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Estimation of critical properties of reaction mixtures obtained in different reaction conditions during the synthesis of biodiesel with supercritical methanol from soybean oil

Pilar Olivares-Carrillo [a], Joaquín Quesada-Medina [a,*], Antonia Pérez de los Ríos [a], Francisco J. Hernández-Fernández [b]

[a] Department of Chemical Engineering, Faculty of Chemistry, University of Murcia (UMU), P.O. Box 4021, Campus of Espinardo, E-30071 Murcia, Spain
[b] Department of Chemical and Environmental Engineering, Technical University of Cartagena (UPCT), Campus La Muralla, C/Doctor Fleming S/N, E-30202 Cartagena, Murcia, Spain

HIGHLIGHTS

- Critical properties of 20 individual components were estimated by different methods.
- Critical properties of more than 150 reaction mixtures were estimated by different methods.
- Critical property data are very interesting for estimating other thermodynamic properties.

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ABSTRACT

The methods of Constantinou and Gani, Ambrose, Joback, Fedors, and Klincewicz were used to estimate the critical temperatures and pressures of the pure components present during the synthesis of biodiesel from soybean oil using supercritical methanol, and the results obtained were compared. Based on the critical properties calculated for the pure components, the pseudocritical and true critical properties of the reaction mixtures obtained in different experimental reaction conditions [temperature, reaction time and methanol-to-oil molar ratio ranges of 523–623 K (8–43 MPa), 15–90 min and 13:1–53:1, respectively] were estimated by means of Kay's rule and the modified Prausnitz and Gunn combination, and by Li's method, respectively. The estimated data of critical properties of the reaction mixtures appearing during the synthesis of biodiesel in supercritical methanol will be very interesting for the calculation of other thermodynamic properties, including the phase behavior of the medium.

1. Introduction

Biodiesel is a promising source of energy because it is a renewable and biodegradable fuel that produces less harmful emissions than petroleum-based diesel; furthermore, it can be used in its pure form or blended with petroleum-based diesel.

The synthesis of biodiesel consists in the transformation of the triglycerides present in vegetable oils and animal fats into fatty acid methyl esters (biodiesel). The transesterification reaction to produce biodiesel is developed in three consecutive stages: 1st stage, triglycerides react with methanol to produce diglycerides and fatty acid methyl esters; 2nd stage, diglycerides react with more methanol to produce monoglycerides and more fatty acid methyl esters; and 3rd stage, monoglycerides react with even more methanol to produce glycerin and more fatty acid methyl esters. Therefore, monoglycerides and diglycerides are formed during the transesterification of triglycerides. These intermediate products can be generated in great amounts during the supercritical reaction [1].

There are different ways of producing biodiesel according to the kind of material used, the most widely used methods focusing on catalyst or non-catalyst transesterification reactions. As regards the catalyst methods, traditional chemical reactions use different types of catalyst, such as sodium or potassium hydroxides, sulfuric acid, ion exchange resins and lipases [2]. The synthesis of biodiesel through alkaline catalytic transesterification reactions has several drawbacks: it is energy intensive, the recovery of glycerol is difficult, the alkaline wastewater retains fatty acids, and water interferes with the reaction. In addition, alkaline transesterification shows low selectivity, leading to undesirable side reactions [3,4]. Lipase has been used as a biocatalyst to synthesize biodiesel from

* Corresponding author. Tel.: +34 868 88 7228; fax: +34 868 88 4148.
E-mail address: quesamed@um.es (J. Quesada-Medina).

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vegetable oils or animal fats and may overcome several of the problems of conventional chemical processes. However, due to the high price of the enzyme and the time-consuming reaction process, this method is not widely used in large scale production [5,6]. Saka was the first to suggest that biodiesel may be prepared from vegetable oil via a non-catalytic method with supercritical alcohols [7]. Compared with the traditional chemistry method, not only does this method require no catalyst, but nearly complete conversions can be achieved in a very short time. In this way successfully resolves most of the problems associated with conventional chemical processes.

However, for the design, simulation and optimization of chemical plants for the production of biodiesel using supercritical methanol we need to further our knowledge of the critical properties of all the compounds present during the transesterification of triglycerides with supercritical methanol [triglycerides, diglycerides, monoglycerides, glycerol, fatty acid methyl esters and methanol] and their mixtures, which are generated during the supercritical reaction. Unfortunately, the experimental determination of the critical temperature and pressure of some compounds is difficult and, in many cases, impossible since they decompose (chemically degrade), especially those of a larger structure and/or which are strongly associated, before the critical point is reached. Consequently, prediction methods are the only means by which these properties may be determined. Since the first development of group contribution methods by Riedel [8] and Lydersen [9], a large number of methods have been developed to obtain critical property data. However, while various approaches can be found in the literature, the use of group contribution methods still seems to provide the most reliable and simple approach with which to obtain reliable results. A variety of methods for estimating critical property data are available in the open literature. A broad overview of these methods together with a detailed discussion of their reliability was given by Poling et al. [10] and in earlier versions by Joback and Reid [11], and Reid et al. [12]. In addition, several authors have evaluated the performance of models using a large common set of experimental data [13]. Indeed, it is possible to estimate the critical properties of each pure component and then compute the properties of their mixtures based on some mixing rules.

