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Model-based run-to-run optimization under uncertainty of biodiesel production

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Abstract

A significant source of uncertainty in biodiesel production is the variability of feed composition since the percentage and type of triglycerides varies considerably across different raw materials. Also, due to the complexity of both transesterification and saponification kinetics, first-principles models of biodiesel production typically have built-in errors (structural and parametric uncertainty) which give rise to the need for obtaining relevant data through experimental design in modeling for optimization. A run-to-run optimization strategy which integrates tendency models with Bayesian active learning is proposed. Parameter distributions in a probabilistic model of process performance are re-estimated using data from experiments designed for maximizing information and performance. Results obtained highlight that Bayesian optimal design of experiments using a probabilistic tendency model is effective in achieving the maximum ester content and yield in biodiesel production even though significant uncertainty in feed composition and modeling errors are present.

Keywords: biodiesel, modeling for optimization, tendency models, uncertainty.

1. Introduction

Biodiesel is an alternative fuel produced from renewable vegetable oils, animal fats or recycled cooking oils whose transesterification with methanol produces glycerol and methyl esters (Ma and Hanna, 1999). Biodiesel would be an ideal substitute for the conventional diesel fuel if only it was more competitive economically. Efforts have been made to reduce its production cost by optimizing biodiesel yield in the face of different sources of uncertainty (Leung and Guo, 2006; Eevera, et al., 2009). In order to make biodiesel more competitive, oil conversion into methyl esters is of paramount importance since in biodiesel production the most contributing factor to the total manufacturing cost is the raw material which represents between 80 and 90% of the total estimate production cost (Benavides and Diwekar, 2012a). Several controllable factors can affect the productivity of alkaline-catalyzed transesterification in terms of yield and biodiesel final concentration. Among these factors, the most relevant are: the alcohol ratio, catalyst concentration, reaction temperature, and reaction time. The optimal values of these parameters for achieving maximum conversion of triglycerides to esters depend on the chemical and physical properties of the feedstock oils and the kinetics of alkali catalyzed alcoholysis. However, in optimizing the operating policy, there are inherent uncertainties that can have a significant impact on the product quantity, quality and process economics. In vegetal oils and animal fats the percentage and type of triglycerides varies considerably. For example, triglyceride composition soybean oils reveals five types of hydrocarbon chains which are: tripalmitin, tristearin, triolein, trilinolein, trilinolein, and trilinolenin and their percentage in triglycerides are 6–10%, 20–30%, 2–5%, 50–60%, and 5–11%, respectively (Linstromberg, 1970; Benavides and Diwekar, 2012b) .

2. Modeling biodiesel production

2.1. Basic chemical reactions

Common vegetable oils or animal fats are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters are called triglycerides, which can react with alcohol in the presence of a catalyst, a process known as *transesterification* or alcoholysis (Ma and Hanna, 1999). The simplified form of its chemical reaction is shown in Fig. 1a, where $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$ are long-chain hydrocarbons, sometimes called fatty acid chains. When the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally to glycerol, 1 mol of fatty ester is liberated at each reaction step.A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). The alcoholysis reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. For an alkali-catalyzed transesterification, the alkali catalyst that is used will also react with biodiesel and triglycerides to form soap. Fig. 1b shows the saponification reaction of the catalyst (sodium hydroxide) and the esters, forming soap and alcohol. This reaction is undesirable because the soap lowers the yield of the biodiesel and makes more difficult to separate esters from glycerol.

