Applied Energy 102 (2013) 647–656

Contents lists available at SciVerse ScienceDirect

Applied Energy

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

Detailed physical properties prediction of pure methyl esters for biodiesel combustion modeling

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HIGHLIGHTS

- Group contribution methods from molecular level have been used for the prediction.
- Complete prediction of the physical properties for 5 methyl esters has been done.
- The predicted results can be very useful for biodiesel combustion modeling.
- Various models have been compared and the best model has been identified.
- Predicted properties are over large temperature ranges with excellent accuracies.

ARTICLE INFO

Article history:
Received 14 May 2012
Received in revised form 29 July 2012
Accepted 10 August 2012
Available online 7 September 2012

Keywords:
Biodiesel
Methyl ester
Physical properties
Combustion modeling

ABSTRACT

In order to accurately simulate the fuel spray, atomization, combustion and emission formation processes of a diesel engine fueled with biodiesel, adequate knowledge of biodiesel's physical properties is desired. The objective of this work is to do a detailed physical properties prediction for the five major methyl esters of biodiesel for combustion modeling. The physical properties considered in this study are: normal boiling point, critical properties, vapor pressure, and latent heat of vaporization, liquid density, liquid viscosity, liquid thermal conductivity, gas diffusion coefficients and surface tension. For each physical property, the best prediction model has been identified, and very good agreements have been obtained between the predicted results and the published data where available. The calculated results can be used as key references for biodiesel combustion modeling.

1. Introduction

In recent years, biodiesel is seen as a promising alternative to conventional diesel due to its desirable attributes such as biodegradable, renewable, sustainable and carbon neutral [1]. It can directly replace petroleum diesel and be used in diesel engines without the requirement of any major modifications, reducing the country's dependence on imported oil. In terms of emissions, researchers have shown that the use of biodiesel can result in a substantial reduction in the unburned hydro-carbon (HC), particulate matter (PM) and carbon monoxide (CO) emissions [2–4], even though a slight increase in nitrogen oxides (NO_x) emission is observed [3–6].

Biodiesel produced from either vegetable oil or animal fats consists of long chain monoalkyl esters derived through transeterification process. It contains five typical methyl esters having the molecular structure of R—(C═O)—O—R′, where R and R′ are chains of alkyl and alkenyl groups with as many as 17–19 total carbon atoms [7]. With the differences in its molecular structure, the physical and chemical properties of biodiesel are quite different from those of conventional diesel. This can have a significant effect on the fuel atomization, evaporation, and the subsequent combustion and emission formation processes. In engine applications, although there have been extensive experimental studies related to biofuels [4,8–18], the combustion and emission characteristics of biodiesel are still not so well understood as compared to diesel. On the other hand, numerical study on the combustion and emission characteristics of biodiesel can be used as an effective tool. However, it needs comprehensive computational workstation, taking into account effects of 3D flow field in conjunction with the application of reliable reaction mechanism. Meanwhile, the accuracy of numerical prediction is highly dependent on biodiesel's fuel properties. Although accurate experimental data [19–23] for various properties can be used for some biodiesel combustion simulations, it is still difficult to provide all the data especially over a large temperature range. Hence, a proper characterization of the fuel using predictive methodologies is desired. The key issue in characterization of a fuel is the selection of a proper and reliable method.

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0306-2619/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2012.08.009

Numerous empirical methods have been proposed to predict the physical properties of a fuel. Allen and his coworkers [24] proposed a method which was verified experimentally to predict the viscosities of biodiesel fuel at 40 °C based on the carbon atoms as well as the number of double bonds. A similar work was also done by Marrero-Morejon and Pardillo-Fontdevila where a more generalized method was developed to predict the liquid viscosity of pure organic compounds at ambient temperature (20 °C) by using group-interaction contributions. And most recently, Ramirez-Verduzco et al. [25] developed four new empirical correlations to estimate the cetane number, kinematic viscosity, density, and higher heating value of fatty acid methyl esters from their molecular weight and the degree of unsaturation. From the above we can see, most of the predictions are either for a specific fuel property, or only valid at a fix temperature, or over limited temperature ranges. However, for combustion modeling, detailed physical properties of a fuel should be provided from the lowest expected temperature to the critical temperature of the fuel. Among the literatures, a relatively more detailed documentation of physical properties prediction was done by Yuan et al. [26]. In their work, the critical properties, vapor pressure, latent heat of vaporization, density, surface tension, and liquid viscosity of biodiesel was predicted and compared with published data available. However, the physical properties considered in this study were still not complete for combustion modeling. Furthermore, the predicted results were only compared and reported for biodiesel but not for the pure methyl esters, and it is believed that it is of critical importance to accurately predict the physical properties for each pure methyl ester before the mixing rules can be applied to calculate the physical properties of biodiesel.

