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Dynamical modeling for biodiesel production from grease trap wastes

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HIGHLIGHTS

- A dynamical model for biodiesel production was proposed.
- The biodiesel was produced via the esterification of grease trap wastes within a CSTR.
- The esterification runs were conducted under load and temperature variations.
- Esterification data were fitted to the model with a proposed regression algorithm.
- The proposed model has been validated with the runs test using low-cost measurements.

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ABSTRACT

Grease trap wastes have been recently considered as an alternative feedstock for biodiesel production due to its relatively low cost and availability. These wastes are characterized by a high content of free fatty acids (FFA) and then, its processing towards biodiesel requires an esterification. In this paper, a dynamical model for the esterification of grease trap wastes was constructed. Specifically, this process has been conducted within a continuous stirred tank reactor. Almost all the parameters contained in the dynamical model were deduced from a series of batch temperature-controlled esterification experiments and from thermodynamic essays. The rest of the model parameters have been successfully estimated by means of a proposed algorithm that combines the notion of sensitivity with the Levenberg–Marquardt procedure. This regression procedure provides the estimates in spite of load and temperature variations and processing low-cost measurements. Finally, the proposed dynamical model has been validated with the runs test.

1. Introduction

Biodiesel is a mixture of organic esters that has been recently considered as a renewable and biodegradable fuel capable of reducing CO emissions and eliminating sulfur emissions in comparison to the conventional fuel, known as diesel or petrodiesel (Knothe et al., 2005). This alternative fuel is usually produced from refined raw materials with a high content of triglycerides and a low content ($<5\%$) of free fatty acids (FFAs) in a process known as transesterification. In this process, the raw material reacts with a short-chain alcohol (usually methanol) in the presence of alkaline catalysts such as the sodium or potassium hydroxides (Ma and Hanna, 1999). Nevertheless, biodiesel prices are not currently competitive with petrodiesel because of the high cost of the refined raw material, which makes up 60–80% of the production costs (Wen et al., 2010). For this reason, it has been proposed to produce biodiesel from cheaper feedstock such as waste cooking oils, rendered animal fats or grease trap wastes whose common characteristic resides in their relatively high FFA content. Specifically, grease trap wastes are recovered from grease interceptors (located in restaurants, hospitals, universities, etc.) before entering the municipal sanitary sewer lines. Although these wastes can be disposed for soil regeneration or converted into inert solids through a bioremediation process (Wiltsee, 1998) or digested in anaerobic processes (López et al., 2014), they can be used as a feedstock for biodiesel production because they are inexpensive (even attainable at zero-cost) and abundantly available. For example, in the U.S. these wastes represent one-third of the total fat and oil production (Canacki, 2007) while approximately 20,000 t are produced annually in Guangzhou, the third largest

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city in China (Park et al., 2010). If it is desired to produce biodiesel from feedstock with a high FFA content through the conventional transesterification process, then soap will be formed and, as a consequence, the reaction yield will fall. Thus, in this case it is recommended to transform the feedstock in a process known as esterification in which the raw material also reacts with a short-chain alcohol although the reaction is catalyzed by an inorganic acid (e.g., sulfuric acid) instead of an alkaline catalyst (Canacki and Van Gerpen, 2001).

Traditionally, both the transesterification and the esterification processes are conducted in the form of batch operations whose mathematical models (or kinetic studies) have been extensively studied. For instance, Freedman et al. (1986), Noureddini and Zhu (1997) and Darnoko and Cheryan (2007) have proposed diverse mathematical models for describing batch transesterification processes; Kamarudin et al. (1998), Sendzikiene et al. (2004), Zheng et al. (2006), Berrios et al. (2007), Aranda et al. (2008), Rani et al. (2013) and Hassan and Vinjamur (2013, 2014) have obtained noteworthy results concerning the mathematical description of the batch esterification processes. The transesterification and esterification processes conducted within batch reactors show flexibility in deployment and relatively high yields; however, it is well-known that the batch processes could increase their production level and can be performed still more efficiently when they are developed within a continuous stirred tank reactor (CSTR) (Levenspiel, 1999). Besides, the operation of a CSTR allows the development and implementation of robust control schemes for the regulation (at certain set-points) of critical state variables. Nevertheless, these regulation tasks are usually performed when a validated mathematical model describing such state variables is known.

To the very best of our knowledge, little has been undertaken to propose and to validate mathematical models for biodiesel production processes conducted within CSTRs. In this paper, we propose a dynamical mathematical model for the esterification of grease trap wastes which is being carried out in a CSTR. The kinetic parameters and some physical parameters that are involved in the proposed model were computed from batch esterification experiments of the grease trap wastes and from thermodynamic essays. The rest of the parameters that cannot be determined from such experiments, were estimated through a proposed nonlinear regression algorithm. This algorithm uses the notion of sensitivity for the estimation of these parameters but also for the estimation of initial conditions that correspond to state variables whose measurement is relatively expensive and difficult. Finally, the proposed model was validated with a statistical tool known as runs test.

