



## Kinetics of soybean oil epoxidation in a semibatch reactor

Elio Santacesaria<sup>1</sup>, Rosa Turco<sup>2</sup>, Vincenzo Russo<sup>2</sup>, Riccardo Tesser<sup>2</sup>, Martino Di Serio<sup>2</sup>

<sup>1</sup> CEO of Eurochem Engineering Ltd, Milano Italy; <sup>2</sup> NICL - Department of Chemical Science, University of Naples Federico II Italy

\*Corresponding author E-Mail: elio.santacesaria@eurochemengineering.com

### 1. Introduction

In this work, the kinetics of soybean oil epoxidation with hydrogen peroxide, in the presence of formic acid as oxygen carrier and phosphoric acid as catalyst, was studied. A biphasic kinetic model developed in a previous work [1] was improved considering the concomitant evolution of 4 different reactions: (1) the oxidation of formic acid to performic; (2) the epoxidation reaction; (3) the ring opening reaction; (4) the performic acid decomposition. The kinetics of the reactions 1, 3 and 4 were studied in independent way and the best kinetic parameters found were applied to interpret the results obtained for the reaction 2.

### 2. Methods

A weighed amount of pre-heated soybean oil was initially put in contact with a concentrated solution of phosphoric acid. Then, hydrogen peroxide and formic acid were slowly added at a constant flowrate for about one hour. Afterwards, the reaction proceeded for 3-4 hours to complete the reaction. Samples of the two phases were withdrawn at different times and analysed for evaluating: (i) the residual Iodine Number, related to the residual double bonds and (ii) the Epoxide Number, related to the epoxide yields. A model was developed considering: (i) performic acid decomposition; (ii) CO<sub>2</sub> formation; (iii) H<sub>2</sub>O<sub>2</sub> consumption; (iv) the partition of performic acid in the two phases; (v) the change of pH in the aqueous phase. Moreover, the reactor was constantly monitored for what concerns the temperature, as the reaction is extremely exothermic (55 Kcal/mol). The temperature profile along the time in the reactor was also simulated. The kinetic model solves 19 differential equations and related kinetic-equilibrium parameters.

### 3. Results and discussion

The reactions studied were:



This reaction is promoted by the acidity of the aqueous phase and occurs with a kinetic law of the type [2]:

$$r_1 = k_1[H^+][\text{HCOOH}]_w[\text{H}_2\text{O}_2] \left(1 - \frac{1}{K_{e1}} \frac{[\text{HCOOOH}]_w[\text{H}_2\text{O}]}{[\text{HCOOH}]_w[\text{H}_2\text{O}_2]}\right)$$

$$k_1 = k_1(323\text{K}) \exp \left[ \left( \frac{-E_{a1}}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{kref}} \right) \right] = 0.078 \exp \left[ \left( \frac{-19830}{R} \right) \left( \frac{1}{T} - \frac{1}{323} \right) \right] \text{ (L}^2\text{/mol}^2\text{/min)}, E_{a1}=\text{cal/mol}$$

$$K_e = K_e(298\text{K}) \exp \left[ \left( \frac{-\Delta H_{e1}}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{kref}} \right) \right] = 1.60 \exp \left[ \left( \frac{10000}{R} \right) \left( \frac{1}{T} - \frac{1}{298} \right) \right], \Delta H_{e1}=\text{cal/mol}$$

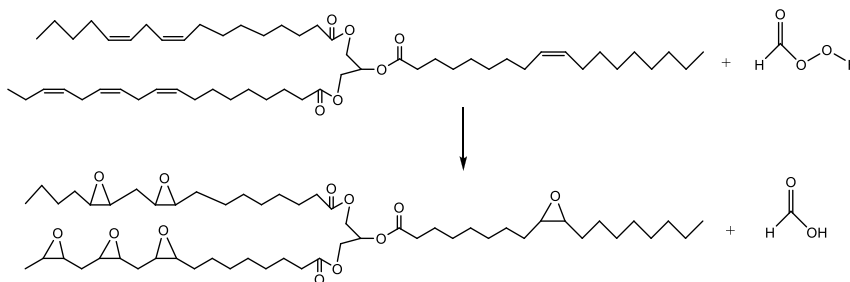


The kinetics of this reaction was studied independently [2]:

$$r_2 = k_2[\text{HCOOOH}]_w$$

$$k_2 = k_2(323\text{K}) \exp \left[ \left( \frac{-E_{a2}}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{kref}} \right) \right] = 0.0084 \exp \left[ \left( \frac{-23180}{R} \right) \left( \frac{1}{T} - \frac{1}{323} \right) \right] \text{ (1/min)}, E_{a2}=\text{cal/mol}$$

