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Article

A comparative study on the effect of unsaturation degree of camelina and canola oils on the optimization of biodiesel production

Energy Reports

Provided in Cooperation with: Elsevier

Suggested Citation: Yang, Jie; Astatkie, Tess; He, Quan Sophia (2016) : A comparative study on the effect of unsaturation degree of camelina and canola oils on the optimization of bio-diesel production, Energy Reports, ISSN 2352-4847, Elsevier, Amsterdam, Vol. 2, pp. 211-217, https://doi.org/10.1016/j.egyr.2016.08.003

This Version is available at: https://hdl.handle.net/10419/187863

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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



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ARTICLE INFO

Article history: Received 11 April 2016 Received in revised form 19 July 2016 Accepted 12 August 2016 Available online 24 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.

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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

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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

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

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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 \times 0.25 mm internal diameter \times 0.25 μ m 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 water bath at a set temperature. A pre-calculated amount of methanol solution containing completely dissolved KOH was added to the oil. The reaction was carried out with a constant 300 rpm agitation rate and stopped once the preset time was reached. The reaction mixture was transferred to a separatory funnel and allowed to stand for 30 min for phase separation, and then the glycerol layer under the crude biodiesel was drawn off. The crude biodiesel remaining in the separatory funnel was washed by a few batches of distilled water until the water layer became completely translucent. The resulting biodiesel (after the water washing) was dried by adding calcium chloride and then centrifuged to remove the water-saturated calcium chloride, giving purified biodiesel for further analysis.

2.4. Product analysis

There are three ways to express the yield of biodiesel obtained from a transesterification process: product yield, FAME yield, and biodiesel yield. The product yield shown in Eq. (1) indicates the quantity of the biodiesel produced with respect to the raw oil feed. The FAME yield in Eq. (2) is determined by the amount of FAME with respect to the resulting biodiesel product, which is an indicator of the quality of the biodiesel. The biodiesel yield in Eq. (3), the product of product yield and FAME yield, represents the quantity of FAME over the parent raw oil.

Product yield (%) =
$$\frac{\text{mass of biodiesel}}{\text{mass of oil}} \times 100\%$$
 (1)

FAME yield (%) =
$$\frac{\text{mass of FAME}}{\text{mass of biodiesel}} \times 100\%$$
 (2)

Biodiesel yield (%) =
$$\frac{\text{mass of FAME}}{\text{mass of oil}} \times 100\%.$$
 (3)

The FAME yield was determined by using Agilent 7890A gas chromatography (GC) with an external calibration method as described in Section 2.2. The properties of the resulting biodiesel were characterized against ASTM D6751-15a, including the kinematic viscosity at 40 °C (ASTM D445), water content (ASTM D4377), acid number (ASTM D664) and flash point (ASTM D93).

2.5. Statistical analysis

A face-centered central composite design (FCCCD) that uses 31 runs at low, center, and high levels of the four factors, namely temperature (30 °C, 40 °C, 50 °C respectively), time (20 min, 30 min, 40 min respectively), molar ratio of methanol to oil (6:1, 8:1, 10:1 respectively), and catalyst loading (0.75 wt.%, 1.25 wt.%, 1.75 wt.% respectively) was generated and analyzed using Minitab Version 17 software to determine the optimum settings of the factors to maximize product yield (%), FAME yield (%), and biodiesel yield (%) from refined canola oil, unrefined canola, and unrefined camelina oil. The three levels of these factors were selected based on preliminary experiments, as well as relevant research reported in the literature. The FCCCD design is an effective second-order design for any number of design factors and has several desirable properties (Myers et al., 2009). Complete analyses of the nine response variables for the three feedstocks measured from the 31 runs were conducted using the methods described in Myers et al. (2009) and Montgomery (2013). The analyses included verifying that the model did not have significant lack-of-fit, and the normal distribution and constant variance assumptions on the error terms were valid. Independence assumption was valid through the random order of the runs. This was followed by testing the significance of each model term, and performing response optimization to identify the combination of the factor settings that jointly maximized product, FAME, and biodiesel yields for each feedstock oil. The fitted model equations for each of the nine response variables using the uncoded units of temperature, time, molar ratio and catalysis loading that can be used to predict the responses at any setting of these factors were also calculated and presented in Table 5. The adjusted coefficient of determination (R^{2}_{adi}), which is the appropriate indicator of the percentage of the variability in the response variable accounted for by the model when multiple factors are used, was also given for each fitted model in Table 5. In all cases, since the temperature by catalyst loading interaction effect was highly significant, the results from response optimizer were used to determine the hold values for time and molar ratio of methanol to oil. This was followed by constructing an overlaid contour plot to determine the "sweet spot" that maximizes all three response variables for each of refined canola, unrefined canola, and unrefined camelina feedstocks.