2. Materials and methods

2.1. Materials

The grease trap wastes used in this study were recovered by a local cleaning company (Solución Ambiental de México, Guadalajara, Jalisco, Mexico). These wastes contained suspended solids, moisture, triglycerides and FFAs. The suspended solids were removed when the wastes (previously heated to 50 °C) were passed through a 100 mesh stainless steel screen. Next, the wastes were reheated to 105 °C for 2 h to remove the moisture content. The dry wastes contained 83.61% FFAs. This global content on FFAs was computed following the method Ca 5a-40 of the AOCS and the method Ch 2-91 was performed over the dry wastes obtaining the following FFA profile: 44.72% oleic acid; 20.31% palmitic acid; 13.50% linoleic acid and 11.83% stearic acid. This profile was determined using a GC (Agilent 6980) analysis confirming the *absence of esters in the wastes*. Additionally, commercial canola oil (Capullo, Mexico) was selected to prepare a 4:1 (m/m) mixture with the dry grease trap wastes. The result was a type of diluted grease trap waste. Furthermore, industrial reagent grade methanol with 0.3% moisture content was supplied by Pochteca (Mexico), and industrial reagent grade sulfuric acid was purchased at Químicos Márquez (Mexico). In the near future, it would be desirable to scale-up the esterification process studied here. In this case, industrial grade reagents might be economically attractive and for this reason they have been used. The remaining reactants are as follows: KOH (Golden Bell, USA); phenolptalein (Golden Bell, USA), isopropyl alcohol and toluene (Fermont, purity $>99.7\%$). The standard substances for the GC analysis were all purchased at Sigma-Aldrich.

2.2. Scheme for the esterification of grease trap wastes conducted in a CSTR

The esterification reaction was carried out in a 1 L, three-necked glass reactor with a mechanical agitator. The temperature of the reactor (T) was recorded by an Xplorer GLX PS-2002 multisensor. The reactor was immersed in a water bath whose temperature (T_J) was monitored with a J-type thermocouple and regulated using a PID controller. The grease trap wastes were supplied to the top of the glass reactor with a concentration C_{Ai}, a temperature T_{AG} and a constant flow rate F_{AG} along with a mixture of methanol/H_2SO_4 entering with a flow rate F_{Mix} and a temperature T_{Mix}. Both flows were supplied using peristaltic pumps (Thomas Scientific 7892K09) and they were calibrated to have a residence time of 1 h employing a 1:2.2:0.05 mass ratio of FFA to methanol and sulfuric acid, respectively (Canacki and Van Gerpen, 2001). *In molar terms, the relationship among methanol and the FFA content is about* 20:1 *which makes methanol the reagent in excess*. Also, the agitation was settled to 200 rpm and the output flow F had been selected to be $F_{AG}+F_{Mix}$ and adjusted using a peristaltic pump to avoid any total mass accumulation within the reactor. Fig. 1 describes the CSTR where the grease trap wastes esterification took place using slight variations in the input concentration of FFAs ($0.675\text{ M}<C_{Ai}<2.7\text{ M}$) and variations in the water bath temperature ($40\,^\circ\text{C}<T_J<60\,^\circ\text{C}$). The variation of C_{Ai} was carried out to consider load disturbances that are likely to be present in an industrial process due to the heterogeneous nature of grease trap wastes, whereas the temperature disturbances were used to verify whether they significantly affected the output concentration of FFAs (C_A) (i.e., the process yield). These variations are further depicted and analyzed in Section 3. In addition, the sampling and analysis of the samples were carried out as it is described below.

2.2.1. Sampling and analysis

At certain time instants, a sample was manually withdrawn from the reaction medium and then cooled by immersion into cold water (7 °C) for several minutes to terminate the reaction (Erciyes et al., 1991). The concentration of FFAs (mol FFAs/L) at such sample time was computed with

$$C_A=\frac{2(\%\text{FFA})m_r}{1000(56.1)V_r} \tag{1}$$

where m_r (g) is the weight of the reactor medium whose volume is V_r (L). The FFA percentage (%FFA) was computed using the AOCS official Method Ca 5a-40. For this technique, the sample was dissolved in a mixture of solvents (50% isopropyl alcohol–50% toluene) and subsequently titrated with a 0.1 N KOH solution using phenolphthalein as the indicator. The FFA percentage of the sample can then be computed from $\%\text{FFA}=(5.61V_n)/(2m_n)$ where V_n is the volume of KOH required to neutralize the sample and m_n is the exact weight of the sample (~ 0.5 g). The remainder of the