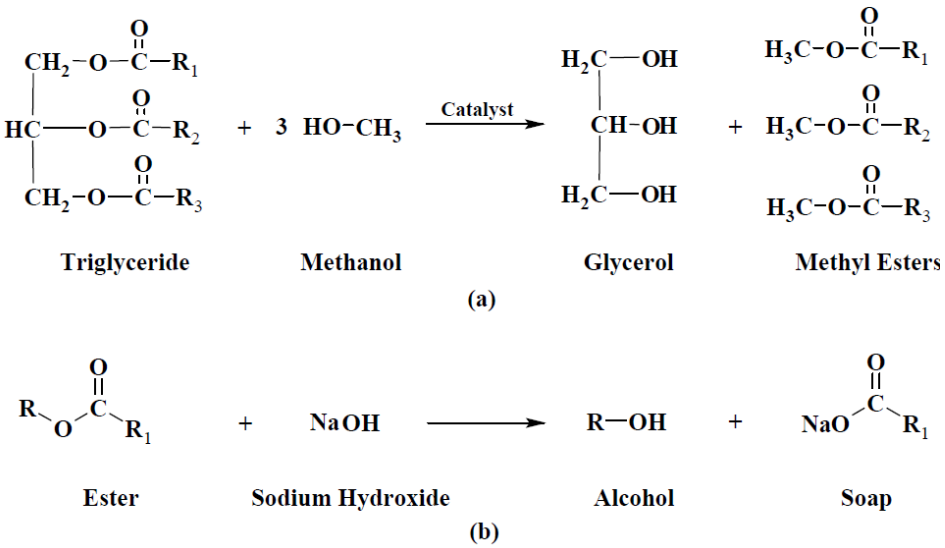

Fig. 1. Main reaction pathways. (a) Overall transesterification; (b) Saponification.

2.2. Kinetics and tendency model

Transesterification kinetics (Komers, et al., 2002) corresponds to the following set of reversible reactions:

$$TG + CH_3OH \leftrightarrow DG + E; DG + CH_3OH \leftrightarrow MG + E; MG + CH_3OH \leftrightarrow G + E \quad (1)$$

whereas the saponification of glycerides and ester can be described by

$$TG + OH \rightarrow S + DG; DG + OH \rightarrow S + MG; MG + OH \rightarrow S + G;\ E + OH \rightarrow S + CH_3OH \quad (2)$$

Basic reaction rates are written using mass action law and Arrhenius equation as follows

$$r_1 = k_1 * OH * TG * CH_3OH;\quad r_2 = k_2 * OH * DG * E; r_3 = k_3 * OH * DG * CH_3OH$$
$$r_4 = k_4 * OH * MG * E;\ r_5 = k_5 * OH * MG * CH_3OH\ ,\quad r_6 = k_6 * OH * G * E$$
$$r_7 = k_7 * OH * E\ ; r_8 = k_8 * OH * TG; r_9 = k_9 * OH * DG; r_{10} = k_{10} * OH * MG$$
$$k_i = {k_i}^o * \left[B_i * \left(\frac{1}{T^o} - \frac{1}{T}\right)\right]; T^o = 295.75\ K \quad (3)$$

For the *in silico* model of biodiesel production, parameters are given in Table 1. The dynamics for a batch reactor are the corresponding mass balances:

$$\frac{dTG}{dt} = -r_1 + r_2 - r_8\ ; \qquad \frac{dDG}{dt} = r_1 - r_2 - r_3 + r_4 + r_8 - r_9;$$
$$\frac{dMG}{dt} = r_3 - r_4 - r_5 + r_6 + r_9 - r_{10}\ ; \quad \frac{dE}{dt} = r_1 + r_3 + r_5 - r_2 - r_4 - r_6 - r_7;$$
$$\frac{dCH_3OH}{dt} = -\frac{dC_E}{dt}; \frac{dG}{dt} = r_5 - r_6 + r_{10}\ ; \quad \frac{dOH}{dt} = -r_7 - r_8 - r_9 - r_{10} \quad (4)$$

To account for the available measurement in sampled data, a tendency model is proposed to optimize the operating policy. The simplified dynamic model for biodiesel production is made up of the following kinetics and mass balances

$$TG + 3 * CH_3OH \rightarrow G + 3 * E\ ; r_1 = k_1 * OH * TG * CH_3OH$$
$$TG + OH \rightarrow S + G; \qquad r_2 = k_2 * OH * TG$$
$$E + OH \rightarrow S + CH_3OH; \qquad r_3 = k_3 * OH * E \quad (5)$$

$$\frac{dTG}{dt} = -r_1 - r_2; \frac{dE}{dt} = 3\,r_1 - r_3; \frac{dCH_3OH}{dt} = -\frac{dE}{dt}; \frac{dOH}{dt} = -r_2 - r_3$$

Table 1. In silico Model Parameters

${k_1}^o$ [l².mol⁻².s⁻¹]	0,1586	${k_6}^o$ [l².mol⁻².s⁻¹]	0,0186	B_1 [K]	7208	B_6 [K]	2022
${k_2}^o$ [l².mol⁻².s⁻¹]	0,0795	${k_7}^o$ [l.mol⁻¹.s⁻¹]	0,0009	B_2 [K]	3891	B_7 [K]	167
${k_3}^o$ [l².mol⁻².s⁻¹]	0,2506	${k_8}^o$ [l.mol⁻¹.s⁻¹]	0,0229	B_3 [K]	12473	B_8 [K]	6626
${k_4}^o$ [l².mol⁻².s⁻¹]	0,1950	${k_9}^o$ [l.mol⁻¹.s⁻¹]	0,0498	B_4 [K]	10103	B_9 [K]	1416
${k_5}^o$ [l².mol⁻².s⁻¹]	0,4048	${k_{10}}^o$ [l.mol⁻¹.s⁻¹]	0,0233	B_5 [K]	5081	B_{10} [K]	9743