3. Results and discussions

3.1. Characterization of parent feedstock oils and the corresponding biodiesel products

The fatty acid composition of feedstock oils (refined canola oil, unrefined canola oil, and unrefined camelina oil) are listed in Table 1. Refined canola oil (food grade) had a similar fatty acid composition to unrefined canola oil. Both were comprised of a higher percentage of oleic acid (C18:1, 63.2-63.5 wt.%) compared to camelina oil (C18:1, 14.4 wt.%). Linolenic acid (C18:3, 33.5 wt.%) was the primary fatty acid in camelina oil, followed by 19.1 wt.% linoleic acid (C18:2) and 15.0 wt.% gadoleic acid (C20:1). Canola oil also had about 18.6-19.2 wt.% linoleic acid, but only 8.9-9.6 wt.% linolenic acid. In terms of degree of saturation, canola oil consisted of 6.3-6.7 wt.% saturated, 65.2-65.5 wt.% monounsaturated, and 28 wt.% polyunsaturated fatty acids, and had a total unsaturation degree of 131 wt.%. Camelina oil with a total unsaturation degree of 179 wt.% contained more than twice the polyunsaturated fatty acids (56.8 wt.%) and half of the monounsaturated fatty acid (33.2 wt.%) compared to canola oil. The properties of the three feedstock oils were assessed by standard testing methods regulated by AOCS, including water content, free fatty acid content, insoluble impurities, unsaponifiable matter, and phosphorus content, listed in Table 2.

The properties of the resulting biodiesel under optimized reaction conditions in this study are summarized in Table 3 together with the standards specified in ASTM D6751 and EN 14214. The EN 14214 standards indicate a satisfactory fatty acid methyl esters (FAMEs) content to be 96.5 wt.%, while FAMEs content is not specified in the ASTM D6751. In this study, the FAME contents were above 96.5% for each feedstock oil, complying with the EN14214 standard. The flash points (>150 $^{\circ}$ C) were higher than 96 °C and 101 °C as specified in ASTM D6751 and EN14214, respectively, implying that the resulting biodiesel fuels are safe to be handled during the process of transportation and storage. The kinematic viscosity, water content, and acid number were tested and all biodiesels produced adhered to the specifications in the ASTM D6751 and EN 14214 standards. These properties are also comparable to the reported data in other studies (Ciubota-Rosie et al., 2013; Leung et al., 2010).

3.2. Optimum settings and factor interaction effects

Biodiesel was synthesized using an alkali-catalyzed transesterification process as described in Section 2.3. Response surface

Fatty acid	C·D	Refined canola oil	Unrefined canola oil	Unrefined camelina oil
ratty acid	C.D			
		(Wt.%)		
Myristic acid	C14:0	-	-	0.1
Palmitic acid	C16:0	4.1	3.7	5.5
Palmitoleic acid	C16:1	0.4	0.2	0.1
Stearic acid	C18:0	1.8	1.6	2.4
Oleic acid	C18:1	63.2	63.5	14.4
Linoleic acid	C18:2	19.2	18.6	19.1
Linolenic acid	C18:3	8.9	9.6	33.5
Arachidic acid	C20:0	0.6	0.5	1.5
Gadoleic acid	C20:1	1.2	1.2	15.0
Eicosadienoic acid	C20:2	-	0.1	2.2
Eicosatrienoic acid	C20:3	-	-	-
Arachidonic acid	C20:4	-	-	1.4
Behenic acid	C22:0	0.1	0.3	0.3
Erucic acid	C22:1	0.3	0.4	3.1
Clupanodinic acid	C22:2	-	-	0.2
Docosatrienoic acid	C22:3	-	-	0.4
Docosahexaenoic acid	C22:6	-	-	
Lignoceric acid	C24:0	0.1	0.2	0.2
Nervonic acid	C24:1	0.1	0.2	0.6
Saturation degree		6.7	6.3	10.0
Monosaturation degree		65.2	65.5	33.2
Polysaturation degree		28.1	28.2	56.8
Total unsaturation degree		130.3	131.5	179.1

Table I					
Fatty acid composition of refined	canola oil,	unrefined	canola and	camelina	oil.

