Biomass and Bioenergy 81 (2015) 544–555

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Modeling and parameters fitting of chemical and phase equilibria in reactive systems for biodiesel production

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ARTICLE INFO

Article history:
Received 29 September 2012
Received in revised form
16 July 2014
Accepted 21 May 2015
Available online 29 August 2015

Keywords:
Biodiesel
Optimization
Gibbs energy minimization
Chemical and phase equilibrium
Non-linear programming

ABSTRACT

Biodiesel, a non-toxic biodegradable fuel from renewable sources such as vegetable oils, has been developed in order to reduce dependence on crude oil and enable sustainable development. The knowledge of phase equilibrium in systems containing compounds for biodiesel production is valuable, especially in the purification stage of the biodiesel. Nonetheless, the refining process of biodiesel and by-products can be difficult and can elevate the production costs considerably unless it has an appropriate knowledge about the phase separation behavior. In addition, the transesterification reaction yield for producing biodiesel depends upon several operation parameters *e.g.* the feed molar ratio oil-to-alcohol and the temperature. These parameters were analyzed through a thermodynamic analysis by direct Gibbs energy minimization method in this paper, with the purpose of calculating the chemical and phase equilibrium of some mixtures containing compounds found in biodiesel production. For this, optimization techniques associated with the GAMS® 2.5 software were utilized and the UNIQUAC and NRTL models were applied to represent the non-idealities of the liquid phases. Also, binary interaction parameters of studied compounds were correlated for NRTL and UNIQUAC models by using the least squares principle. The results showed that the use of optimization techniques associated with the GAMS software are useful and efficient tools to calculate the chemical and phase equilibrium by minimizing the Gibbs energy. Moreover, a good agreement was observed in cases in which calculated data were compared with experimental data.

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1. Introduction

The development of new alternative fuels has been studied over the past decades because of the environmental preoccupations and the possibility of depletion of crude oil reserves. In this manner, there has emerged a significant volume of research and review works about replacing conventional fuels by biodiesel [1–9]. This biofuel represents an attractive alternative due to its environmental advantages (a non-toxic and biodegradable fuel), when it is compared with the petroleum-based diesel. Biodiesel is produced from renewable resources, such as vegetable oils and animal fats. For this reason, this contributes to the reduction of emissions of toxic gases, as SO_2, CO and hydrocarbons [1,5,10].

Biodiesel can be produced from several vegetable oils by using different techniques, including esterification, transesterification, blending, cracking, microemulsification, and pyrolysis [1,11–13]. The most commonly used technique to obtain biodiesel is the transesterification. It is a reaction in which a fat or oil and an alcohol react to produce fatty acid alkyl esters (biodiesel) and glycerol as by-product. This reaction consists of a sequence of three consecutive reversible reactions, in which the oil (mixture of triacylglycerols) is stepwise converted into diacylglycerol, monoacylglycerol and finally glycerol; resulting a fatty acid ester at each step of the reaction as is shown in Fig. 1. The vegetable oils transesterification is catalyzed by both acid/base catalysts to increase the reaction rate and its yield. An excess of alcohol is frequently employed to shift the equilibrium of the reaction [14,15].

The most widely used vegetable oils to produce biodiesel are canola, sunflower, cotton, palm, soybean, coconut, jatropha oils etc [7]. Among these oils, the soybean oil is currently being utilized by many countries because of its large production and availability *e.g.* the United States, Argentina and Brazil. Methanol is the most frequently used alcohol because it is cheaper than other alcohols (ethanol, propanol, butanol and amyl alcohol) and it is also recovered more easily than other ones. Ethanol is the predominant alcohol in Brazil for biodiesel production due to its low cost and

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http://dx.doi.org/10.1016/j.biombioe.2015.05.015
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Nomenclature

