

Phase equilibria of triolein to biodiesel reactor systems



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ARTICLE INFO

Article history:

Received 15 July 2015

Received in revised form

13 September 2015

Accepted 24 September 2015

Available online 30 September 2015

Keywords:

SAFT

GXL

Supercritical

CO₂

ABSTRACT

The phase equilibria of biodiesel systems, which are comprised of mixtures of triolein, methanol, carbon dioxide, methyl-oleate, glycerol, and water, are analyzed using PC-SAFT in ASPEN PLUS and SAFT- γ Mie in gPROMS (gSAFT) for systems in the vicinity of their critical point. Pure-species density and liquid vapor-pressure data were used to regress pure-species parameters for both variants of the SAFT equations. Binary vapor–liquid and liquid–liquid equilibrium data for the six species were used to obtain binary interaction parameters in PC-SAFT and cross parameters in SAFT- γ Mie. Vapor–liquid and liquid–liquid equilibria data from the literature were supplemented with experimental data taken herein to obtain a complete set of binary parameters. Overall, SAFT- γ Mie gave the best agreement with binary data, but had difficulty predicting liquid–liquid behavior in ternary systems. PC-SAFT showed good agreement with experimental data, especially for LLE systems. However, the *Gibbs flash method* in ASPEN PLUS yielded poor predictions for the triolein, methanol, and carbon dioxide mixture in the VLE and VLLE regions – but, addition of a tangent-plane-distance code revealed the prediction of unstable phases. Similarly, gSAFT in gPROMS, was unable to predict correct phase distributions, using parameters regressed in prior studies. Consequently, to examine the conversion of triolein to methyl-oleate observed experimentally at VLLE conditions (95 °C 9.65 MPa), RK-ASPEN (without binary interaction parameters) was used in a custom-written FORTRAN reactor program.

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1. Introduction

Biodiesel offers a renewable, carbon-neutral alternative to its fossil fuel counterpart. However, with plummeting oil prices, alternative fuels have become less competitive, and thus, improved processes are needed to reduce costs. In a previous study, which examined algae-to-biodiesel ventures, the extraction step was found to be energy intensive and have widely variable economic estimates [1]. An alternative, using high-pressure CO₂, has been demonstrated experimentally [2] and found to be highly-effective and selective at extracting algae-oil. Similarly, several studies have shown the potential of supercritical CO₂ as a co-solvent in the transesterification reactions [3–5], allowing high conversions at relatively low temperatures. It is thus possible that these two steps could be combined, although this has not been demonstrated yet. However, performing the oil-extraction and conversion in the same step or at least the same process should yield considerable cost savings by eliminating pre-processing and purification steps that

are currently required [1].

This paper focuses on the conversion of triglyceride to biodiesel using supercritical CO₂—with the kinetic mechanism shown in Fig. 1, rather than the extraction of oil from algae. Given that the objective is to use algae-derived oils, water is assumed to be present. Due to lack of data, diglycerides and monoglycerides are excluded from the calculations herein. Further, triolein and methyl-oleate were used as exemplars of algal oil and biodiesel for this study as they are the only triglyceride and fatty acid methyl ester (FAME) molecules having sufficient data to be included. As such, this analysis involves just six chemical species: triolein, methyl-oleate, methanol, glycerol, water, and carbon dioxide. In future studies, the number of triglycerides will be increased to accurately represent algae-oils, allowing the extraction step to be modeled.

Kinetic pre-exponential factors and activation energies for the conversion of algae-oils to biofuels are available [5–7]. However, previous studies that modeled the phase behavior for transesterification reactions used crude models (like Redlich–Kwong in ASPEN PLUS [3,4,8], which are not suitable in the critical region or with large, asymmetric molecules. The most advanced equations-of-state (EoS) used for supercritical systems have been the Cubic