Notes: C:D denotes the number of carbons and the number of double bonds in each fatty acid. Total unsaturation degree = 1% monounsaturated fatty acids +2% diunsaturated fatty acids +3% triunsaturated fatty acids +4% guadunsaturated fatty acid.

Table 2

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Properties of feedstock oil (refined canola, unrefined canola and camelina).

Characteristics	Refined canola oil	Unrefined canola oil	Unrefined camelina oil
Water content (ppm)	534	838	489
Moisture and volatiles (%)	0.02	0.06	0.01
Free fatty acid (%)	0.15	2.07	0.65
Insoluble impurities (%)	0.02	0.07	0.05
Unsaponifiable matter (%)	0.99	0.86	0.70
Phosphorus in oil (ppm)	<20	<20	<20
Calculated iodine value	120.3	121.6	166.2

Table 3

The properties of resulting biodiesel from three feedstock oils.

Properties	Units	Refined canola	Unrefined canola	Unrefined camelina	ASTM D6751-09	EN 14214-10
Kinematic viscosity at 40 °C	mm ² /s	4.1	4.2	3.9	1.9–6	3.5-5
Acid number	mg KOH/g	0.01	0.01	0.25	≤0.5	≤ 0.5
Water content	mg/kg	489	353	427	-	\leq 500
Flash point	°C	168	160	152	≥93	≥101
Methyl ester content	wt.%	98.2	98.7	98.5	-	≥96.5
Linolenic acid methyl ester	wt.%	8.5	9.4	32.7	-	≤12.0

Notes: ASTM = American Society and Testing Methods; EN = European standard.

analysis of the FCCCD design results for the nine response variables are summarized in the Analysis of variance (ANOVA) *p*-values shown in Table 4. The fitted equations and the adjusted R² are shown in Table 5; and the factor settings that jointly maximized product, FAME, and biodiesel yields for each feedstock oil as well as the predicted values of product, FAME and biodiesel yields at these settings are shown in Table 6. Validation experiments were conducted in duplicate under such optimized conditions, and experimental and model-determined values were in a good agreement.

For all responses, since the temperature by catalyst loading (Te * C) interaction effect was highly significant (Table 4), contour plots of Te * C were produced using hold values for time and molar ratio of methanol to oil determined by response optimizer in Minitab. Then the overlaid contour plots that show the "sweet spot" that maximizes all three response variables for each of the refined canola, unrefined canola, and unrefined camelina shown in Fig. 1 were produced.

The optimal settings of reaction time and molar ratio of methanol/oil for refined canola, unrefined canola, and unrefined camelina found through response optimizer and the overlaid contour plots were 40 min and 7.5:1, 40 min and 10:1, and 40 min and 7:1, respectively. The sweet spot (white color area) in the overlaid contour plot maximized the product, FAME, and biodiesel yields jointly for each feedstock oil.

Fig. 1(a) clearly shows that catalyst loading for refined canola decreased from 1.7 wt.% at 30 °C to 1.3 wt.% at 45 °C, indicating reaction temperature increase resulted from the decrease of catalyst loading for maximizing refined canola product, FAME and biodiesel yield. Therefore, a significant Te * C interaction existed. For unrefined canola, catalyst loading was diminished from 1.45 wt.% to as low as 0.95 wt.% by increasing reaction temperature from 36 °C to 50 °C as shown at Fig. 1(b). A similar interaction pattern could be observed in the case of optimization of unrefined camelina as shown in Fig. 1(c). The reduction of catalyst loading



Fig. 1. Overlaid contour plot that shows the sweet spot of product, FAME and biodiesel from (a) refined canola, (b) unrefined canola, and (c) unrefined camelina.

