Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 76–84

Contents lists available at SciVerse ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Design and control of a biodiesel production process using sugar catalyst for oil feedstock with different free fatty acid concentrations

Jian-Kai Cheng, Chuan-Chen Chao, Jeffrey D. Ward, I-Lung Chien *

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 6 December 2012
Received in revised form 8 April 2013
Accepted 11 April 2013
Available online 14 May 2013

Keywords:
Biodiesel
Free fatty acids
Sugar catalyst
Process design
Process control

ABSTRACT

This manuscript reports on the plant-wide design and control of a biodiesel process using a sugar catalyst. This catalyst is less expensive and more environmentally friendly than the conventional catalyst because it does not have to be neutralized and there is no resulting waste salt. Also, the acid catalyst can be used for simultaneous esterification of free fatty acids (FFA) and transesterification of triglyceride because there is no concern about the formation of soap, which is a problem with the conventional base catalyst. Two issues are addressed in this work. The first one is to find the effect of FFA content in oil feed to the optimal design of this process. The second one is to investigate the operability of the proposed process. The results show that total annual cost of the plant-wide process is not significantly changed when the FFA content greater than 15 wt%. As compared to a two-step process in literature, the energy consumption per tons of biodiesel production of our proposed process gives significant 65.8% saving for an oil feed with 5 wt% FFA. Dynamic simulations demonstrate that the proposed process can accommodate production rate and feed composition changes using a decentralized plant-wide control structure.

1. Introduction

Biodiesel, an alternative fuel that can be made from renewable resources or waste oil, has attracted increasing attention recently because of concerns about global climate change and the diminishing global supply of crude oil. Biodiesel can be manufactured from biological feedstock such as soybean oil by transesterification with an alcohol such as methanol. In the conventional biodiesel process, the reaction is catalyzed with a homogeneous base catalyst such as sodium hydroxide. This catalyst has the disadvantage that in the presence of even trace amounts of water it will react to form a soapy byproduct which is difficult to remove from the reactor effluent. Furthermore, free fatty acids (FFAs) containing in lower-quality feedstock such as waste cooking oil can be esterified with alcohol to form biodiesel but producing water as a byproduct of that reaction.

Van Gerpen *et al.* [1] reported that used cooking oils typically contain 2–7 wt% FFAs, animal fats contain from 5 wt% to 30 wt% FFAs, and lower quality feedstock, such as trap grease, could contain over 75 wt% FFAs. Therefore, in the conventional process for the conversion of such lower quality feedstock to biodiesel, all of the free fatty acid is first esterified using a homogeneous acid catalyst [2], all of the water is then removed and the remaining oil is transesterified using a homogeneous base catalyst. The resulting process consumes a great deal of acid and base catalysts and produces a great deal of waste salt.

In 2005, Toda *et al.* [3] first reported the discovery of a new heterogeneous acid catalyst that was active for the esterification and transesterification reactions. The catalyst was made by partially carbonizing a mixture of saccharides and then sulphonating the resulting product in concentrated sulphuric acid. The resulting catalyst was found to be less active than liquid sulphuric acid but more active than commercial heterogeneous acid catalysts. Since that time, other researchers have also reported success using such sugar catalysts for biodiesel production [4–6].

Although there have been many reports about catalysis and reaction engineering for biodiesel production, the process development aspect has received less attention. Most processes reported in the literature use an excess of alcohol to achieve high conversion of the oil in a single pass. Therefore the feed ratio of alcohol to oil is an important design variable. If the reactor system is inefficient, a higher feed ratio will be required and this will result in greater cost in the separation section. Shen *et al.* [7] reported that the efficiency of the reaction section could be improved by separating and partially recycling the glycerol phase of the reactor effluent (which contains a great deal of the reactant methanol).

While considering economic assessment, plant-wide processes including reactor, recycle and purification systems were presented

---

* Corresponding author. Tel.: +886 3 3366 3063; fax: +886 2 2362 3040.
E-mail address: ilungchien@ntu.edu.tw (I.-L. Chien).

1876-1070/$ – see front matter © 2013 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jtice.2013.04.005

to deal with oils containing free fatty acids, such as a homogeneous alkali-catalyzed process with esterification pretreatment, a homogeneous acid-catalyzed process, a heterogeneous acid-catalyzed process, and a supercritical process [8,9]. West *et al.* [8] concluded that the heterogeneous acid-catalyzed process had the lowest total annual cost while Marchetti *et al.* [9] concluded that it gave the most profit in terms of the net present value (NPV).

We are not aware of any researchers that have presented a plant-wide process of the biodiesel production using the sugar catalyst, where the esterification and transesterification react simultaneously in the same reactors. Since the sugar catalyst is less active, it can be expected that the reaction section will be less efficient. However, this may be offset by a reduction in overall catalyst cost since no recovery and recycling of this heterogeneous catalyst is necessary as opposed to a homogeneous catalyst. Another potential advantage of using sugar catalyst is that the equipment cost can be reduced since the esterification and transesterification can be carried out simultaneously in the same reactors.

In addition, the controllability of biodiesel processes is also an important issue while the FFA content in oil feedstock is uncertain. In the literatures, the control design of the biodiesel processes for the vegetable oil has been discussed [7,10]. However, the study on the control of the biodiesel plant with FFA content in oil feedstock has not been proposed.

