Effect of thermal decomposition on biodiesel viscosity and cold flow property
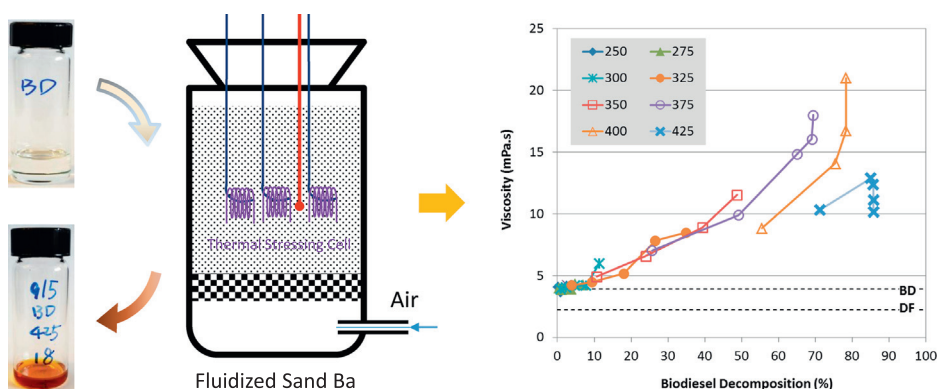
Ronghong Lin, Yiying Zhu [1], Lawrence L. Tavlarides *

Department of Biomedical and Chemical Engineering, Syracuse University, 329 Link Hall, Syracuse, NY 13244, USA

HIGHLIGHTS

- Thermal decomposition has a significant effect on biodiesel viscosity and cold flow property.
- Polymerization products determine the viscosity of thermally-stressed biodiesel.
- Pyrolysis products reduce biodiesel viscosity and improve biodiesel cold flow properties.
- Dynamic viscosities of biodiesel, diesel and their blends were determined at 40 °C.
- Biodiesel thermal decomposition involves isomerization, polymerization and pyrolysis reactions.

GRAPHICAL ABSTRACT

ABSTRACT

Thermal stressing experiments were performed in batch reactors at 250–425 °C for 3–63 min to evaluate the influence of thermal decomposition on biodiesel viscosity and cold flow properties. Dynamic viscosity was measured by a micro viscometer, and cold flow properties were characterized by differential scanning calorimetry (DSC). The crystallization onset temperature determined by DSC correlates with cold flow properties. Results showed that the *cis–trans* isomerization reactions had a minimal effect on both viscosity and cold flow properties of biodiesel, but polymerization and pyrolysis reactions had significant influence on both properties. Polymerization reactions resulted in increases in both viscosity and the crystallization onset temperature, while pyrolysis reactions showed the opposite effect. The current study suggests that polymerization reactions should be avoided or minimized during high-temperature non-catalytic homogeneous transesterification reactions for biodiesel production.

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1. Introduction

Biodiesel, a substitute for petroleum diesel fuel, produced from renewable resources such as vegetable oils, animal fats, algal oils and waste cooking oils, provides superior environmental benefits over conventional diesel fuel [1]. It is produced through transesterification reactions either under low temperature heterogeneous conditions using alkaline, acid, enzyme or heterogeneous solid catalysts or under high temperature (usually >250 °C) homogeneous conditions without using a catalyst [2–4]. Compared with conventional catalytic methods, the homogeneous non-catalytic method offers many attractive advantages including short reaction time, high water and free fatty acid tolerance, simple and environmental friendly process, and potential reduction in the production cost [5,6]. Despite these advantages, concerns about the application of the high-temperature non-catalytic transesterification method for biodiesel production include reduced biodiesel yield and possible influence on biodiesel

* Corresponding author. Tel.: +1 315 443 1883; fax: +1 315 443 9175.
E-mail addresses: rlin01@syr.edu (R. Lin), lltavlar@syr.edu (L.L. Tavlarides).
[1] Current address: Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, NC 27695, USA.

quality due to thermal decomposition of biodiesel at high temperature [7,8]. Some researchers [7,9] recommended that high-temperature non-catalytic transesterification reactions for biodiesel production should be conducted below the minimum decomposition temperature to avoid biodiesel decomposition, while others [10] argued that the low content of decomposition products in biodiesel produced in the best reaction conditions should not affect fuel properties. Others also argued that the decomposition would be acceptable as long as fuel properties such as the viscosity and cold flow properties were improved due to the presence of lower molecular weight decomposition products [8]. Still others proposed the use of thermal cracking to improve cold flow and stability properties of biodiesel fuels [11].

Biodiesel is unstable and starts to decompose upon thermal stressing at 275 °C and above. The decomposition mainly involves isomerization reactions to transfer unsaturated *cis*-type fatty acid methyl esters (FAMEs) to *trans*-type FAMEs, dimerization or polymerization reactions to form higher molecular weight (MW) components, pyrolysis reactions to break down FAMEs to form lower MW FAMEs and hydrocarbons. Our previous study showed that these reactions occurred at 275–400 °C, 300–425 °C and >350 °C, respectively [12]. Consequently, the thermally-stressed biodiesel may contain not only higher MW compounds but also lower MW ones, and these species must influence fuel characteristics [7].