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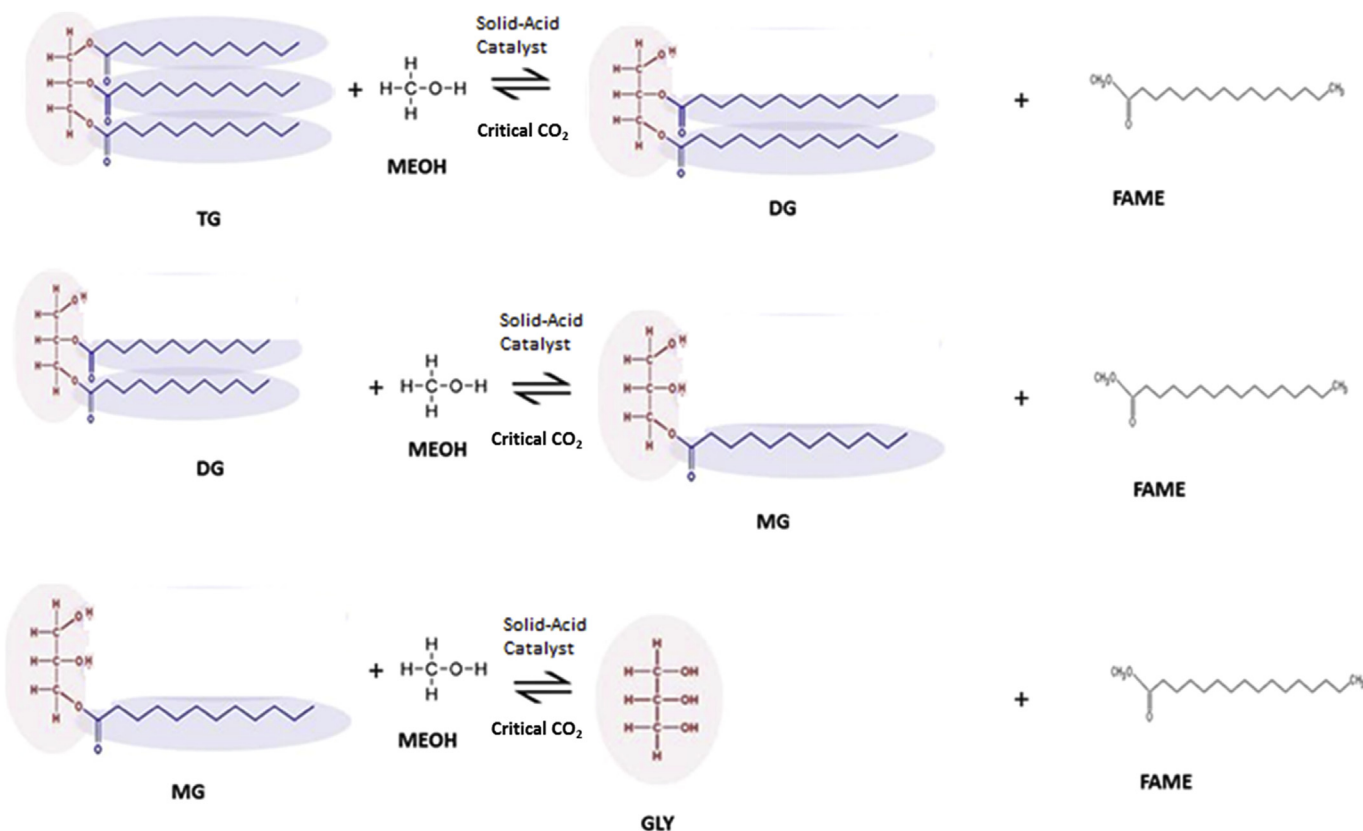


Fig. 1. Triolein to biodiesel conversion mechanism. TG is triglyceride (triolein), MEOH is methanol, DG is diglyceride, FAME is fatty-acid methyl-ester (biodiesel), MG is monoglyceride, GLY is glycerol, and critical CO_2 is carbon dioxide in or near the critical region.

Plus Association (CPA) EoS, which was used to study supercritical alcohols [9–15], and the soft-SAFT, which was used to study binary systems of CO_2 and water, and CO_2 and FAME [16].

The objective of this transesterification study is to use the SAFT EoS to model the phase behavior of a biodiesel reactor [up to three phases (vapor, polar liquid, nonpolar liquid) or as few as one supercritical phase [17]]. The miscibility between the phases has drastic effects on the concentrations (and reaction rates). It will be shown that a reliable phase equilibria model is needed to describe the reactor conversions; however, predictions with commercially-available SAFT phase-equilibria models are not yet sufficiently reliable in the critical region for triolein, methanol and CO_2 . This paper presents experimental data and shows the reason for the inadequacy of their predictions, along with suggestions to improve their predictive capability in future work.

In the sections that follow, cubic and SAFT equations-of-state are reviewed, the latter designed for use with long-chain hydrocarbons. Experimental methods are presented, which were used to generate data herein for binary systems, where data were unavailable or unreliable. Most of these data were for liquid–liquid systems, although one vapor–liquid system was studied experimentally. Then, pure-species, binary, and ternary data are used to compare two SAFT variants [PC-SAFT in ASPEN PLUS [18,19] and SAFT- γ Mie in gPROMS (gSAFT¹) [20,21]] and RK-ASPEN. Finally, a

multiphase-reactor model, using approximate RK-ASPEN to model VLE, is formulated and evaluated with experimental data.

2. Theory

2.1. Cubic equations-of-state

Cubic equations-of-state (EoS) were first developed roughly 130 years ago and have become the industry standard since the development of computer-aided process design in the 1970s. The cubic EoSs are named as such because they contain a cubed molar volume term (Eq. (1)). Numerous variants exist, the most popular of which are the van der Waals, Soave–Redlich–Kwong [22], and Peng–Robinson [23] equations. Herein, a variant of Soave–Redlich–Kwong (RK-ASPEN) will be used for comparative purposes with the SAFT EoS. The equations that describe RK-ASPEN are shown below.

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \quad (1)$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - K_{a,ij}) \quad (2)$$

$$b = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - K_{b,ij}) \quad (3)$$

where R is the gas constant (8.314 J/mol-K), T is temperature, V is

¹ Note that the equation-of-state is known as SAFT- γ Mie. gSAFT is the thermodynamics package developed by Process System Enterprise, which contains the SAFT- γ Mie equation-of-state. Note that these two terms are used interchangeably throughout this paper.

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