3. Run-to-run optimization

3.1. Methodology

In order for a tendency model to reflect the observed dynamics as accurately as possible it must faithfully represent its own accuracy. A probabilistic model quantifies this uncertainty by integrating first-principles knowledge with data to capture all plausible dynamics in a distribution over model predictions for state transitions between samples in a batch run (Martinez et al., 2009, 2013). To this aim, let us assume that process dynamics is modeled using a number of state variables $x(t)$ that can be measured and the vector $y(t)$ represents measured values of the outputs at a given sampling time t. Also, it

is assumed that the probabilistic tendency model can be described by a dynamic stochastic model constituted by

$$f(\dot{x}, x, \boldsymbol{u}(t), w, \Theta, t)\ ,\ y = g(x(t)) \tag{6}$$

with the set of initial conditions $x(0)=x_0$, $\boldsymbol{u}(t)$ and w are, respectively, the time-dependent and time-invariant control variables (manipulated inputs), Θ is the set of i.i.d. model parameters with given *a priori* distributions $p(\theta_i), i = 1,\ldots,k$, and t is time.

Model-based policy iteration aims at optimizing the objective function $J(t_f, x_f)$ at the end of each run by acting on the following design vector for the operating policy:

$$\varphi(y_0, \boldsymbol{u}(t), w, \mathbf{t}^{sp}, t_f) \tag{7}$$

where y_0 is the set of initial conditions of the measured variables, and t_f is the duration of an experiment. The set of time instants at which the output variables are sampled is a design variable itself, and is expressed through the vector $\mathbf{t}^{sp} = [t_1 \ \ldots \ t_n]^T$ of n sampling times. Control vector parameterization techniques are used to discretize the control input $\boldsymbol{u}(t)$ profiles.

A high-level description of the model-based policy iteration framework is given in Fig. 2 (see Martinez et al., 2013, for details). It is important to highlight that the activity called *policy evaluation* corresponds to the actual running of a designed experimental run whereas other activities such as *policy optimization*, *experimental design* and *sensitivity analysis* are entirely based on model simulations. The operating policy is first initialized by resorting to expert judgment and a priori knowledge from lab scale to avoid undesirable states. Samples are taken along this experiment so as to make a rough estimation of probability distributions or histograms for parameters in the tendency model. Equipped with a probabilistic model which explicitly addressed its own uncertainty, the policy iteration loop can be entered. First, the "most probable" model parameterization is used to find a model-optimized operating policy. Using this policy an optimally informative experiment is designed to define informative sampling times along the next evaluation run. The policy is then evaluated experimentally and new data is gathered. To use incoming data more efficiently, a sensitivity analysis is made to pinpoint which is the subset of parameters that explain most of the variance of the chosen performance J. Finally, the probabilistic tendency model is updated by selectively re-estimating the distributions of sensitive parameters, and a new policy improvement round begins.

1: *Policy evaluation* ▷ Exploratory run.
2: *Model initialization* ▷ Define priors for parameter distributions.
3: **Loop**
4: *Policy optimization* ▷ Performance improvement.
5: *Experimental design* ▷ Optimal sampling times.
6: *Policy evaluation* ▷ Collect observations.
7: *Sensitivity analysis* ▷ Introduce modeling bias.
8: Probabilistic *model update* ▷ Bootstrapping.
9: **End loop**

Fig. 2. High-level description of the model-based policy iteration.

3.2. Simulation results

Based on sample data from the foregoing *in silico* model run-to-run optimization has been addressed. Measurement errors are modeled using a normal distribution with zero mean and a standard deviation of 5% regarding the corresponding noise-free data. The operating policy has four parameters: initial hydroxyle concentration C_{OH}, switching time t_{SW} and two temperature levels T_1 and T_2. Yield is defined on the basis of the initial lump of tryglycerides regardless of its composition. The final time is set to 60 min whereas the methanol to oil ratio is chosen as 6:1. Results obtained are summarized in Table 2. As can be seen, the methodology in Fig. 2 only requires two iterations to achieve a near-optimal operating condition (see Table 2).

