Energy Reports 2 (2016) 211–217

Contents lists available at ScienceDirect

Energy Reports

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

A comparative study on the effect of unsaturation degree of camelina and canola oils on the optimization of bio-diesel production

Jie Yang, Tess Astatkie, Quan Sophia He *

Department of Engineering, Faculty of Agriculture, Dalhousie University, Truro, NS B2N 5E3, Canada

ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form
19 July 2016
Accepted 12 August 2016

Keywords:
Transesterification
Fatty acid composition
Unsaturation degree
Camelina
Canola
Response surface methodology

ABSTRACT

Transesterification is the most common method of producing biodiesel from vegetable oils. A comparative study on the optimization of reaction variables for refined canola oil, unrefined canola oil, and unrefined camelina oil using a four-factor (temperature, time, molar ratio of methanol to oil, and catalyst loading) face-centered central composite design (FCCCD) was carried out. The optimum settings of these four factors that jointly maximize product, fatty acid methyl ester (FAME) and biodiesel yields for each of refined canola, unrefined canola and unrefined camelina were determined. Results showed that the optimized conditions were associated with the fatty acid profile and physical properties of the parent oils. The optimum temperature of vegetable oil with low polyunsaturation degree was higher than that of oils with high polyunsaturation degree. High free fatty acid content in parent oils led to low optimized catalyst concentration, and the decreased reaction rate could be compensated by increased reaction temperature due to significant interaction effect between reaction temperature and catalyst loading in the transesterification process. The highest biodiesel yields from the optimum setting for refined canola oil, unrefined canola oil, and unrefined camelina oil were 97.7%, 95.2%, and 95.6%, respectively. This study provided guidelines on how to optimize different reaction variables taking economic viability and feedstock availability into consideration when producing biodiesel at plant scale.

1. Introduction

The inherent conflict between global energy demand increase and fossil fuel reserve depletion, along with environmental concerns, is driving researchers and industry practitioners to seek viable fuel alternatives. Biodiesel, a renewable, biodegradable, and environmentally innocuous biofuel, has shown promise as a substitute for conventional petro-diesel. The global production of biodiesel is estimated to have reached 29.1 million tons in 2014 and this industry is one of the most rapidly growing industries in the world (Ruitenberg, 0000; Lam et al., 2010).

In response to the increasing demand, numerous efforts have been made to identify feedstock suitability and reliability, develop high performance catalysts for conversion, and evaluate the impact of biodiesel fuel properties on diesel engine performance and exhaust emissions (Lam et al., 2010; Patil and Deng, 2009; Moser, 2010; Yang et al., 2016; Atadashi et al., 2013; Zhang et al., 2010; Wan Ghazali et al., 2015). This has also stimulated interest in optimization of the conversion process, which is essential for large scale production. Optimized reaction parameters would provide valuable fundamental information for evaluating economic viability and commercialization of biodiesel production.

The most commonly used method for biodiesel production is transesterification, a process in which vegetable oils (triglycerides) react with alcohol (usually methanol) to generate fatty acid monoalkyl esters in the presence of alkaline catalysts (usually NaOH or KOH). Transesterification is a reversible reaction; the yield and quality of biodiesel strongly depend on reaction variables such as reaction temperature, reaction time, molar ratio of methanol/oil, and catalyst loading, which can drive the equilibrium toward the product side or vice versa (Ma and Hanna, 1999; Pullen and Saeed, 2015). As early as the 1980s, Freedman et al. (1984) examined the variables affecting the yields of fatty acid methyl ester (FAME) derived from vegetable oils such as soybean, sunflower, peanut, and cottonseed oil, with or without refining, and provided the most fundamental information. They reported that a molar ratio of alcohol to oil of 6:1 gave optimum conversion to the ester, 1% sodium hydroxide was an effective catalyst, and ester conversions of 96%–98% were obtained by transesterifying refined oils with methanol at 60 °C. Following that, more research that focused on parameter effects and transesterification reaction optimization has

* Corresponding author.
E-mail address: quan.he@dal.ca (Q.S. He).

http://dx.doi.org/10.1016/j.egyr.2016.08.003

been conducted. It is generally believed that temperature and catalyst concentration are the most important factors impacting the reaction, while reaction time and molar ratio of methanol/feedstock oil are less important. Recently, statistical optimization methods such as factorial design and response surface methodology (RSM) have also been employed to optimize transesterification conditions and study the interaction effects among the reaction variables.

However, there are considerable inconsistencies in the optimization results reported in the literature, not only for the emerging feedstocks such as camelina, Jatropha, castor, and algal oil, but also for the most extensively researched feedstocks such as canola, soy bean, palm, and sunflower oils (Wu and Leung, 2011; Rashid and Anwar, 2008; Leung and Guo, 2006; Vicente et al., 2006; Dorado et al., 2004). This is most likely caused by the following factors, which could impact transesterification parameters optimization significantly:

1.1. The fatty acid profile of parent oils

The structural feature of vegetable oils such as length of fatty acid chains and unsaturation degree may influence the reaction greatly, thus impacting the optimization of conversion conditions. Very limited, but valuable research reported that the oil with long fatty acid chains (maize, sunflower, linseed oils etc.) needed only half of the reaction time required by oils with short carbon chains (coconut oil) to achieve maximum yield (Pinzi et al., 2011b). However, it was not safe to draw such conclusions based on the reported experiments, as coconut oil was the only oil with high saturation degree (89%) among the feedstocks of interest in this study. It is difficult to determine whether the chain length or saturation degree contributed to such a low conversion rate. Asakuma et al. (2009) studied the kinetics of transesterification and gave different statements. They concluded that the chain length and unsaturation degree had no significant effects on reaction rate. However, in another study conducted by Pinzi et al. (2011a), a correlation between optimized reaction temperature and unsaturation degree of the parent oils was established, indicating that highly unsaturated oils required lower reaction temperatures.