Dunn [13] examined the effect of oxidation under high temperatures on biodiesel fuel properties and found that the kinematic viscosity of biodiesel increased as the oxidation reaction temperature increased possibly due to the Diels–Alder reaction which results in the formation of dimers and polymers [14]. Yuan et al. [15] demonstrated by modeling that long-chain unsaturated FAMEs significantly affected fuel properties such as critical temperature, critical volume, liquid density, liquid viscosity, surface tension, vapor pressure and heat of vaporization. Xin et al. [16] reported that the oxidation stability of biodiesel produced from waste cooking oils having high peroxide values by the high-temperature supercritical methanol method (270 °C, 17 MPa, 30 min) was improved over biodiesel made from the same feedstock by the conventional alkali-catalyzed method. Imahara et al. [7] observed that the cloud point and the pour point of biodiesel produced in supercritical methanol at 350 °C and 43 MPa increased slightly due to the *cis*–*trans* isomerization. Luo et al. [17] showed that biodiesel could be upgrade to fuel products with significantly improved cold flow properties using thermal cracking. Windom

and Bruno [18] found that the cracking and polymerization of unsaturated FAMEs significantly influenced the volatility of biodiesel fuel.

Despite the quality research in this field, the effects of thermal decomposition on biodiesel properties have not been well addressed. The current work is a continuation of our previous study on biodiesel thermal decomposition [12], and the main objective is to understand the influence of thermal stressing on the viscosity and cold flow properties of biodiesel. Viscosity is one important parameter that affects fuel spray characteristics and hence engine brake effective power and emissions [19,20]. Cold flow properties (cloud point, pour point and cold filter plugging point) characterize the performance of liquid fuels during cold weather, and these properties for biodiesel must be acquired for designing storage procedures and conditions and to ensure safe operation of fuel systems and engines [21]. In this work, fresh soy biodiesel fuel was thermally stressed in batch reactors at varying temperatures for a length of time up to 63 min. Viscosity and cold flow properties of the stressed biodiesel were characterized, and the effects of thermal stressing conditions (temperature and duration) and thermal decomposition on these two fuel properties were evaluated.

2. Material and methods

2.1. Material

Commercial soy biodiesel fuel (Nexsol BD-0100, ASTM D 6751, CAS# 67784-80-9) was purchased from Peter Cremer North America. The density of biodiesel was 0.880 g/ml [12]. The gas chromatography analysis showed that the biodiesel contains by mass 80.8% unsaturated FAMEs and 19.2% saturated FAMEs [12]. Detailed composition of the biodiesel and properties of individual pure FAME are given in Table 1. It should be pointed out that natural vegetable oils and biodiesel derived from them by conventional catalytic methods contain exclusively *cis*-type unsaturated fatty acid structures [22,23].

The Grunberg–Nissan equation [27] was applied to predict the dynamic viscosity of biodiesel using either mass fraction or molar fraction [28]:

$$\ln \eta_m = \sum_{i=1}^{n} a_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1, j \neq i}^{n} a_i a_j G_{ij} \qquad (1)$$

Table 1
Property of FAMEs and predicted viscosity of biodiesel.

FAMEs	MW (g/mol)	ρ^a (g/ml)	η^b (mPa·s)	Mass frac. (x_i) [12]	$x_i \ln \eta$	Mol. frac. (y_i)	$y_i \ln \eta$
Palmitic acid methyl ester (C16:0)	270.5	0.850	3.78	0.106	0.141	0.115	0.153
Stearic acid methyl ester (C18:0)	298.5	0.851	4.76	0.060	0.094	0.059	0.092
Oleic acid methyl ester (C18:1)							
(*cis*)	296.5	0.864	3.84	0.300[d]	0.404	0.297	0.400
(*trans*)			5.06[c]		0.487		0.482
Linoleic acid methyl ester (C18:2)							
(*cis*)	294.5	0.879	3.19	0.508[d]	0.590	0.507	0.588
(*trans*)			4.69[c]		0.785		0.782
Arachidic acid methyl ester (C20:0)	326.6	n/a	6.05	0.009	0.016	0.008	0.015
Behenic acid methyl ester (C22:0)	354.6	n/a	7.51	0.017	0.034	0.014	0.028
Total				1.000	1.279	1.000	1.276
					1.556		1.552
Predicted biodiesel viscosity (mPa·s)							
(*cis*)					3.59		3.58
(*trans*)					4.74[e]		4.72[e]

[a] Densities of pure FAMEs were predicted by the correlation equation $\rho = mT + b$ with coefficients determined by Yuan et al. [24].
[b] Otherwise noted, viscosities of pure FAMEs were predicted by the Vogel equation with coefficients determined by Yuan et al. [24].
[c] Viscosity of *trans*-type FAMEs from Ref. [25].
[d] Mass fractions of C18:1 and C18:2 were not determined in Ref. [12]. The values presented in this table were estimated based on the analysis for the same brand of biodiesel samples [26].
[e] Predicted viscosity of biodiesel assuming all *cis*-type C18:1 and C18:2 were isomerized to *trans*-type isomers.