Hence, the objective of this work is to do a more complete prediction on the physical properties of the five typical methyl esters over a large temperature range.

2. Physical properties prediction models

Table 1 shows the chemical formula, molecular weight, number of atoms and molecular structure of the five typical methyl esters of biodiesel. These data will be used for the latter physical properties predictions. For each physical property, various prediction methods are introduced in this section.

2.1. Normal boiling point

The normal boiling point of a fluid is the temperature in Kelvins at which the vapor pressure is equal to one atmospheric pressure. It can be predicted using the correlation proposed by Yuan et al. [27] as shown below:

$$T_b = 218.49\ln(CN) - 6.933 \tag{1}$$

where T_b is the normal boiling temperature (K); and CN is the number of carbon atoms in the methyl esters.

Another one is the model proposed by Reid et al. [28] based on the group contributions method:

$$T_b = 198 + \sum \Delta b \tag{2}$$

where Δb quantities can be calculated by summing contributions of various atoms or groups of atoms as shown in [28].

2.2. Critical properties

Critical pressure, critical temperature and critical volume are the three widely used pure component constants, which cannot be easily obtained through experiments. In physical properties prediction, they are usually used as key inputs.

2.2.1. Ambrose method

$$T_c = T_b\left[1 + \left(1.242 + \sum \Delta_T\right)^{-1}\right] \tag{3}$$

$$P_c = M\left(0.339 + \sum \Delta_P\right)^{-2} \tag{4}$$

$$V_c = 40 + \sum \Delta_V \tag{5}$$

where T_c is the critical temperature (K); P_c is the critical pressure (bar); M is the molecular weight (g/mol) and V_c is the critical volume (cm^3/mol). The Δ_T, Δ_P, and Δ_V values can be calculated by summing the group contributions of various atoms or groups of atoms listed in [28].

2.2.2. Joback method

$$T_c = T_b\left[0.584 + 0.965\sum \Delta_T - \left(\sum \Delta_T\right)^2\right]^{-1} \tag{6}$$

$$P_c = \left(0.113 + 0.0032n_A - \sum \Delta_P\right)^{-2} \tag{7}$$

$$V_c = 17.5 + \sum \Delta_V \tag{8}$$

The units employed in Joback method are the same as those in Ambrose method.

2.2.3. Fedors method

Fedors group contribution method is only valid for critical temperature prediction. The advantage of this method is it does not require the normal boiling point. The drawback of this method is that it is less accurate compared to the other two methods mentioned above.

$$T_c = 535\log\sum \Delta_T \tag{9}$$

The Δ_T values can be calculated by summing the group contributions of various atoms or groups of atoms listed in [28].

2.3. Vapor pressure

2.3.1. Lee–Kesler method

The Lee–Kesler method [28] is one of the very successful methods to predict the vapor pressure. It requires the knowledge of critical pressure, critical temperature and acentric factor of the fluid as inputs.

$$\ln P_{vpr} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \tag{10}$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862\ln T_r + 0.169347T_r^6 \tag{11}$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721\ln T_r + 0.43577T_r^6 \tag{12}$$

where P_{vpr} is the reduced vapor pressure = P/P_c; ω is the acentric factor which can be found in [28,29] or computed using Eq. (13); T_r is the reduced temperature = T/T_c.

$$\omega = \frac{\alpha}{\beta} \tag{13}$$

where

$$\alpha = -\ln P_c - 5.97214 + 6.09648\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^6 \tag{14}$$

$$\beta = 15.2518 - 15.6875\theta^{-1} - 13.4721\ln\theta + 0.43577\theta^6 \tag{15}$$