



A New Kinetic Biphasic Approach Applied to Biodiesel Process Intensification



NICL - Naples Industrial Chemistry Laboratory



NICL - Naples Industrial Chemistry Laboratory

Introduction

Many different papers have been published on the kinetics of the **transesterification of vegetable oil with methanol**, in the presence of alkaline catalysts to produce biodiesel. All the proposed approaches are based on the assumption of a pseudo-monophasic system. The consequence of these approaches is that some experimental aspects cannot be described. For the reaction performed in batch conditions, for example, the monophasic approach is not able to reproduce the different plateau obtained by using different amount of catalyst or the induction time observed at low stirring rates. Moreover, it has been observed by operating in continuous reactors that micromixing has a dramatic effect on the reaction rate. We have recently observed that it is possible to obtain a complete conversion to biodiesel in less than 10 seconds of reaction time. This observation is confirmed also by other authors using different types of reactors like: **static mixers, micro-reactors, oscillatory-flow reactors, cavitation reactors, microwave reactors or centrifugal contactors**. In this work we will show that a recently proposed biphasic kinetic approach is able to describe all the aspects before mentioned that cannot be described by the monophasic kinetic model. In particular, we will show that the biphasic kinetic model can describe both the induction time observed in the batch reactors, at low stirring rate, and the very high conversions obtainable in a micro-channel reactor. The adopted biphasic kinetic model is based on a reliable reaction mechanism that will be validated by the experimental evidences reported in this work.

Kinetic Model

Polar phase	Apolar phase	Reaction rate expressions
$K^+OH^- + CH_3OH \leftrightarrow K^+OCH_3^- + H_2O$		
$CH_3O^- + T \rightarrow D^- + E$	$D^- + CH_3OH \rightarrow M^- + E$	$r_1 = k_1 \cdot a_L \cdot [CH_3O^-]^p \cdot [T]^q$
	$M^- + CH_3OH \rightarrow G^- + E$	$r_2 = k_2 \cdot [D^-] \cdot [CH_3OH]^p$
	$T + CH_3OH \rightarrow D + E$	$r_3 = k_3 \cdot [M^-] \cdot [CH_3OH]^p$
	$D + CH_3OH \rightarrow M + E$	$r_4 = k_4 \cdot [D^- + M^-] \cdot [T]^q \cdot [CH_3OH]^p$
	$M + CH_3OH \rightarrow G + E$	$r_5 = k_5 \cdot [D^- + M^-] \cdot [D]^q \cdot [CH_3OH]^p$
		$r_6 = k_6 \cdot [M^-] \cdot [CH_3OH]^p$
		$r_7 = k_7 \cdot [CH_3OH]^p \cdot [G^-]^q \cdot \frac{1}{K_{eq,7}} \cdot [CH_3O^-]^p \cdot [G]^q$
$G^- + CH_3OH \rightarrow CH_3O^- + G$		

- The liquid-liquid interfacial area is a key factor in determining the reaction rate of the transesterification reaction.
- D⁻ is involved in a successive reaction step giving monoacylglycerolates (M⁻) and methyl ester
- M⁻ reacts with the same mechanism giving glycerolate anion (G⁻) that is not soluble in oil phase
- The transesterification proceeds in oil phase, catalyzed by D⁻ and M⁻ until these catalytic species, soluble in oil, are present, that is, until G⁻ is formed
- Glycerolate anion is not soluble in the oil phase and promptly migrates in the polar phase; consequently, the reaction rate rapidly slows down, because, G⁻ is much less active than D⁻ and M⁻.
- It retains a low catalytic action probably due to the equilibrium with CH₃O⁻ formed by exchange with G⁻ and methanol as in the following reaction scheme:

$$\frac{dY_m^k}{dz} = \pm \sum r_z \pm \sum J_m$$

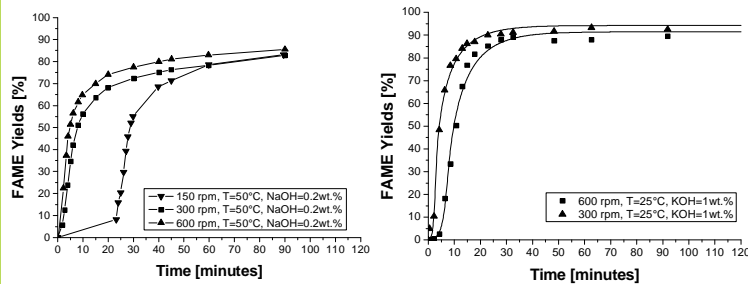
z: integration variable (time for batch and volume for continuous reactors)
 Y_m^k is either the concentration of the m component (batch), of the molar flow-rate of the m component (PFR) in the phase k
 r_n the reaction rate of equation n
 J_m the mass transfer rate related to the component m.

