



Key factors in the Process Intensification of the Soybean Oil Epoxidation



NICL- Naples Industrial Chemistry Laboratory



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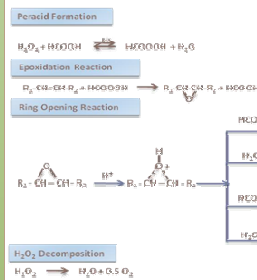
Introduction

Epoxidation of Soybean Oil production is growing in interest, being ESBO a building-block in the chemical industry. This product is normally obtained by performing a reaction between soybean oil and a percarboxylic acid generated in-situ, by putting in contact a small excess of hydrogen peroxide (60wt.%), formic acid (95wt.%) with a strong mineral catalyst (H_2SO_4 or H_3PO_4). Being the epoxidation reaction extremely exothermic ($\Delta H = -55$ Kcal/mol of unsaturation), this reaction is currently performed in industry by using Pulse-Fed-Batch reactors (PFBR), where small amounts of the oxidizing mixture are gradually added to the batch reactor, that is previously loaded with soybean oil and the catalyst, in order to keep the process temperature in a range of 65-75 °C. Therefore, the current industrial reactors presents several problems, such as the management of the heat and the mass transfer (the reactions occurs between a polar and an apolar phase), the selectivity of the PFBR, the reaction time (that usually requires about 10 hours), the hydrogen peroxide decomposition (occurring at high temperatures) and the low selectivity to the epoxidized product. To adopt continuous reactors can be a way to solve the mentioned problems, but in order to opportunely design a continuous reactor, it is necessary to have a complete knowledge about the kinetics, the mass and the heat transfer for the epoxidation reaction, paying attention also to the main side-reactions that are: hydrogen peroxide decomposition and oxirane ring-opening reaction. Recently, our group have developed a biphasic kinetic model [1], based on several experimental runs, that is capable to describe properly all the kinetic aspects of the soybean oil epoxidation.

Aim of the work

- Investigation on both the kinetics and the mechanism of ESBO production in the presence of both H_2SO_4 and H_3PO_4 as catalysts.
- Study of the effects of catalyst concentration and reaction temperature on both the main and the side reactions.
- Study of the operation modality by adopting both Fed-Batch and Pulse-Fed-Batch reactors.
- Development of a biphasic mathematical model able to opportunely interpret the collected experimental data.
- Design and installation of continuous reactors for the model validation.

Reaction Scheme



- The Performic acid formation occurs in the aqueous phase between hydrogen peroxide and formic acid in the presence of a strong mineral acid.
- The epoxidation reaction is an irreversible reaction. This steps occurs between the soybean oil unsaturations with the dissolved performic acid.
- Accordingly with our observations and literature findings, the ring opening reaction occurs at the interphase. Being this reaction extremely influenced by the pH of the aqueous media, the ring protonation is the rate determining step. The nature of the by-product depends on the nucleophile concentration.
- Hydrogen peroxide decomposition occurs in the aqueous media.

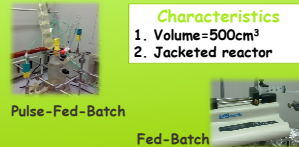
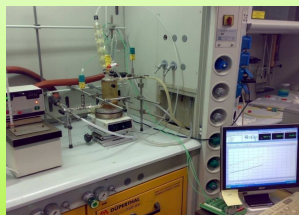
Batch Runs

Experimental Modalities (EM):

- Fed-batch: a continuous flow of 0.3 cm³/min of the oxidizing mixture has been imposed, working in isothermal conditions.
- Pulse-fed-batch: the oxidizing mixture was added pulse by pulse, keeping the temperature in the range 65-75°C.

Run	Oil (g)	H ₂ O ₂ (g)	Formic Acid (g)	Catalyst	Mass of catalyst (g)	EM
1	100	36.7	5.38	H ₂ SO ₄	0.64	B
2	100	36.7	5.38	H ₂ SO ₄	0.64	A
3	100	42.0	10.76	H ₂ SO ₄	0.84	A
4	100	33.4	2.69	H ₂ SO ₄	0.57	A
5	100	36.7	5.38	H ₂ SO ₄	0.64	B
6	100	36.7	5.38	H ₂ SO ₄	0.32	B
7	100	36.7	5.38	H ₂ SO ₄	0.64	B
8	100	36.7	5.38	H ₂ SO ₄	1.28	B
9	100	36.7	5.38	H ₃ PO ₄	0.98	B
10	80	29.5	4.41	H ₃ PO ₄	0.78	B