Therefore, in this work we will develop and optimize a process for the production of biodiesel using a sugar catalyst. We will also try to develop a decentralized control structure for the process and simulated the dynamic response of the proposed process for changes in feed flow rate and feed composition.

2. Reaction kinetics and thermodynamics of the studied system

Van Gerpen *et al.* [1] reported that a molecule of triolein has near the actual number of atoms of carbon and hydrogen and has a molecular weight that is near the value for soybean oil. To simplify the analysis of kinetics and thermodynamics, oil can be regarded as a mixture of pure triolein (TG) and pure oleic acid (FFA). Note that all three fatty acid chain of triolein are oleic acid. Consequently, methyl-oleate (FAME) can be used to represent a biodiesel product. Note that the assumption of the representative compounds may not fit all different oil sources but overall properties would still be very similar.

2.1. Thermodynamics

Since the biodiesel process involves highly non-ideal components in the system, proper modeling of the thermodynamic behavior is important to achieve a reliable design. Table 1 shows the sources of thermodynamic parameters used in this study. Fig. 1 shows the regression results (model and experimental data) for the ternary system MeOH/TG/FAME from Cheng *et al.* [11]. Fig. 2 shows the four-component (quaternary) liquid–liquid equilibrium diagram for the components including methanol, water, FAME and glycerol. Table 2 shows the normal boiling points of all pure components and azeotropes.

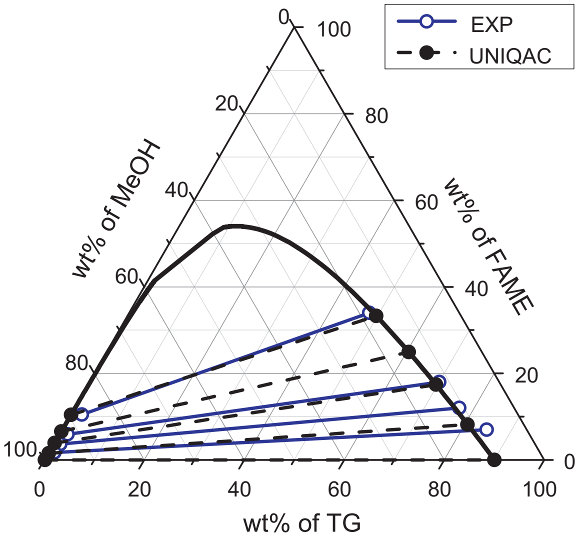

Fig. 1. Regression results for liquid–liquid equilibrium (mass basis) in the ternary system FAME/MeOH/TG at $t = 60\,^{\circ}C$. (solid circle: predicted data; circle: experimental data [10]).

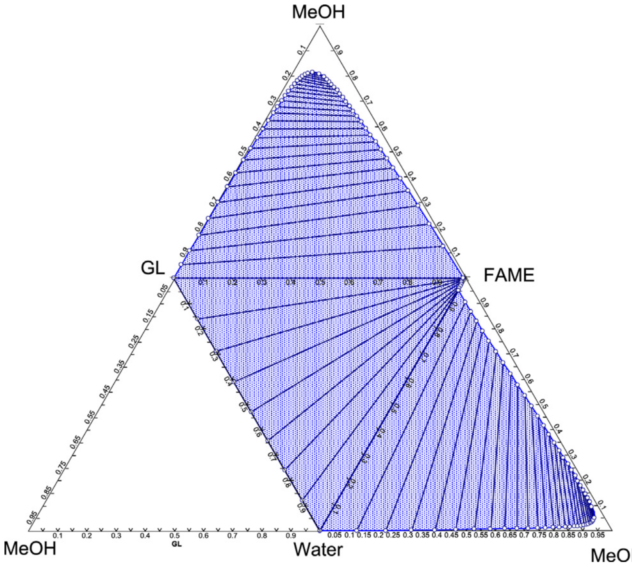

Fig. 2. Quaternary liquid–liquid equilibrium diagram (mole basis) for FAME/MeOH/water/GL at $T = 150\,^{\circ}C$ and $P = 15$ atm.

2.2. Reaction kinetics

For the simultaneous esterification and transesterification reactions using the heterogeneous sugar catalyst, experimental data from Lien *et al.* [4] were used to obtain kinetic parameters. For the transesterification to produce FAME, the reaction is shown in

Table 1
Sources of liquid–liquid equilibrium thermodynamic model parameters.

	TG	OA	MeOH	FAME	GL	Water
TG	–	UNIFAC	Cheng	Cheng	UNIFAC	UNIFAC
OA	–	–	Aspen	UNIFAC	UNIFAC	UNIFAC
MeOH	–	–	–	Lee	Lee	Aspen
FAME	–	–	–	–	Lee	Lee
GL	–	–	–	–	–	Aspen

UNIFAC: predicted by UNIFAC Method in Aspen Plus; Aspen: built in the databank of Aspen Plus; Cheng: binary parameters are regressed from experimental data by Cheng *et al.* [11]; Lee: binary parameters are given by Lee *et al.* [14].