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Acquisition of non-linear kinetics from linear relations: modelling of transesterification reactions for biodiesel production

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1. Introduction

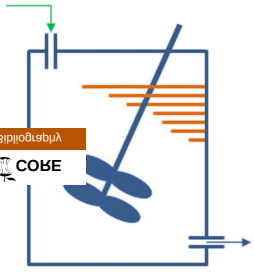
Esterification and transesterification are important reactions in industrial chemistry and especially in the production of biodiesel. A key point for these reactions is their reaction kinetics, used in reactor simulations to (a) describe pilot plant facilities or larger scale industrial reactors and (b) to optimize the output, i.e., to improve selectivity of desired products. However, a significant drawback of these corresponding kinetics is the non-linear behavior and the need for sophisticated software to obtain them from experimental laboratory data.

This research proposes a fast and easy method to determine kinetic parameters in systems with non-linear concentration dependencies via semi-batch operation of a laboratory continuous stirred tank reactor. The experimental set-up is chosen in such a way that the non-linear equations can be transformed into linear algebraic equations. Since linear dependencies are derived, the solution is trivially found, because it does not depend on the initial guesses of the kinetic parameters. Moreover, simple software like Excel, accessible to everybody for daily use, can be addressed to this extent.

Transesterification reactions, applied to obtain biodiesel from triglycerides, are taken as a worked out example to indicate the fast and reliable method for parameter estimation via linear relations [1].

Table 1. Reaction conditions (initial concentrations and inlet conditions) for the performed work.

Initial and inlet conditions		
Component i	$C_{i,0}$ (mol L^{-1})	$C_{i,0,f}$ (mol L^{-1})
TG	1.0	0
DG, MG, GL	0	0
M	0	0.01, 0.02, 0.04, 0.08
Reactor conditions		
V_{rx} (mL)	500	
$F_{V,0}$ (mL s^{-1})	1, 2, 5, 10	
τ (s)	250	
T (K)	293, 313, 333, 353	



2. Experimental

In this work, so-called 'synthetic data' are used, i.e., existing kinetic parameters are used in a reactor model giving rise to continuous output data. Superposing artificial experimental error (noise) on discrete points,

taken from these continuous data, creates these synthetic data. This is a common practice in literature when no experimental set-up is available.

The given reactor model considers semi-batch operation using the data from Noureddini and Zhu [2], in which the kinetics of the transesterification of soybean oil are considered: transesterification of a triglyceride (TG) is performed with methanol (M), in the presence of an alkaline homogeneous catalyst, yielding esters of fatty acids ($E_i = R_iCOOCH_3$, and i = 1, 2 and 3) and glycerol (GL). The governing chemical reactions are given by Eqs. (1) to (3), with the intermediate products diglyceride (DG) and monoglyceride (MG):

$$TG + CH_3OH \rightleftarrows DG + R_1COOCH_3 \qquad k_1 \text{ (forward)}, k_2 \text{ (backward)} \qquad (1)$$

$$DG + CH_3OH \rightleftarrows MG + R_2COOCH_3 \qquad k_3 \text{ (forward)}, k_4 \text{ (backward)} \qquad (2)$$

$$MG + CH_3OH \rightleftarrows GL + R_3COOCH_3 \qquad k_5 \text{ (forward)}, k_6 \text{ (backward)} \qquad (3)$$

3. Results and discussion

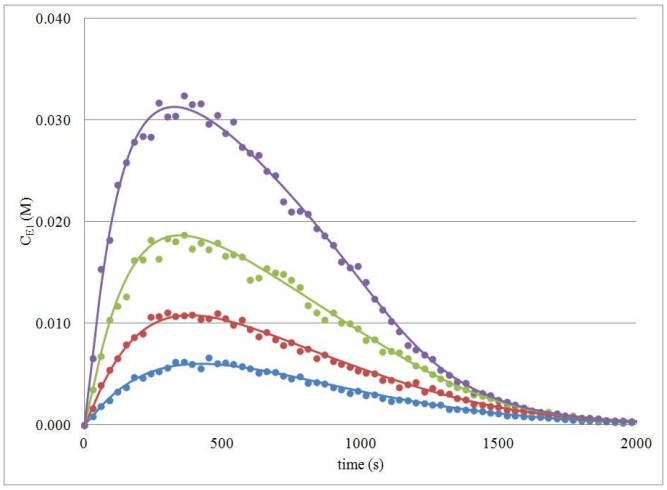


Figure 1. Example of synthetic data, used in this work. Level of error = 5%, colors correspond the conditions mentioned in Table 1.

Figure 1 gives the simulation result, corresponding to the conditions mentioned in Table 1. Due to the re-actor operation, typical concentration profiles like this are obtained. In this work, synthetic exper-imental error is varied up to 20% for a broad range of conditions: temperature is varied at 4 levels and input concentrations are varied, see Table 1. Math-ematical details are omitted here for conciseness of the abstract. Synthetic data are used to estimate the transesterification reaction parameters, k_1 to k_6, via the linear relations proposed in this work. As men-tioned in Table 1, a striking resemblance is ob-tained, but the author did not have to endure the tedious non-linear parameter estimation procedure.

Table 1. Parameter estimation results, presented in this work at 313 K.

i	k_i from ref [2]	k_i from this work
1	0.163	0.176 ± 0.034
2	0.269	0.268 ± 0.123
3	1.281	1.425 ± 0.284
4	4.577	4.038 ± 0.589
5	4.310	4.627 ± 0.461
6	0.166	0.165 ± 0.066

4. Conclusions

Kinetics for esterification reactions, which are very important in the development of biodiesel production, are obtained via linear relations, rather than complex non-linear differential equations. To this extent, a smart reactor design and operation is explained in this contribution. It is believed that this approach will broaden the work field of many researchers in the field of biodiesel research, since no tedious and special software is needed; daily accessible Excel can do the job.

References

[1] Heynderickx P. M. Acquisition of non-linear kinetics from linear relations: modelling of transesterification reactions for biodiesel production, submitted to Chem. Eng. J.

[2] Nourredini H. and Zhu D. Kinetics of transesterification of soybean oil, J. Am. Oil Chem. Soc., 74, 1457-1463 (1997)