Batch Setup

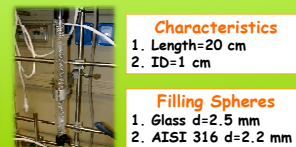
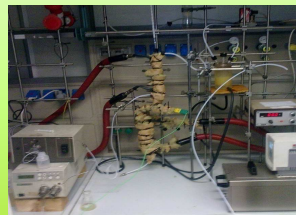


Pulse-Fed-Batch

Fed-Batch

- Characteristics**
- Volume=500cm³
 - Jacketed reactor

Continuous Setup



- Characteristics**
- Length=20 cm
 - ID=1 cm

- Filling Spheres**
- Glass d=2.5 mm
 - AISI 316 d=2.2 mm

Continuous Runs

Experimental Fillings (EF):

- Glass spheres of 2.5 mm of diameter. 7 cm³ of void volume on 15.7 cm³.
- AISI 316 stainless steel spheres of 2.2 mm of diameter. 12 cm³ of void volume on 18 cm³.

The temperature of the jacket is equal to the temperature at the outlet of the reactor.

Run	EF	Q _{oil}	Q _{ox}	τ (min)	T ⁱⁿ (°C)	T ^{out} (°C)	X _{DB} (%)		Yield (%)	
							EXP	SIM	EXP	SIM
1	A	4	1	1.4	68	71	14.8	14.5	4.9	12.5
2	A	4	1	1.4	69	71	12.5	14.7	5.8	12.7
3	B	4	1	2.4	66	70	2.3	2.4	2.2	2.11
4	B	4	1	2.4	78	77	8.6	8.7	8.1	7.54
5	B	4	1	2.4	83	93	7.8	7.9	6.7	6.53
6	B	3	2	2.4	66	67	11.2	10.2	10.9	9.2
7	B	3	2	2.4	78	78	20.0	20.2	19.5	18.4

*Flowrates expressed in cm³/min

Biphasic Kinetic Model

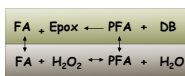
Main hypothesis

- Whitman's two films theory
- Partition coefficient H₁ calculated by SPARC¹
- Linear dependence of mass transfer rate with the volume of the realtive phase:

$$\beta_1^{aq} = k_1 \frac{A}{V^{aq}} = \beta_1^{org}$$

$$\beta_2^{aq} = k_2 \frac{A}{V^{aq}} = k_2 \frac{A}{V^{org}} \cdot \frac{V^{org}}{V^{aq}} = \beta_2^{org} \frac{V^{org}}{V^{aq}}$$

- Linear dependence of global heat exchange coefficient with the conversion degree $U = U_0 \alpha X_{DB}$



Aqueous phase

$$r_1^{aq} = k_1 [H_2O_2] \left\{ [H_2O_2]_{aq} [FA]_{aq} - \frac{1}{K_1} [PFA]_{aq} [H_2O]_{aq} \right\}$$

Organic phase

$$r_2^{org} (i) = k_2 (i) [DB]_{org} [PFA]_{org}$$

Interphase

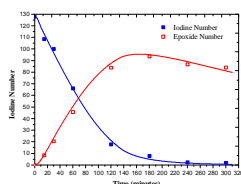
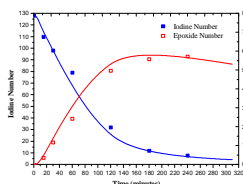
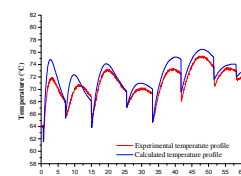
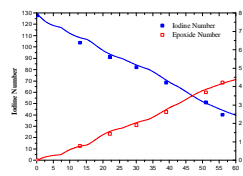
$$r_3^{int} (i) = k_3 (i) [Epox]_{org} [H^+]_{org}$$

Balances equations and Agreements

The following mass and heat balances equations are applied to all the components involved in each phase.

$$\frac{dn_j^i}{dt} = F_j + (\sum r_j + \sum J_j) \cdot V^i$$

$$\frac{dT}{dt} = \frac{Q_{ex} + Q_{cool} + Q_c}{C_p \cdot M_{Tot}}$$



Conclusions

A kinetic biphasic model has been developed considering:

- All the reactions respectively occurring in the aqueous phase (oxidation of formic to performic acid and hydrogen peroxide decomposition), in the oil phase (epoxidation) and at the water/oil interphase (epoxide ring opening reaction).
- The partition equilibria of reactants and products, between the two phase.
- The eventual mass transfer limitation

The model and related parameters have been verified by interpreting kinetic runs performed in continuous reactors.

Cited Literature

[1] E. Santacesaria, R. Tesser, M. Di Serio, R. Turco, V. Russo, D. Verde; A biphasic model describing soybean oil epoxidation with H₂O₂ in a fed-batch reactor; Chem. Eng. J. (2011), doi:10.1016/j.cej.2011.05.018