM S/A (Campo Grande, MS, Brazil) companies. Ethanol 99.7% (v/v) was of commercial quality. Catalyst used was sodium hydroxide (NaOH), 99% ethanol and anhydrous sodium sulfate. All other reagents were analytical grade.

2.2. Soybean oil extraction with ethanol

Extraction was conducted by soybean flakes immersion in the solvent in stainless steel equipment described by Saad et al. [30], consisting of a stainless steel tank (13 liters capacity), with double wall for hot water circulation, an internal screen basket that held a cotton bag and flaked soybean. During extraction agitation (200 rpm) was provided by a propeller. The system comprised also a thermostat, a condenser and thermometer. The extraction temperature conditions, ethanolic solvent concentration and extraction periods (cycle duration) were defined based on the work by Rao and Arnold [31] and Arnold and Choudhury [32]. The temperature for extraction was ethanol boiling point (78 °C), the proportion soybean flakes:solvent ratio of 1:2 w/v for extraction period of 60 min (one cycle). Total extraction time was 4 h, where the first, second and third cycles applied had poor miscella as solvent and the fourth, 99% ethanol to ensure maximum oil removal from the matrix, according to procedure adopted by Regitano-d'Arce and Lima [33]. After cooling of the miscella, three phases were identified: the gum phase, the rich-in-oil phase (rich miscella) and the rich-in-ethanol phase (poor miscella). The gum phase deposited at the bottom of the oil container was recovered by siphoning. The rich-in-oil miscella was separated from the poor miscella and filtered through qualitative filter paper under vacuum. Poor miscella was reused in the subsequent extractions. Rich miscella was chemically and physically characterized.

2.2.1. Rich miscella characterization

The rich miscella was analyzed for iodine value (AOCS [34] Cd 1d-92), peroxide value (meq/kg) (AOCS [34] Cd 8b-90), kinematic viscosity at 40 °C (mm^2/s) using a capillary viscometer Ostwald-Fenske n° 100, water content (ASTM [35] D6304), specific gravity at 20 °C using a manual densimeter, unsaponifiable matter (wt%) (AOCS [34] Ca 6b-53); lipid contents [36]; phosphorus content (mg/kg) (ASTM [35] D 4951); acid value (mg KOH/g) and free fatty acids (% FFA) (AOCS [34] Ca 5a-40), alcohol content (%), by distillation and digital densimeter model DMA-48 mark Anton Paar and non-volatile matter (AOCS [34] Ca 2b-38), and its fatty acid composition (%). The phospholipids content was calculated by multiplying phosphorus content by factor 30 according to AOCS [34].

2.2.1.1. GC analysis of the fatty acids composition. Samples were prepared according to AOCS [34] Ce 1b-89 and the fatty acids composition was determined by high resolution gas chromatography using CG (HP 5890) and a flame ionization detector, fitted with capillary column SUPELCO-SP 2560 (100 m × 0.25 mm). The temperature program was 130 °C (1.0 min) to 170 °C (6.5 °C/min), 170–215 °C (2.75 °C/min), 215 °C (12 min), 215–230 °C (40 °C/min), 230 °C (6 min). The injector and detector temperatures were 270 and 280 °C, respectively. The samples (0.3 μl) were directly injected. Fatty acids of 6, 8, 10, 12, 14, 15, 16 (cis and trans), 17, 18 (cis and trans), 20, 22 and 24 carbon atoms, saturated and unsaturated, were identified by comparison with data obtained from CG and methyl esters authentic standards eluted under the same conditions.

2.2.2. Flaked soybean and meal characterization

Extraction meals were desolventized in a laminar air flow at 25 °C for 24 h. Soybean flakes and meals had total lipids contents determined according to AOCS [34] Ba 3-38 method. Moisture and volatile matter were determined by method AOCS [34] Ba 2a-38. Protein content was determined by the Kjeldhal method using the 5.71 conversion factor [34,37], the nitrogen solubility index (NSI) and the urease activity were performed by AOCS method [34] Ba 11-65 and Ba 9-58, respectively. All data are provided on a wet base. All analytical determinations were performed in duplicate.