 Table 4

 Analysis of variance (ANOVA) p-values that show the significance of the coefficient of the regression models.

SV	Refined canola		Unrefined can	Unrefined canola			Unrefined camelina		
	Product	FAME	Biodiesel	Product	FAME	Biodiesel	Product	FAME	Biodiesel
Те	0.014	0.001	0.001	0.196	0.002	0.007	0.002	0.000	0.000
Ti	0.771	0.010	0.557	0.101	0.631	0.207	0.002	0.028	0.002
R	0.294	0.010	0.066	0.028	0.016	0.005	0.158	0.003	0.008
С	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000
Te * Te	0.116	0.278	0.065	0.341	0.933	0.511	0.295	0.241	0.178
Ti * Ti	0.925	0.311	0.834	0.479	0.429	0.917	0.925	0.848	0.918
R * R	0.349	0.497	0.492	0.736	0.504	0.799	0.875	0.488	0.617
C * C	0.446	0.326	0.300	0.003	0.002	0.001	0.028	0.017	0.007
Te * Ti	0.272	0.027	0.735	0.554	0.107	0.472	0.004	0.764	0.057
Te * R	0.013	0.163	0.032	0.018	0.839	0.096	0.050	0.287	0.625
Te * C	0.001	0.001	0.001	0.001	0.006	0.001	0.000	0.000	0.000
Ti * R	0.620	0.343	0.421	0.541	0.798	0.672	0.013	0.446	0.053
Ti * C	0.593	0.568	0.738	0.010	0.760	0.070	0.003	0.086	0.008
R * C	0.370	0.001	0.648	0.921	0.107	0.344	0.063	0.022	0.015

Notes: product yield (%), FAME yield (%) and biodiesel yield (%) of refined canola, unrefined canola, and unrefined camelina, Te = Temperature (°C), Ti = Time (minute), R = Molar ratio of methanol to oil, <math>C = Catalyst loading (wt.%); SV = Sources of variance;*p*-value < 0.05 indicates significant effect at the 5% level of significance.

Table 5

Fitted model equations for Product, FAME and Biodiesel yields from refined canola, unrefined canola and unrefined camelina using uncoded (original) units along with the corresponding Adjusted R^2 values.

