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Experimental and computational study on the compatibility of biodiesel/diesel/methanol blended fuel

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HIGHLIGHTS

- LLE data containing n-alkane, fatty acid methyl ester and methanol were measured.
- The experimental data were well modeled using NRTL and UNIFAC-Dortmund models.
- The new and reliable model parameters were obtained.
- Phase chart for the diesel/biodiesel/methanol blends was successfully simulated.

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ABSTRACT

In order to obtain the solubility values for the diesel/biodiesel/methanol blends and prepare the homogeneous single blended fuels, biodiesel or diesel was composed approximately of a series of model compounds and the liquid–liquid equilibrium (LLE) data for the seven ternary and one quaternary systems involving in n-alkane, fatty acid methyl ester and methanol have been measured and performed thermodynamic modeling. The experimental data were correlated by NRTL model and UNIFAC-Dortmund model with a good accuracy. The new parameters of NRTL and UNIFAC-Dortmund models were obtained systematically and they were tested to be reliable for the (diesel + biodiesel + methanol) system through the prediction of some experimental and literature data. Meanwhile, the phase chart for the (diesel + biodiesel + methanol) mixture was successfully simulated using Aspen Plus software based on the obtained NRTL and UNIFAC-Dortmund models parameters, which was applied to investigate the compatibility of biodiesel/diesel/methanol blended fuel. In this work, the diesel/biodiesel/methanol blended fuel containing 30% biodiesel is likely to be border-line in terms of homogeneous system.

1. Introduction

Due to the extensive utilization of fossil fuel, the world's petroleum reserves are exhausted gradually and the ecological environment is destroyed and polluted seriously, such as atmospheric haze and global warming. Therefore, it is very urgent to develop an alternative to fossil energy. Biodiesel, known as fatty acid monoalkyl ester, is regarded as a promising fuel and has received great attention because of its renewable and environmental benefits [1].

The biodiesel, obtained from vegetable oils or animal fats, has a lot of advantages, such as non-toxicity, renewability, the minimal sulfur, biodegradability, high flash point and cetane number [2]. However, some poor properties of biodiesel, including high viscosities, low volatilities and poor cold flow properties, led ignition delay and higher carbon built up when biodiesel was used as fuel for the long-term engine test [3]. Therefore, biodiesel is not suitable well to use directly in the existing diesel engines. Fortunately, the utilization of diesel/biodiesel blends or diesel/biodiesel/methanol blends at a certain proportion does not require any modification of the car engine [4]. Li et al. [5] investigated the combustion and emission characteristics of diesel engine fueled with diesel/biodiesel/pentanol blended fuel and suggested that the addition of alcohols with lower viscosity and high volatility could improve the atomization quality of diesel–biodiesel blends. Methanol is often used as additive to the diesel/biodiesel blended fuel to decrease the density, viscosity and surface tension of the mixed fuel and reduce harmful exhaust emission [6]. The mutual solubility of diesel, biodiesel and methanol is important and must be investigated for the design, simulation and optimization of the

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Nomenclature

Abbreviations

LLE	liquid–liquid equilibrium
VLE	vapor–liquid equilibrium
NRTL	non-random two liquids
UNIFAC	universal quasi-chemical functional group activity coefficient
FID	flame ionization detector
RMSD	root mean square deviation

Symbols

x	molar fraction
G_{ij}	the NRTL parameter
T	the absolute temperature
R	the universal gas constant
$(g_{12}-g_{22})$ and $(g_{21}-g_{11})$	the binary interaction parameters
V	the auxiliary property
V_i'	the empirically modified V_i-value
q	the surface area parameter
r	the volume parameter
F	the auxiliary property
$v_k^{(i)}$	the number of structural groups of type k in molecule i
R_k	the group volume parameter
Q_k	the group area parameter
X_m	the group mole fraction of group m in the liquid phase
a_{nm}, b_{nm} and c_{nm}	the group interaction parameters
w_{11}	the mass fraction of n-alkane in the alkane-rich phase
w_{33}	the mass fraction of methanol in the methanol-rich phase
a and b	the parameters in Othmer–Tobias equation

Greek letters

γ_i	the activity coefficient
τ_{ij}	the binary molecular energy interaction parameter
α_{12}	the non-randomness binary interaction parameter
Γ_k	the activity coefficient of group k in mixture
θ_m	the surface fraction of group m in the liquid phase
ψ_{nm}	the interaction between groups n and m

Subscripts

i and j	pure component indexes
n and m	group indexes
i, j and k	component, phase, and tie-line in Eqs. (19) and (20)

Superscripts

C	combinatorial term
R	residual term
exp	experimental
cal	calculated
(i)	the pure substance in Eq. (12)

production of the homogeneous diesel/biodiesel/methanol blended fuel. Therefore, it is necessary to study the liquid–liquid equilibrium (LLE) in the systems containing these components.