a_{ij}	parameter associated to the characteristic energy of interaction between the molecules of type i and j [K]
A_i	parameter for saturation pressure in DIPPR correlation of component *i*
b_{ij}	parameter associated to the characteristic energy of interaction between the molecules of type i and j
B_i	parameter for saturation pressure in DIPPR correlation of component *i*
C_i	parameter for saturation pressure in DIPPR correlation of component *i*
Cp_i	ideal-gas heat capacity for component *i* [J mol^{-1} K^{-1}]
D_i	parameter for saturation pressure in DIPPR correlation of component *i*
E_i	parameter for saturation pressure in DIPPR correlation of component *i*
$\widehat{f}_{ij}$	fugacity of component *i* in the mixture in phase *j*
f_i°	fugacity of pure component *i* in the reference state at system temperature and reference pressure
FAEE	fatty acid ethyl esters
FAME	fatty acid methyl esters
FOBJ	objective function
G	total Gibbs energy of the system [kJ]
GAMS	General Algebraic Modeling System
LLE	liquid–liquid equilibrium
MW	molar mass [kg kmol^{-1}]
n_{ij}	number of moles of component *i* in phase *j* [mol]
n_i^0	initial number of moles of component *i*[mol]
n_i^t	total number of moles of component *i*[mol]
nexp	number of experimental data
NC	number of components in the system
NP	number of potential phases in the system
NR	number of independent reactions in the system
NRTL	non-random two liquid
P	absolute pressure of system [kPa]
P_i^{sat}	saturation pressure of component *i* [kPa]
q	molecular surface parameter
Q_k	group surface parameter
RMSD	root mean square deviation
r	molecular–size parameter
R	universal gas constant [kJ mol^{-1} K^{-1}]
R_k	group size parameter
T	absolute temperature of system [K]
TL	number of tie lines
UNIQUAC	universal quasi chemical
VLE	vapor–liquid equilibrium
w	mass fraction
x_i	liquid phase mole fraction of component *i*
y_i	vapor phase mole fraction of component *i*

Greek letters

α_{ij}	empirical parameter associated to the non-randomness in the mixture
μ_{ij}	chemical potential of component *i* in phase *j* [kJ mol^{-1}]
μ_i°	chemical potential of reference at system temperature and reference pressure of pure component *i* [kJ mol^{-1}]
$\widehat{\phi}_i$	fugacity coefficient of component *i* in vapor phase
γ_{ij}	activity coefficient of pure component *i* in liquid phase *j*
ν_{ik}	stoichiometric coefficient of the component *i* in the reaction *k*
ν_k	number of groups *k* of the component *i* or molecule *m*
ξ_k	extent of the reaction *k*
Δg_{ij}	empirical parameter associated to the characteristic energy of interaction between the molecules of type i and j
Δg_f^o	standard-state Gibbs energy of formation [kJ mol^{-1}]
Δh_f^o	standard-state enthalpy of formation [kJ mol^{-1}]

Superscripts

cal	calculated by model
exp	experimental
L	liquid phase
V	vapor phase

Subscripts

i	component in the mixture
j	phase in the system
k	independent reactions in the system

accessibility in this country [1,14,16–18]. The reaction rate depends upon several parameters, that's why if these are not optimized then the reaction will be incomplete. These parameters are: the amounts of free fatty acids, water, catalyst, the reaction temperature, the reaction time and the amount and type of alcohol [7,19]. The effect of some of these parameters on the equilibrium conversion can be predicted through a thermodynamic analysis of reaction [20,21].

It is important to highlight that two liquid phases co-exist in equilibrium at the final system: one of them is rich in glycerol and the other one is rich in fatty acid methyl/ethyl esters. In these two liquid phases, there are amounts of the unreacted alcohol in proportions depending on the characteristic energies of intermolecular

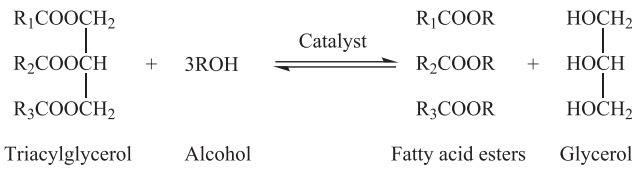

Fig. 1. Scheme of general transesterification reaction.

interactions between each compound [22,23]. A solid phase could be present in the system when a solid catalyst will be used. So, the phases in the final system could have small amounts of catalyst as well as several concentrations of monoacylglycerols and diacylglycerols, and in some cases triacylglycerols that may also no react completely. A stage of purification and separation of phases is necessary in order to separate the esters from mixture at low cost and to obtain a high purity biodiesel [1]. Some methods can be found in literature to predict the chemical and phase equilibrium [24–29], these methods can be divided into two different but equivalents approaches: the method of Gibbs energy minimization and the method of finding the roots of a nonlinear equations system. In latter method, a reliable phase stability analysis is required for verifying whether the calculation of simultaneous chemical and phase equilibrium is correct. By applying of method of direct Gibbs energy minimization, a sufficient condition for achieving the thermodynamic equilibrium (global minimum of Gibbs energy) at temperature and pressure constant is satisfied, provided that the initial estimate has a number of potential phases equal to or larger than the number of phases present at equilibrium. If the number of potential phases is underestimated at the start of the calculation, it

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