Model	R^2_{Adj}
Refined canola	
Product =	72.2%
$-3.2 + 2.6 \\ Te - 0.23 \\ Ti + 3.22 \\ R + 49.3 \\ C - 0.032 \\ Te * \\ Te + 0.002 \\ Ti * \\ Ti - 0.47 \\ R * \\ R - 6.1 \\ C * \\ C + 0.009 \\ Te * \\ Ti + 0.11 \\ Te * \\ R - 0.75 \\ Te * \\ C - 0.02 \\ Ti * \\ R - 0.086 \\ Ti * \\ C + 0.72 \\ R * \\ C + 0.009 \\ Te * \\ Ti + 0.11 \\ Te * \\ R - 0.75 \\ Te * \\ C - 0.02 \\ Ti * \\ R - 0.086 \\ Ti * \\ C + 0.72 \\ R * \\ C + 0.009 \\ Te * \\ Ti + 0.11 \\ Te * \\ R - 0.75 \\ Te * \\ C - 0.02 \\ Ti * \\ R - 0.086 \\ Ti * \\ C + 0.72 \\ R * \\ C + 0.009 \\ Te * \\ Ti + 0.11 \\ Te * \\ R - 0.75 \\ Te * \\ C - 0.02 \\ Ti * \\ R - 0.086 \\ Ti * \\ C + 0.72 \\ R * \\ C + 0.009 \\ Te * \\ Ti + 0.11 \\ Te * \\ R - 0.75 \\ Te * \\ C - 0.02 \\ Ti * \\ R - 0.086 \\ Ti * \\ C + 0.009 \\ Te * \\ Ti + 0.11 \\ Te * \\ R - 0.75 \\ Te * \\ C - 0.02 \\ Ti * \\ R - 0.086 \\ Ti * \\ C + 0.72 \\ Te * $	
<i>FAME</i> = 28.5 + 1.31Te + 0.75Ti + 1.14R + 27.86C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.006Ti * Ti + 0.106R * R - 2.48C * C - 0.006Te * Ti - 0.018Te * R - 0.228Te * C - 0.007Te * Te - 0.007Te * 0.007Te * Te - 0.007Te * 0	87.1%
0.012Ti * R + 0.029Ti * C - 1.133R * C	
Biodiesel = -62.1 + 3.66Te + 0.49Ti + 3.8R + 71.5C - 0.037Te * Te - 0.004Ti e * Ti - 0.329R * R - 8.04C * C + 0.003Te * Ti + 0.089Te * R - 0.913Te *	83.1%
C = 0.03111 * R = 0.05111 * C = 0.351R * C	
Unrefined canola	
Product = 21.8 + 1.097Te + 0.18Ti - 0.12R + 67.1C - 0.01Te * Te + 0.008Ti * Ti - 0.089R * R - 14.44C * C - 0.003Te * Ti + 0.061Te * R - 0.499Te * 0.497Te * 0.499Te * 0.497Te * 0.497Te * 0.499Te * 0.497Te	75.4%
C = 0.014Ti * R = 0.267Ti * C + 0.046R * C	
FAME = 31.6 + 0.36Te + 0.33Ti - 1.46R + 72.6C - 0.001Te * Te - 0.01Ti * Ti + 0.2R * R - 16.97C * C + 0.009Te * Ti + 0.005Te * R - 0.325Te * C - 0.001Te * Te - 0.01Te * Ti + 0.2R * R - 16.97C * C + 0.009Te * Ti + 0.005Te * R - 0.325Te * C - 0.001Te * Te - 0.01Te * Te - 0.01Te * Te - 0.01Te * Te - 0.001Te * 0.	85.2%
0.007Ti * R – 0.032Ti * C – 0.874R * C	
Biodiesel = -31.8 + 1.34Te + 0.44Ti - 1.74R + 125.9C - 0.01Te * Te - 0.002Ti * Ti + 0.102R * R - 28.51C * C + 0.005Te * Ti + 0.061Te * R - 0.747Te *	86.3%
C – 0.015Ti * R – 0.269Ti * C – 0.675R * C	
Unrefined camelina	
Product = -20.4 + 2.03Te + 1.23Ti + 4.2R + 54.27C - 0.009Te * Te - 0.001Ti * Ti - 0.031R * R - 7.61C * C - 0.011Te * Ti - 0.034Te * R - 0.514Te * 1.23Te + 1.23Te	85.7%
C – 0.044Ti * R – 0.227Ti * C – 0.637R * C	
<i>FAME</i> = 5.9 + 1.35Te + 0.28Ti + 3.62R + 55.1C - 0.01Te * Te + 0.002Ti * Ti - 0.147R * R - 8.77C * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.01Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.001Te * Ti + 0.018Te * R - 0.391Te * C - 0.001Te * Ti + 0.001Te * 0.001Te * Ti + 0.001Te * Ti + 0.001Te * 0.001T	89.5%
0.013Ti * R – 0.122Ti * C – 0.848R * C	
Biodiesel = -94.8 + 3.1Te + 1.3Ti + 7.0R + 100.4C - 0.018Te * Te + 0.001Ti * Ti - 0.158R * R - 15.33C * C - 0.01Te * Ti - 0.013Te * R - 0.828Te * C - 0.018Te * 100.4C + 0.018Te * 100.4C + 0.001Ti * 100.4Ti *	90.4%
0.052Ti * R – 0.305Ti * C – 1.353R * C	
Δt_{1}	

Notes: Te = Temperature (°C), Ti = Time (minute), R = Molar ratio of methanol to oil, C = Catalyst loading (wt.%).

Table 6

The optimal transesterification reaction condition settings and the best product, FAME and biodiesel yields at these settings.

