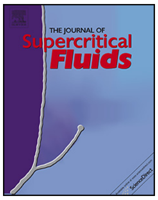
J. of Supercritical Fluids 124 (2017) 57–71

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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



Continuous biodiesel production in supercritical two-step process: phase equilibrium and process design

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ARTICLE INFO

Article history:
Received 26 October 2016
Received in revised form 23 January 2017
Accepted 25 January 2017
Available online 28 January 2017

Keywords:
Simulation
Transesterification
Co-solvent
Vapor-liquid equilibrium
Phase envelope
Validation

ABSTRACT

A supercritical biodiesel production process via transesterification of vegetable oil with methanol, using CO_2 as co-solvent is designed, simulated, and validated with experimental data. A preliminary study of the liquid-vapor equilibrium of the reacting mixture at different compositions was done to determine the supercritical conditions, by means of pressure-temperature diagrams. Under supercritical conditions, the presence of a single phase increases the reaction kinetics, avoiding the limitation by interphase mass transfer, and enabling to carry out the process with low residence time. The proposed process is based on two fixed-bed catalytic reactors in series, with intermediate glycerol separation. CO_2 used as co-solvent decreases the critical temperature, enabling to carry out the process in milder conditions. The intermediate glycerol separation displaces the chemical equilibrium towards higher conversion of triglyceride, increasing biodiesel yield. The results of a complete experimental study are used to validate the model, through a comparison with the simulations result.

1. Introduction

Biodiesel is a fatty acid methyl esters mixture which has been widely used as an engine fuel over the last decades. Interestingly, one of the first fuels tested by Rudolf Diesel in the late 19th century were vegetable oils. In his *Rational Heat Engine* [1], Diesel developed the idea that the very high compression of the cylinder can raise the temperature to values high enough to auto-ignite the fuel. Compression-injection engines rapidly spread in Europe and North America for electricity generation because of their practical efficiency (due to the higher compression ratios used and the non-expensive gas-oil).

An interesting property of biodiesel is its similarity to oil-derived gas-oil as a compression-ignition fuel, both in terms of cetane number and heating value. Biodiesel is mainly produced by transesterification reaction, and could be considered a totally renewable fuel as it can be produced using vegetable oils and a bio-alcohol (e.g., bio-ethanol). If methanol (MeOH) synthesized from fossil fuels-derived (e.g., coal) syngas is used for its production, biodiesel can be only considered as partially renewable. The type of glycerides to be used as raw material, depends on the local availability. The products of transesterification of vegetable oils also offer the advantage of low viscosity and clean combustion. Demirbas compared supercritical (SC) transesterification process with other potential processes [2]. A summary on available biodiesel manufacturing processes was given by Dimian and Sorin Bildea [3]. In this regard, the Henkel process carried out in many European plants is of interest because it uses a continuous, liquid-phase, homogeneously catalysed system based on sodium methylate catalyst. This process produces fatty acid methyl esters (FAME) and raw glycerol, with a standard capacity of 50,000 tons of biodiesel per year. Plants of the original Henkel processes are freely offered for license [4,5]. A useful review on the plants in operation in Europe, USA and Asian Pacific, with about 3 Mtons per year production (from 1992 to 2007), with a total of 12 Mtons per year production worldwide in 2008 was provided by International Energy Agency (IEA) [6].

The Lurgi process is also interesting because it uses a homogeneous sodium methylate catalyst that is converted to methanol in the process [7]. Sodium methylate, a very strong alkali, has to be produced in another plant (that could be located far-off the biodiesel plant), then shipped to the biodiesel plant, and fed continuously to the reactor. Sodium methylate is a relatively inexpensive chemical, but it is dangerous to handle, with consequent high risk during the shipping and operation, and should be neutralized within the biodiesel plant. This requires HCl consumption for NaOH neutralization and water washing for purification. However, many

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http://dx.doi.org/10.1016/j.supflu.2017.01.010
0896-8446/

small-scale local biodiesel producers operate with batch plants and recovery operations, with all sorts of available oils including spent cooking oils, using standard bases. Vila and Salguero [8] showed that using a reactor design based in the low pressure homogeneous kinetics and the Henkel patent data, the two in-series reactors are of quite large size (30 m^3 each), with a powerful agitation requirement.

Glisíc and Skala provided simulation studies regarding biodiesel manufacture [9]. Homogeneous and heterogeneous catalysis (or even no catalyst) can be used, depending on the type of reactor. In our previous work [10], and in another work [11], a solid catalyst, SAC-13® (Engelhard) was used in a packed-bed reactor in a continuous process, which is preferred for a large plant. The results indicate that SAC-13®, as well as other ion-exchange catalysts (i.e., Amberlyst-15®, and Dowex-50® to lesser extent), hold activity for long periods, and can be used in catalytic distillation. The use of solid acid catalysts allows the elimination of the methoxide and the water generation.

He et al. described a SC transesterification process using methanol [12]. Prior to this, Madras et al. [13] studied the biodiesel synthesis with methanol (or ethanol) without a catalyst, to high conversions at 200 bar and the SC reaction using an enzymatic catalyst (lipase) in a CO_2 environment with limited conversion (30% max). It seems that the CO_2 solvent adversely affects interphase mass transfer and/or the fluid-phase equilibrium. This was documented by Pereda et al. [14,15], who showed that phase equilibrium problems occur in the reactor phase condition, and by Nunes da Ponte [16] for the effect of multiphase on kinetics. Härröd et al. [17] and later Ramírez et al. [18] showed that conditions of phase-equilibria are crucial for the case of catalytic (Pd/C) hydrogenations in SC propane, CO_2, and other solvents.