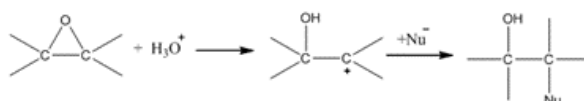
### Reaction 3



$$r_3 = k_3 [HCOOOH]_{oil} [DB]$$

$$k_3 = k_3(323K) \exp \left[ \left( \frac{-E_{a3}}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{kref}} \right) \right] = 0.12 \exp \left[ \left( \frac{-24890}{R} \right) \left( \frac{1}{T} - \frac{1}{323} \right) \right] (\text{L/mol/min}), E_{a3} = \text{cal/mol}$$

### Reaction 4



$$r_4 = k_4 [H^+] [ESBO] (\alpha_1 [FA] + \alpha_2 [H_2O_2] + \alpha_3 [PFA] + \alpha_4 [H_2O]), \alpha_1 \approx 40, \alpha_2 \approx \alpha_3 \approx \alpha_4 \approx 1$$

$$k_4 = k_4(333K) \exp \left[ \left( \frac{-E_{a4}}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{kref}} \right) \right] = 2.0 \cdot 10^{-6} \exp \left[ \left( \frac{-21020}{R} \right) \left( \frac{1}{T} - \frac{1}{333} \right) \right] (\text{L}^2/\text{mol}^2/\text{min}), E_{a4} = \text{cal/mol}$$

Some examples of the agreement between the experimental and calculated data are showed in figure 1. In this run  $H_2O_2$  (60%) and  $HCOOH$  (90%) solutions, kept at  $25^\circ\text{C}$ , were added separately to 100 g of pre-heated oil and catalyst, kept at  $63^\circ\text{C}$ , with respectively a flow rate of 0.54 mL/min the  $H_2O_2$  solution and 0.19 mL/min the  $HCOOH$  solution. Therefore, for 23.15 minutes the two components were fed into the reactor. After this time only hydrogen peroxide was still fed with a flow rate of 0.54 mL/min until an overall volume of 29.8 mL was added: the procedure lasted 55.18 minutes. The initial temperature of  $63^\circ\text{C}$  after 1 hour was increased to  $72^\circ\text{C}$  and kept at this value for other 4 hours.

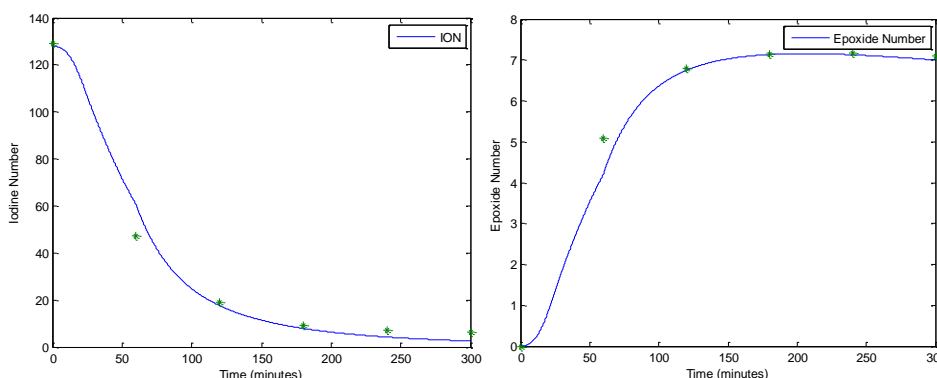


Figure 1 – The evolution with time of the Iodine Number and Epoxide Number values. The lines correspond to simulation profiles and the symbols to experimental data.

## 4. Conclusions

The kinetics of soybean oil epoxidation was studied considering all the occurring reactions and the existence of two phases, one polar and another one apolar. The kinetics of performic acid formation and decomposition and the kinetics of epoxide ring opening reaction were evaluated independently. The obtained kinetic parameters were successfully employed for simulating the soybean oil epoxidation process.

## References

- [1] E.Santacesaria, A. Renken, V. Russo, R.Turco, R.Tesser, M.Di Serio; Ind. Eng. Chem. Res. 51 (2012) 8760-8767
- [2] E.Santacesaria, V. Russo, R.Tesser, R.Turco, M. Di Serio; Ind. Eng. Chem. Res., 56(2017) 12940–12952