Computers and Chemical Engineering 43 (2012) 108–119

Contents lists available at SciVerse ScienceDirect

Computers and Chemical Engineering

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

CFD simulation of transient stage of continuous countercurrent hydrolysis of canola oil

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ARTICLE INFO

Article history:
Received 27 October 2011
Received in revised form 15 April 2012
Accepted 18 April 2012
Available online 27 April 2012

Keywords:
CFD
Continuous hydrolysis
Triglycerides
Free fatty acid
Biofuel production

ABSTRACT

Computational Fluid Dynamic (CFD) modeling of a continuous countercurrent hydrolysis process was performed using ANSYS-CFX. The liquid properties and flow behavior such as density, specific heats, dynamic viscosity, thermal conductivity, and thermal expansivity as well as water solubility of the hydrolysis components triglyceride, diglyceride, monoglyceride, free fatty acid, and glycerol were calculated. Chemical kinetics for the hydrolysis reactions were simulated in this model by applying Arrhenius parameters. The simulation was based on actual experimental reaction conditions including temperature and water-to-oil ratio. The results not only have good agreement with experimental data but also show instantaneous distributions of concentrations of every component in hydrolysis reaction. This model provided visible insight into the continuous countercurrent hydrolysis process.

1. Introduction

Oils and fats are considered one of the dominant renewable raw materials of the chemical industry. They have been hydrolyzed into free fatty acids (FFA) of a high purity grade to be used for chemical conversions and for the synthesis of chemically pure compounds (Metzger & Bornscheuer, 2006). Fatty acids are also utilized in a wide variety of end-use industries, such as commercial soaps, cosmetics, and pharmaceuticals production (Brockmann et al., 2005). Currently, n-alkanes can be produced from FFA through a decarboxylation process (Kubickova, Snåre, Eränen, Mäki-Arvela, & Murzin, 2005), and these hydrocarbons are good replacements for petroleum diesel or other transportation fuels after suitable refining.

Hydrolysis of fats and oils, which are composed of mostly triglycerides, has been performed in industry for many years. Commonly, hydrolysis of esters occurs via the acyl-oxygen fission route (Kirby, 1972). The excess of three moles of subcritical water, at high temperature or over an appropriate acid catalyst, yields hydronium or hydroxide ions to hydrolyze the glycerol backbone at the ester group of any triglyceride (TG), diglyceride (DG), or monoglyceride (MG) (Moquin & Temelli, 2008) and form three moles of FFA and one mole of glycerol (Gly). In practice, the intermediates, such as DG and MG, are stable in small amounts during the reaction and are viewed as impurities in the product (Noureddini, Harkey, & Gutsman, 2004). The three consecutive reversible reaction steps are shown below. The fourth reaction step describes a reaction phenomenon observed in the high temperature range (Moquin & Temelli, 2008; Noureddini et al., 2004).

$$\text{Triglyceride} + \text{H}_2\text{O} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Diglyceride} + \text{FFA} \tag{R1}$$

$$\text{Diglyceride} + \text{H}_2\text{O} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{Monoglyceride} + \text{FFA} \tag{R2}$$

$$\text{Monoglyceride} + \text{H}_2\text{O} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \text{Glycerol} + \text{FFA} \tag{R3}$$

$$\text{Triglyceride} + \text{Monoglyceride} + \text{H}_2\text{O} \underset{k_8}{\overset{k_7}{\rightleftarrows}} 2\text{Diglyceride} \tag{R4}$$

The hydrolysis reaction in continuously operating counter-flow systems, known as Colgate-Emery (Barnebey, 1948) and Foster-Wheeler (Foster-Wheeler Corp., 2011) processes, yields high purity of FFA without using a catalyst. These processes require relatively high temperature, necessary to overcome the activation energy barrier. The high temperature also energizes water to dissociate to hydronium ion. High pressure maintains the reactants in liquid phase. Mass transfer between the lipid and aqueous phases has a predominant effect on the degree of hydrolysis (Barnebey,

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http://dx.doi.org/10.1016/j.compchemeng.2012.04.008

Nomenclature

ρ, ρ_i	density of the hydrolysis components
U	mean velocity vector
∇P	pressure gradient
μ	dynamic viscosity
g	gravity vector
F_D	interphase drag force
F_B	interphase buoyancy force
h_{tot}	total enthalpy
T	reaction temperature
C_p	specific heats of the hydrolysis components
C_P^0	ideal gas specific heat capacity
R	universal gas constant
T_r	reduced temperature
ω	acentric factor
η	dynamic viscosity
M_ω	molecular weight
η_a, η_b	group contribution values
λ	thermal conductivity
T_{br}	reduced normal boiling temperature
α	thermal expansivity
c	solubility of the solute
d	density of the pure solvent
k_m	number of molecules in the solute–solvent complex
ε	dielectric constant
K_w	ion product
T^*	normalized temperature
ρ^*	normalized density
ρ_w	density of water
k	rate constant
A	pre-exponential factor
E_a	activation energy
e	mathematical constant
k_b	Boltzmann's constant
h	Planck's constant
rpd	reaction path degeneracy
$\Delta n_{irot}^{\neq}$	change in the number of free rotors during each reaction step

1948). Higher temperature is necessary not only to increase the oil solubility in water but also to enhance the electrolytic dissociation of water which also accelerates the reaction (King, Holliday, & List, 1999). Water-to-oil ratio also highly influences the degree of hydrolysis at the reaction equilibrium (Wang, Turner, Stikeleather, & Roberts, 2012). A large water-to-oil ratio inflow reduces the glycerol concentration in sweet water (glycerol–water mixture) and drives the reaction toward completion.