1.2. The physical and chemical properties of parent oils

It was reported that even for the same species of vegetable oil, the resultant optimized conditions varied in the literature. This was mainly due to the fact that the reported studies did not include or test the properties of the feedstock used, such as acid number, and water and phosphorus content, as well as whether the feedstock was refined, which could influence reaction performance. For example, acid value represents the content of free fatty acid (FFA) in feedstock oil. Interaction of FFA with alkaline catalyst may form soap and emulsions during transesterification, which decrease FAME yield, and also make biodiesel purification more difficult. Water content indicates moisture, which can react with alkaline catalysts and accelerate the saponification process. Unsaponifiable matter consists of organics such as sterols, higher aliphatic alcohols, pigments, waxes and hydrocarbons, which do not react with bases to form soaps. Phosphorous is a minor oil component typically associated with phospholipids and gums that may act as emulsifiers or cause sediment, lowering yields (Gerpen, 2005; Chaves et al., 2010).

1.3. The optimization method

Each optimization method has an inherently different algorithm. The levels of experimental factors and the target response variables are also influential, affecting the resultant optimum settings. In our previous research regarding the optimization of camelina oil biodiesel synthesis (Yang et al., 2015), the optimum settings were determined to be: reaction temperature of 38.7 °C, KOH catalyst concentration of 1.5 wt.%, reaction time of 40 min, and molar ratio of methanol/oil of 7.7:1, with a resulting product yield of 97% and FAME yield of 98.9%. However, in another study using orthogonal experiment design (Wu and Leung, 2011), the optimized conditions were: reaction temperature of 50 °C, KOH catalyst concentration of 1 wt.%, reaction time of 70 min, and molar ratio of methanol and oil of 8:1 with an achieved product yield of 95.8% and FAME yield of 98.4%.

These facts motivated us to do comparative studies to identify the underlying contributors to the inconsistency in optimization. In this study, refined canola, unrefined canola, and unrefined camelina with similar carbon chain length, were chosen as representative feedstocks to examine the impact of unsaturation degree and feedstock properties on biodiesel optimization. RSM was used in all cases to keep the optimization method consistent, levels of four independent factors (temperature, reaction time, catalyst loading and molar ratio of methanol/oil) were set in the same range, and the responses included product yield, FAME yield, and biodiesel yield. This study aims to provide answers to these questions and invite more research efforts on this topic.

2. Materials and methods

2.1. Materials

Unrefined canola and camelina oil used for biodiesel synthesis were cold pressed from seeds grown in Canning, Nova Scotia, Canada. Commercially available canola oil (refined, good grade) was purchased from Capri, Canada. Potassium hydroxide in the form of pellets, analytical grade methanol (>99%), anhydrous calcium chloride and hexane (>99%) were purchased from Fisher Scientific Ltd., Canada. Sodium methoxide (25 wt.% solution in methanol) and two standard reference solutions (GLC 96, >99%; GLC 428, >99%) were purchased from Sigma Aldrich, Canada and Nu-Chek Prep. Inc., USA, respectively.

2.2. Identification of feedstock oil fatty acid profile and properties

Refined canola oil, unrefined canola oil, and unrefined camelina oil were methylated according to ISO 5509 standard (Animal and vegetable fats and oils—Preparation of methyl esters of fatty acids). The prepared samples were injected into an Agilent 7890A GC equipped with a Flame Ionization Detector (FID) at 260 °C and an Agilent DB-23 column (50%-Cyanopropyl-methylpolysiloxane; 30 m length × 0.25 mm internal diameter × 0.25 μm thickness; high polarity). The carrier gas was helium, and the oven temperature was initially set at 190 °C, then increased to 250 °C at a heating of rate of 40 °C/min and was maintained constant at 250 °C for 3.5 min. The fatty acid methyl esters were identified by comparing their specific retention times to those of a standard reference solutions. The moisture and volatiles, free fatty acid, insoluble impurities, unsaponifiable matter, water content, and calculated iodine of the feedstock oils were determined according to American Oil Chemists' Society (AOCS) standard testing methods, AOCS Ca 2c-25, AOCS Ca 3a-46, AOCS Ca 6a-40, AOCS Ca 5a-40, AOCS Ca 2e-84, and AOCS Cd 1c-85, respectively. The phosphorus content was determined in accordance with Association of Official Agricultural Chemists standard AOAC 984.27.

2.3. Transesterification process

A typical biodiesel synthesis procedure was as follows: 50 g of raw feedstock oil was added to a 300-mL flask and placed in a