Feedstock	Temp (°C)	Time (min)	Molar ratio	Catalyst (wt.%)	Product yield (%)	FAME yield (%)	Biodiesel yield (%)
Refined canola	40.7	36.6	7.4:1	1.75	99.7	98.2	97.7
Unrefined canola	50.0	40.0	10:1	1.14	96.9	98.7	95.2
Unrefined camelina	33.6	40.0	6.9:1	1.66	97.2	98.5	95.6

Note: optimization was achieved by jointly maximizing product, FAME, and biodiesel yield from feedstock oils (refined canola, unrefined canola, and unrefined camelina) via response optimizer, where Temp = temperature; Molar ratio = molar ratio of methanol to oil; Catalyst = catalyst loading (wt.%).

from 1.45–1.75 wt.% to 1.05–1.3 wt.% was caused by increasing temperature from 30 $^\circ\text{C}$ to 50 $^\circ\text{C}$ for unrefined camelina oil transesterification reaction.

3.3. Comparison of optimization results among three feedstocks

The impact of refining on optimization was first examined. As shown in Table 6, the optimal reaction conditions for refined canola oil were determined to be a reaction temperature of 40.7 °C, reaction time of 36.6 min, molar ratio of methanol/ oil of 7.4, and KOH catalyst loading of 1.75 wt.%. Under such an optimum setting, the highest product yield was 99.7 wt.%, FAME yield of 98.2 wt.%, and biodiesel yield of 97.7 wt.%. Compared to refined canola oil, the optimized conditions for unrefined canola were: catalyst loading of 1.14 wt.%, much lower than that of refined canola, reaction temperature of 50 °C, higher than that of refined canola, slightly longer reaction time of 40 min, and higher molar ratio of methanol/oil of 10:1. Maximum yields of biodiesel derived from unrefined canola were close to those of refined canola biodiesel. The differences in the obtained optimal settings in the two case studies could be mainly attributed to varying free fatty acid content (FFT) in the two feedstocks. As shown in Table 2, most properties of refined and unrefined canola were comparable except FFA content. Unrefined canola oil had much higher FFA content (2.07%) than that of refined canola oil (0.15%). High free fatty acid content of parent oil in biodiesel production process is extremely undesirable as it may cause a number of problems. During transesterification, FFA in feedstock oil can react with excess base catalyst to form soap, which decreases the overall yield (Pullen and Saeed, 2015; Wu and Leung, 2011; Vicente et al., 2006; Bouaid et al., 2007). Excess catalysts also cause more triglyceride participation in the saponification reaction, leading to a remarkable reduction in FAME yield. The saponification reaction is usually faster than transesterification. Therefore, optimized catalyst loading of unrefined canola was lower than that of refined canola to maximize biodiesel product yields. On the other hand, as demonstrated in Section 3.2, there was a significant Te * C interaction effect during transesterification. Increasing reaction temperature could sufficiently compensate for the decreased reaction rate caused by a lower catalyst loading in the case of unrefined canola oil. A compromise between strongly interactive variables, temperature and catalyst loading, was observed to reach maximum yields.

The optimized conditions of unrefined camelina present some different features. The optimal reaction temperature was 33.6 °C, the lowest one among those three feedstocks examined in this study. The other optimized variables, the reaction time of 40 min, molar ratio of methanol/oil of 6.9:1 and catalyst loading of 1.66 wt.%, were very close to those of refined canola. This is as expected, as the FFA content in unrefined camelina oil (0.65 wt.%) and refined canola oil (0.15%) were both below 0.8 wt.%. The threshold limit value in which the saponification reaction was almost negligible (Vicente et al., 2006). Therefore, these two feedstock oils required similar amounts of catalyst to accelerate transesterification reaction. However, it is surprising that the optimized temperature of 33.6 °C for camelina was much lower than that of unrefined canola (50 °C), and even refined canola (40.7 °C). Such difference in optimal reaction temperature could be due to the unique fatty acid composition of camelina. As illustrated Table 1, camelina oil was comprised of a much higher percentage of polyunsaturated fatty acid of 56.8% (mainly C18:3) and a relatively low content of monounsaturated fatty acid of 33.2% (mainly C18:1), compared to those of canola with polyunsaturated fatty acid of 28.1% and monounsaturated fatty acid of 65.2%. The total unsaturation degree of camelina was 179.1 while that of canola was 130.3.