At present, some LLE data of binary or multi-component mixtures involving in biodiesel have been reported in the open literatures. Rostami et al. [7] measured liquid–liquid phase equilibria for the binary mixture of water + biodiesel within a temperature range of 297.2–333.2 K. And, the liquid–liquid solubility values for the binary systems (*Jatropha curcas* fatty acid methyl esters/*J. curcas* fatty acid ethyl esters/fatty acid methyl esters/Castor oil fatty acid ethyl esters/Soybean fatty acid methyl esters/Soybean fatty acid ethyl esters + water) have been determined [8–10]. Furthermore, the liquid–liquid equilibrium (LLE) for the ternary and quaternary system (biodiesel + methanol/ethanol + glycerol/water) [10–14], (biodiesel + water + glycerol) [15], (biodiesel + water + glycerol + methanol/ethanol) [10,16] have been reported. In these phase equilibrium systems, biodiesel was regarded as a pseudo-pure component and the corresponding interaction parameters were obtained through the correlation of the experimental LLE data. However, the compositions of biodiesel vary considerably by means of the different raw materials. And, the reported interaction parameters can only be used for the specific biodiesel system and are unable to be spreaded to other relevant systems. Therefore, it is very necessary to investigate the phase equilibrium data of pure alkyl esters of fatty acid and obtain a series of the model parameters. Then, the phase equilibrium data related to biodiesel produced from different raw materials can be calculated by the model parameters.

Currently, there were few phase equilibrium data of model compounds about biodiesel, diesel and methanol in the reported literatures. Benziane et al. [17] measured the isothermal vapor–liquid equilibria of three binary systems (ethyl hexanoate + n-tetradecane), (ethyl decanoate + n-tetradecane), and (ethyl tetradecanoate + n-tetradecane) by means of a static apparatus at temperatures between 373.15 and 453.15 K. Chen et al. [18] reported the isobaric vapor–liquid equilibrium (VLE) data for the binary system of methyl myristate + methyl palmitate at 0.5, 1.0 and 1.4 kPa. A survey of literature showed that the phase equilibrium data containing pure alkyl esters of fatty acid, n-alkanes and alcohol with shorter carbon chain are still scarce, and it is very necessary to get new phase equilibrium data.

Therefore, the objectives of this study were to (1) determine the liquid–liquid equilibrium (LLE) data for the model compounds about n-alkane (diesel), fatty acid methyl ester (biodiesel) and methanol at 303.15 K, including (n-undecane/n-dodecane/n-tridecane/n-tetradecane + methyl laurate + methanol), (n-tetradecane/n-pentadecane/n-hexadecane + methyl myristate + methanol) and (n-dodecane + n-tetradecane + methyl laurate + methanol); (2) correlate the experimental LLE data with the NRTL model and UNIFAC-Dortmund models and obtain the new interaction parameters for the (n-alkane + fatty acid methyl ester + methanol) mixtures systematically; (3) estimate the phase equilibrium data of multi-component system (alkane mixtures + fatty acid methyl ester mixtures + methanol) through the obtained interaction parameters. Furthermore, alkane mixtures and fatty acid methyl ester mixtures were regarded as diesel, and biodiesel, respectively. The compatibility of diesel/biodiesel/methanol blended fuel was discussed, which are of essential for the preparation of the homogeneous single blended fuels.

2. Methods

2.1. Materials

In this study, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane and methyl myristate were obtained from J&K Scientific (China) with 99.00% purity by mass. Methyl laurate (>99.0% in mass fraction, Tianjin Guangfu Reagent Co., China) was used in this work. n-Hexadecane and methanol were provided from J&K Scientific (China), which had a purity of 98.50% and 99.99% in mass fraction, respectively. More details of