Table 2. Run-to-run improvement of the operating policy

Run #	Policy Parameter				J [%]	J_{pred} [%]
	C_{OH} [mol/l]	t_{SW} [min]	T_1 [°C]	T_2 [°C]		
Exploratory	0,0750	30,00	60,0	40,0	81,18	-
1	0,1246	52,65	40,0	44,3	94,36	94,67
2	0,1451	19,54	40,0	40,0	94,44	91,61
3	0,1274	15,57	40,0	40,0	94,25	93,49
4	0,1377	36,47	40,0	40,0	94,40	95,43
In silico **optimum**	**0,1128**	**36,26**	**40,0**	**60,0**	**95,44**	**-**

In Fig. 3, the model-based optimized policy for iteration #1 is shown along with optimal sampling times. Ester and hydroxyle concentrations for this policy are given in Fig. 4. The histograms for some of the tendency model parameters are depicted in Fig. 5 and the corresponding uncertainty in biodiesel time profiles are shown in Fig. 6.

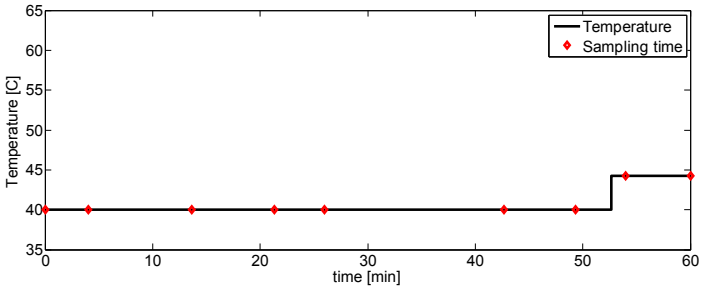

Fig. 3. Optimized policy using the tendency model in iteration #1.

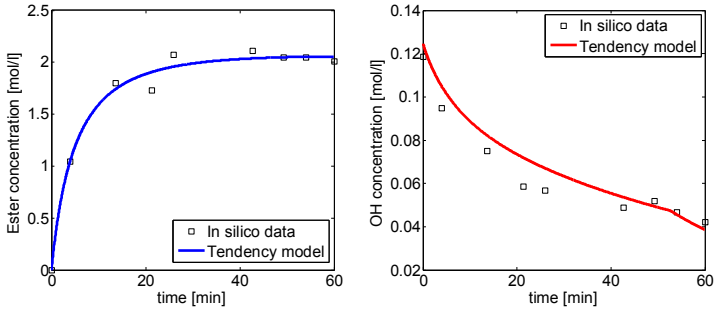

Fig. 4. Product and hydroxyle concentrations in iteration #1

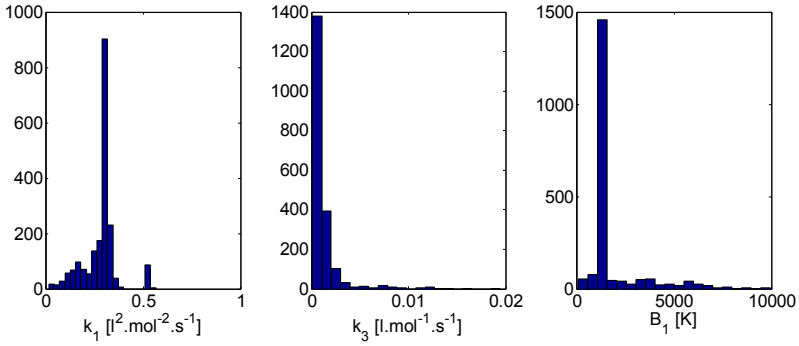

Fig. 5. Histograms for selected parameters in the probabilistic tendency model (run # 1)

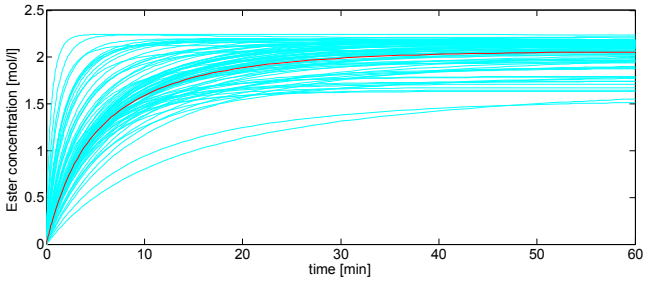

Fig. 6. Characterization of yield prediction uncertainty using the probabilistic tendency model

4. Concluding remarks

In this work, a probabilistic tendency model for approximating the hydroxide-catalyzed methanolysis of vegetal oils that also accounts for the saponification reactions is proposed. Run-to-run optimization based on the probabilistic tendency model demostrates fast convergence to a significantly improved operating policy.

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