Maçaira et al. experimentally demonstrated that biodiesel could be produced in a SC MeOH/CO_2 mixture (8 wt.% vegetable oil + 92 wt.% of a MeOH/CO_2 mixture 25/75 parts by wt.), at 150–250 bar with a solid acid catalyst, using a packed-bed reactor [10,11]. Phase equilibria at the operating pressure and temperatures were rather done by approximation with estimated data. Pereda et al. [15,19] showed the way to the engineering predictions of thermodynamics equilibrium data using Group-Contribution Equation of State (GC-EoS) [20,21], which is one of the most reliable methods available today for multiphase processes. Unless phase equilibrium is well predicted, the engineering for the process reactor (sub- or supercritical) cannot be worked out properly [22]. In this regard, Pereda et al. [23] applied this method to the separation units of the plant as well. This opens up the question as to which equations of state have to be used, as will be addressed in this work.

The overall stoichiometry for the biodiesel (FAME) formation from vegetable oil by transesterification, is as follows:

$$\text{Triglyceryde} + 3\text{MeOH} \rightleftarrows \text{Glycerol} + 3\text{FAME} \tag{1}$$

The reaction proceeds stepwise as three reversible reactions in series, where each reaction gives one FAME molecule, but only in the last one glycerol is generated:

$$\begin{aligned} &A + B \underset{k2}{\overset{k1}{\rightleftarrows}} D + E \\ &D + B \underset{k4}{\overset{k3}{\rightleftarrows}} M + E \\ &M + B \underset{k6}{\overset{k5}{\rightleftarrows}} G + E \end{aligned} \tag{2}$$

where: A = triglyceride, B = methanol, D = diglyceride, M = monogyceride, E = FAME, G = glycerol. It is interesting to point out that a rapid transfer of the glycerol (reaction product) to another phase will shift the chemical equilibrium toward the formation of more FAME.

In this work, our purpose was two-fold. First, as glycerol is the component with the highest boiling point (290 °C) and density (1.261 g cm^{-3}), we wanted to simulate its partial condensation from the fluid coming out from the reactor using a reliable equation of state (EoS). In particular, we wanted to find the pressure-temperature (P–T) ranges where glycerol separation is favored. The use of CO_2 in combination with SC methanol is of fundamental value in the proposed process as a way to lower the mixture's critical point and monitor how this evolves with the reaction advance. To this end, we followed the approach of Poliakoff et al. [24], who obtained a moving envelope on the P–T plane for critical points and retrograde condensation regions. Our last purpose was to rewrite the reactor mass balance equations for suitable use in reaction engineering, that is, in terms of unit mass of catalyst (a standard in heterogeneous catalysis). In this way, we propose a continuous two-reactor process, with inter-stage glycerol separation and recompression of the reactive mixture, as an improved method to increase triglyceride conversion to near full completion. The model used for the simulations was validated by a complete experimental study comprising several tests at 250 bar, with different space-time values (form 0.5 to 4 min), and temperatures (form 180 to 205 °C). Comparing the experimental data with the ones predicted by the simulations, provided a direct proof of the validity of the results predicted by the model.

2. Phase equilibrium calculation

The objective of this part is to determine the pressure (P) and temperature (T) of the reactants mixture to have SC conditions inside the first reactor. In general, SC fluids have intermediate properties between a gas and a liquid phase. Moreover, in a SC fluid there is not any surface tension, since there are not liquid-gas bonds. All the SC fluids are completely miscible by each other. Consequently, it is possible to obtain a one-phase, multi-component mixture if the critical point of the mixture is overcame.

The desired condition for this process is to have in the reactor a single homogeneous reacting phase, which presence depends on chemical composition, T and P of the system. To this purpose, it is necessary to calculate the vapor-liquid equilibrium conditions for the system having the same composition of the mixture fed to the reactor (which is made by triglycerides, methanol and a co-solvent, CO_2 in this case).

In the experimental tests where the values of the kinetic constants used in this work were calculated, a refined sunflower oil was used [10]. Similarly to other vegetable oils, sunflower oil is a mixture of different triglycerides [3]. In this work, as an approximation, the vegetable oil was represented by a unique component, that was chosen to be triolein (glycerol trioleate). The average content of triolein in sunflower oil is about 17%, being linolein the other main triglyceride component (74%). As triolein, linolein has 18C atoms in the side hydrocarbon chains. Other two minor components of sunflower oil are stearin (3%) and tripalmitin (6%). In addition, triolein is the triglyceride for which a greater amount of thermodynamic data are available in the literature [25].

The decision to use triolein as unique component to represent the vegetable oil could be considered a good approximation if one considers the molecular structure of triglycerides and the transesterification reaction. In facts, triglycerides are glycerol tri-esters, differing from one another only for the side hydrocarbon chains. Transesterification involves only the carbonyl group and the alcoholic oxygen, and for this reason, the differences between the long side hydrocarbon chains on the reactivity have been neglected. The influence of the different triglycerides (i.e. molecular weight and chemical structure) on the physical properties of the reactant mixture has been neglected as well.