It has been demonstrated in a study by Pinzi et al. (2011a) that the optimized temperature of transesterification decreased with an increase in polyunsaturation degree. They researched the optimization of a number of vegetable oils and established a relationship, namely, the optimized temperature as a function of carbon chain length, monounsaturation degree, polyunsaturation degree, and total unsaturation degree. Experimental result in this study is in good agreement with their relationship. Sharma et al. (2014) reported that transesterification was an endothermic reaction and the activation energy for C18:1, C18:2, and C18:3 methanolysis was 23.8 kJ/mol, 17.9 kJ/mol, and 9.9 kJ/mol respectively. It offered additional support for the experimental results. 56.8% of fatty acids in camelina oil were C18:3; therefore, a relatively low temperature was sufficient to convert camelina oil into biodiesel. Moreover, a transesterification reaction comprises of three consecutive reversible reactions, first, triglyceride to diglyceride, then diglyceride to monoglyceride, and finally monoglyceride to FAME, among which converting diglyceride to monoglyceride is the rate-limiting step (Asakuma et al., 2009; Stavarache et al., 2007; Komers et al., 2001; Freedman et al., 1986). However, Pinzi et al. (2011a) found that diglyceride to monoglyceride conversion was generally faster for unsaturated fatty acids than for saturated fatty acids. All the above factors led to the low optimized temperature in the case of transesterification of camelina oil.

Table 7 presents the comparison of the optimal reaction conditions for alkali-catalyzed transesterification among different feedstock oils. It is important to point out that this comparison is a generally qualitative comparison as the optimal reaction conditions are also associated with feedstock properties and experimental procedures which might vary in each reported study.

4. Conclusion

A comparative study on the transesterification optimization of refined canola, and unrefined canola and camelina was conducted using response surface methodology. This study found: (1) there was a significant interaction effect between the reaction temperature and catalyst loading (Te * C). Such interaction effect allowed compromises between reaction temperature and catalyst loading during transesterification to cope with high free fatty acid content in parent oils. For the parent oils with high free fatty acid content, a relatively low catalyst loading and high reaction temperature were desirable. The decreased reaction rate caused by low catalyst loading could be effectively compensated for by increasing reaction temperature to maximize yields; and (2) the optimum reaction temperature for vegetable oils with high polyunsaturation degree was much lower than that required by feedstock oils with lower polyunsaturation degree. This is due to the fact that the rate-limiting step in transesterification, diglyceride to monoglyceride, was faster for highly unsaturated oils than for saturated oils. Additional contribution came from the activation energy of C18:3 being much lower than those of C18:2 and C18:1.

The results in this study cannot fully explain the inconsistency found in transesterification optimization, but provides interesting information on the impact of refining and parent oils' unsaturation degree on the optimized reaction conditions. The results also offer basic guidelines on how to optimize different reaction variables taking economic viability and feedstock availability into account. Especially when considering establishing a biodiesel production plant with multiple feedstocks, different optimized conditions should be applied to achieve overall maximum yield.

Acknowledgments

The authors acknowledge the financial support from NSERC Discovery (RGPIN 04211), and Xingyu Peng for carrying out preliminary experiments.

Table /

Comparison of optimal reaction conditions among different feedstock oils.

Feedstock	Temp (°C)	Time (min)	Molar ratio	Catalyst (wt.%)	Biodiesel yield (%)	Reference
Unrefined rapeseed	65	120	6:1	KOH: 1.0	95-96	Rashid and Anwar (2008)
Unrefined sunflower	60	120	6:1	NaOH: 1.0	97.1	Rashid et al. (2008)
Refined canola	60	60	9:1	KOH: 1.0	80–95	Patil and Deng (2009)
Refined canola	40.7	36.6	7.4:1	KOH: 1.75	97.7	Current study
Unrefined canola	50	40	10:1	KOH: 1.14	95.2	Current study
Refined camelina	50	70	8:1	KOH: 1.0	95.8	Wu and Leung (2011)
Unrefined camelina	36.6	40	6.9:1	KOH: 1.66	95.6	Current study

Temp: temperature; Molar ratio: molar ratio of methanol to oil; Catalyst: catalyst concentration. KOH: potassium hydroxide; NaOH: sodium hydroxide.

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