In the literature, very few papers calculate the critical parameters of the principal triglycerides that constitute the different oils used to produce biodiesel [14–19], the fatty acid methyl esters generated from them [20–25] and only some intermediate reaction products (monoglycerides and diglycerides) [22,26]. Furthermore, there are no data available on the critical properties of the reaction mixtures generated during the methanolysis in supercritical conditions.

The purpose of the present paper is to determine by various methods (Constantinou and Gani, Ambrose, Joback, Fedors, and Klincewicz) the critical temperature and pressure of the pure components present during the supercritical methanol transesterification of refined soybean oil. Moreover, based on the critical properties calculated for the pure components, the critical temperature and pressure of the reaction mixtures obtained in different experimental reaction conditions [reaction temperature, reaction time and methanol-to-oil molar ratio ranges of 523–623 K (8–43 MPa), 15–90 min and 13:1–53:1, respectively] will be estimated by Kay's rule, the modified Prausnitz and Gunn combination, and Li's method. The results provided by the prediction methods will be compared with each other.

2. Methodology for estimating the critical properties of individual components present during the reaction

The accurate prediction of critical properties of pure components is of particular importance because of the influence they have on the selection of the optimal conditions for synthesizing biodiesel with supercritical methanol. The critical properties of interest (temperature, pressure and molar volume) are generally estimated using existing property correlations available in the literature. These correlations are selected on the basis of their applicability to the chemical structure of the components and simplicity of use, and include the effects of the structure and molecular composition of the required compounds.

Among the large number of estimation methods available, several are derived from correlations of experimental data. The best are based on theory with empirical corrections for the theory's defects. Others are based on generalizations that are partly empirical but nevertheless have application to a remarkably wide range of properties. Totally empirical correlations are useful only when applied to situations very similar to those used to establish the correlations. In this research, five methods based on theory with empirical corrections were studied (Constantinou and Gani [27], Ambrose [28–30], Joback [11,31], Fedors [32], and Klincewicz [33]). These five prediction methods were selected based on the fact that they are (i) among the most commonly used in the literature to predict the critical properties of the individual compounds involved during the transesterification of triglycerides (in this way, we will be able to compare our results with the few already published in the literature), (ii) easy to use, (iv) accurate, and (v) are not restricted to a certain types of substances. The different equations used in each method are shown in Table 1.

All these methods (described in Appendix A) use group contribution techniques, except that of Klincewicz, to determine contribution factors for specific groups of atoms constituting the molecule of interest. Values of these contribution factors for each critical property are tabulated for every method and their sum represents the final correction applied to the calculation of the critical property. These specific methods differ according to the definition of different groups and contribution factor values. Application of these methods requires knowledge of the group contribution models based on the molecular structure, molecular weight (M) and the normal boiling point (T_b) of the compound.

The group contribution methods for calculating critical properties belong to two distinctive classes: (a) the "First Order" group techniques, which determine the molecule structure by means of simple group contribution, neglecting the next-nearest neighbor effects (methods of Ambrose, Joback, and Fedors); and (b) the "Second Order" group techniques, which take into consideration the influence of first and second level neighbors of a given group (method of Constantinou–Gani).

The method of Ambrose is one of the best estimating methods used in the literature to calculate the critical temperature of individual organic compounds because it provides the smallest errors (0.7%) and is simple to apply [30]. Joback's method is somewhat more complicated than that of Ambrose, but covers the broadest range of compounds [10]; the error in this method tends to increase considerably when there is no measured boiling temperature available and, therefore, estimated values must be used. Regarding the method of Constantinou and Gani, this generally gives good results for large and complex structure substances (0.85% average error) because calculations do not require knowledge of the boiling temperatures but, however, is more complicated to use than that of Joback. The method of Fedors, which is only valid for estimating critical temperatures, does not require the use of boiling temperatures and gives the highest errors (4%).

As regards the critical pressures, all the methods chosen give average errors of about 3–6%, except that of Klincewicz and Reid, for which a 12% average error was obtained. The Constantinou–Gani Second Order contributions do not significantly improve the results. Thus, there is little to choose among the methods and the decision must be based less on accuracy and reliability than on breadth of applicability and ease of use.