Batch Runs Interpretation

Noureddini and Stamenkovic' [1,2], have shown that in batch conditions, at low stirring rate, an induction time more or less long occurs. After the induction time, the slopes of the curves are quite similar to the ones observed at higher stirring rates.

The induction time can be attributed to a delay in the CH₃O⁻ depletion. This delay is attenuated by the formation of D and M exerting a tensile effect so increasing the liquid-liquid interfacial area.

$$a_L = a_L^0 + \varepsilon \cdot ([M] + [D]) = [cm^2 / cm^3]$$



The two simulated runs, performed by Aracil et al. [3,4] were only interpreted by determining only the following parameters $\gamma_1 = k_1 \cdot a_L$ and $\beta = k_1 \cdot a_L$.

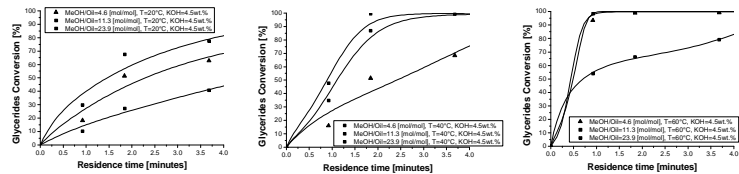
	300 rpm	600 rpm	Unit
k ₁	1.02 e-1	1.02 e-1	(L ^p /(mol·min)) · (cm ³ /cm ²)
k _L	3.55 e-1	3.55 e-1	cm/min
a _L ⁰	6.72 e-2	2.93 e-1	cm ² /cm ³
ε	2.9	11.6	(cm ² /cm ³) · (L/mol)
k ₂	0.225	0.225	L ³ /(mol·min)
k ₃	0.225	0.225	L ³ /(mol·min)
k ₄	18.16	18.16	L ² /(mol ² ·min)
k ₅	4.61	4.61	L ² /(mol ² ·min)
k ₆	1.92	1.92	L ² /(mol ² ·min)
K _{eq,7}	1.69 e-3	1.69 e-3	-
Ea ₁	≈ 0	≈ 0	kcal/mol
Ea ₂	17.61	17.61	kcal/mol
Ea ₃	26.62	26.62	kcal/mol

Continuous Runs Interpretation

The model was able to describe continuous runs at different catalyst concentration and performed with different reactors [5,6], for example by adopting static mixer or micromixer reactors. In the best conditions an almost complete conversion in less than 10-30 seconds has been achieved.

Here we have applied the biphasic kinetic model to the experimental runs performed by Guan et al. [7] in a micro-tubular reactor.

I.D.: 0.8 mm; Length: 250, 500, 1000 mm; Q= 8.2 cm³/h; 4.5 wt.% KOH .
 T: 20, 40, 60 °C; methanol/oil molar ratios: 4.6, 11.3, 23.9.



Methanol/ oil [mol/mol]	T=20°C		T=40°C		T=60°C	
	γ ₁	β	γ ₁	β	γ ₁	β
4.6	48	0.78	107	0.53	450	0.25
11.3	245	7	293	2	300	4.79
23.9	959	5.6	1800	1.78	1264	2.92

β becomes not significant for values >3.

Conclusions

The presented kinetic model is suitable to describe many experimental evidences. In particular:

- Very fast kinetic runs characterized by a very intense local micromixing
- Both batch and continuous runs performed at different experimental conditions
- Batch runs that present an induction time at low stirring rate.

Cited literature

- [1] H. Noureddini, D. Zhu; *J. Am. Oil Chem. Soc.* 1997, 74, 1457-1463.
- [2] S. O. Stamenkovic', Z. B. Todorovic', M. L. Lazic', V. B. Veljkovic', D. U. Skala; *Bioresource Technology* 2008, 99, 1131-1140.
- [3] G. Vicente, M. Martinez, J. Aracil, A. Esteban; *Ind. Eng. Chem. Res.* 2005, 44, 5447-5454.
- [4] G. Vicente, M. Martinez, J. Aracil; *Energy Fuels* 2006, 20, 1722-1726.
- [5] E. Santacesaria, R. Turco, M. Tortorelli, V. Russo, M. Di Serio, R. Tesser; *Green Processing and Synthesis* 2012, 1 (2), 181-189.
- [6] E. Santacesaria, R. Turco, M. Tortorelli, V. Russo, M. Di Serio, R. Tesser; *Industrial & Engineering Chemistry Research* 2012, 51 (26), 8777-8787.
- [7] G. Guan, K. Kusakabe, K. Moriyama, N. Sakurai; *Ind. Eng. Chem. Res.* 2009, 48, 1357-1363.