A Computational Fluid Dynamics (CFD) model that described the liquid–liquid flow phenomena observed in a reaction medium was investigated by Nikou, Ehsani, and Emami (2008) and represented a promising use of CFD for the design, scale-up, and optimal operation of various chemical processes. In their study, the velocity distribution, pressure, concentration, and temperature profiles were accurately predicted by the CFD model. ANSYS-CFX, the package used in this work, is a high-performance, general purpose fluid dynamics software package that has been used to solve many fluid flow problems and achieve reliable and accurate solutions quickly and robustly. The solver is able to capture virtual images for any type of phenomena related to fluid flow. It is also capable of showing the geometry of the computational domain used and the various boundary conditions incorporated with the actual experimental setup (Gobby, Hamill, Jones, Lewin, & Montavon, 2002; Nikou et al., 2008). It can be applied to model the chemical kinetics within a reaction by incorporating kinetic parameters. ANSYS-CFX has been used for developing a CFD model to simulate the biodiesel transesterification process (De Boer & Bahri, 2009). Their analysis focused on the reactant mixture and achieving simulation convergence. In order to realistically simulate the process, the turbulent dispersion forces, reaction kinetics and the component solubilities and dissociations need to be considered.

In this study, attention was focused on the contribution of multi-component liquid flow behavior and reaction kinetics in a continuous countercurrent hydrolysis process. Based on the solubilities, dissociation rates, density differences and thermal and physical properties, the distribution of the reactants and products were determined. Also, Arrhenius parameters were applied to both the forward and backward reaction steps listed above to simulate the reaction kinetics. Finally, the computational results were compared with actual experimental data for model validation.

2. Experimental method

To quantitatively validate the CFD model, a lab-scale countercurrent continuous hydrolysis system was designed and built, as shown in Figs. 1 and 2. The hydrolysis reactions were performed in a 316 SS reactor with a length of 150 cm and 8.9 cm inner diameter. The heat of the reaction was provided by electromagnetic induction coils driven by two modified induction oven cooktops (Stikeleather & Singleton, 2001). The top and bottom halves of the vessel were heated via two separated coils which could be operated at two different temperatures. Temperature was measured via K-type thermocouple attached on the surface of the reactor. Temperature controllers (Delta DTB 4824, Delta Electronics Inc., Fremont, CA), connected to the thermocouple, modulated the induction ovens in on–off mode. The reaction pressure, necessary to maintain the reactants in liquid phase at the saturation temperature, was controlled via back pressure relief valves (Swagelok, SS-4R3A).

Commercial off-the-shelf distilled water and canola oil were used in this study as the feedstock. From the beginning of the reaction, water and oil with volume ratios of 2:1 were continuously and simultaneously fed into the hydrolysis reactor through two separated ports via proportional pumps (Model: 515-S-N1, Neptune Chemical Pump Company, Inc., Buffalo, NY) and HPLC pumps (Model: 510, WATERS Corporation, Milford, MA), respectively. Both inputs were heated to 250 °C by induction coils similar to the reactor coils. Distilled water was injected at a point 25 cm below the top of the reactor and canola oil was injected 120 cm below the top of the vessel. Due to the differences in densities, water and oil flow in opposite directions, which also enhances mixing. The FFA product, with the lowest specific gravity, floats to the top of the reactor and the sweet water, which has the highest density, sinks to the bottom. During the reaction, the FFA and sweet water were continuously removed and the outflow rates were controlled via metering valves (Swagelok, SS-4MA-MH). The FFA flow rate was maintained at the same value as the oil feed rate, and sweet water was removed at the same rate as the fresh water feed rate.

The lipid samples, containing TG, DG, MG, and FFA, as well as sweet water samples, containing a few percent Gly, were acquired periodically during the reaction. Composition was quantified via gas chromatography (GC; Shimadzu QP2010, Shimadzu Scientific Instruments, Columbia, MD) equipped with a RESTEK MXT®-Biodiesel TG column (15 m length, 0.32 mm ID, 0.1 μm film thickness, Restek Co., Bellefonte, PA) coupled to a flame ionization detector (FID). Extracted product samples, 60 mg each, were dissolved in 4 mL HPLC grade hexane and a 1 μL sample of this mixture was injected into the GC with a split ratio 10:1 and a carrier gas (helium) flow rate of 32.9 mL/min. The injector temperature was 380 °C. The initial oven temperature was 50 °C, was