

## Facing the Hazard of Biphasic, Unstable, Highly Exothermic Process: the Case of Epoxidation of Vegetable Oils

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Vegetable oils are epoxidized by peroxy-acid in the presence of mineral catalysts. Besides, the risk of thermal explosion due to the decomposition of reactants (hydrogen peroxides and peroxyacids) is very high.

This contribution examines the hazards of epoxidation and explores different possibility to reduce the risks of thermal explosion pro-actively, starting from the biphasic kinetic model developed based on lab-scale experimental tests published in previous works.

Variable reactant feeding intensity for the peroxy-reactants, heat losses at wall have been set, in the light of the Quick, Fair conversion, Safe (QFS) criterion, by adopting the Cooling number methodology and by analyzing divergence criterion. Results allow best operating conditions and safety considerations either for lab-scale or for industrial scale when standard techniques cannot be adopted.

### 1. Introduction

Epoxidation of vegetable oils is commonly performed by in-situ formation of performic acid in the presence of mineral catalysts, by using highly concentrated hydrogen peroxide:

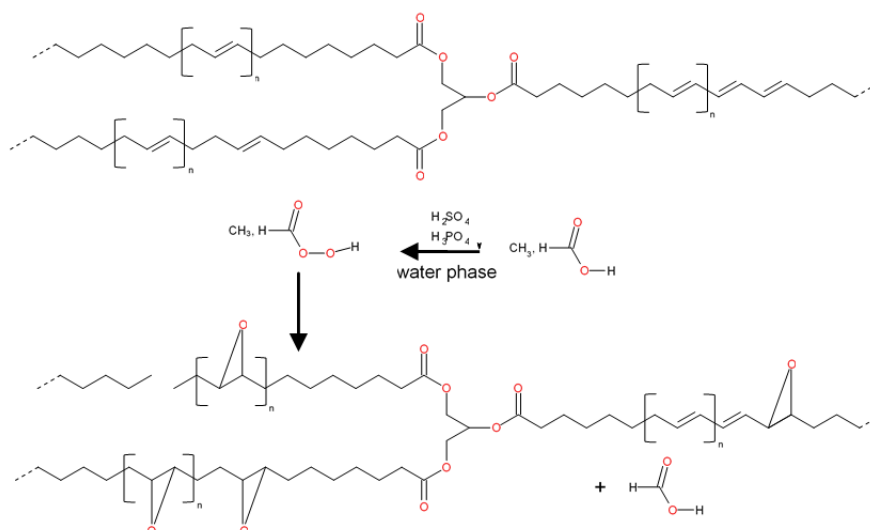
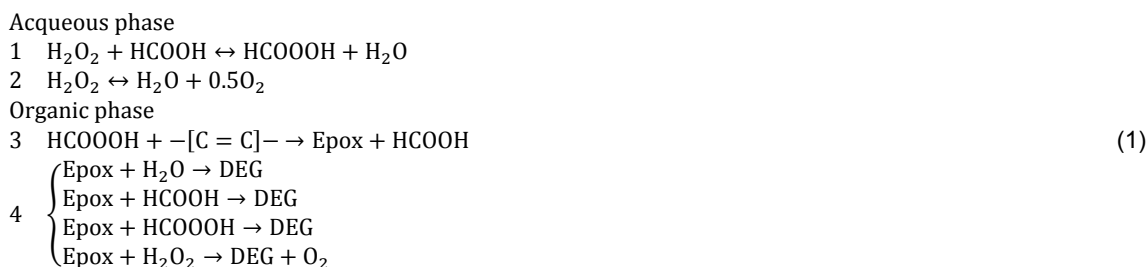


Figure 1. Epoxidation reaction of vegetable oils by means of in-situ preparation of peroxy-acids using mineral acids as catalysts.

The reaction is very exothermic and the risk of thermal explosion due to the decomposition of peroxides, which may be further catalysed by process conditions and by the presence of other components, is very high. Furthermore, standard techniques for safety cannot be adopted (Leveneur, 2014). Consequently, the scale-up of reactors is not straightforward.

This contribution examines the hazards of epoxidation and explores different possibility to reduce the risks, however aiming at the best yield and selectivity, which is one of the main economic issue of the bio-derived chemical process, hence in the light of the Quick, Fair conversion, Safe (QFS) criterion as defined by Westerterp & Molga (2004).

Variable feed intensity for the peroxy-reactants (hydrogen peroxide, formic or acetic acid), heat losses at wall, and Cooling number have been then analysed starting from the existing kinetic model previously developed on lab-scale experimental tests (Santacesaria et al., 2011) (Eq.1):



As it can be seen, the reaction network is complex, including both side reactions responsible of lowering the yield and the selectivity of the process. Therefore, both the hydrogen peroxide decomposition and the ring opening reactions are exothermic.

The reactive system is defined by the set of mass balance equations (Eq. 1) for each component  $j$  participating to the overall epoxidation reaction, either in aqueous (aq) or in organic (org) phase (ph):

$$\frac{dn_j^{ph}}{dt} = F_j + \sum_j r_j \cdot V_{ph} + J_i^{ph} \cdot V_{ph} \quad (2)$$

where  $n$  are the moles,  $F$  the molar flow rate,  $r_j$  the reaction rate,  $V$  the volume,  $J$  is the mass transfer rate for the component  $j$  in the given phase, and by the energy equation:

$$c_p \cdot M_{tot} \cdot \frac{dT}{dt} = (W_{\text{H}_2\text{O}_2} \cdot c_{p,\text{H}_2\text{O}_2} + W_{\text{FA}} \cdot c_{p,\text{FA}} + W_{\text{H}_2\text{O}} \cdot c_{p,\text{H}_2\text{O}}) \cdot (T_{add} - T) + [\Delta H_3 \cdot (-r_3) + \Delta H_4 \cdot (-r_4)] \cdot V_{org} + [\Delta H_1 \cdot (-r_1) + \Delta H_2 \cdot (-r_2)] \cdot V_{aq} - U \cdot A \cdot (T - T_w) \quad (3)$$

where  $M_{tot}$  is the total mass,  $c_p$  is the mean specific heat capacity at constant pressure,  $W$  is the inlet mass flow rate of the reactant,  $T_{add}$  is the inlet flow temperature,  $\Delta H$  is the reaction heat,  $U$  is global thermal exchange coefficient of equipment,  $A$  is the exchange area, and  $T_w$  is the temperature of the jacket. Finally, the corresponding set of kinetic constants for the Arrhenius law is given in Table 1.

Table 1. The set of kinetic constant and reaction parameter. Reference temperature for the kinetic constant is 25 °C.

Kinetic constant			Pre-Exponential factor (J/mol)
$k_1$	0.00104	$\text{L}^{1.5} \text{mol}^{-1.5} \text{min}^{-1}$	-
$k_{dec}$	0.37546	$\text{L}^2 \text{mol}^{-2} \text{min}^{-1}$	22795.70
$k_2$	0.05263	$\text{L}^2 \text{mol}^{-2} \text{min}^{-1}$	11390.00
$K_{eq,2}$	5.17000	-	-
$k_3$	0.00045	$\text{L mol}^{-1} \text{min}^{-1}$	24890.00
$k_{tri,3}$	133.037	$\text{L mol}^{-1} \text{min}^{-1}$	-
$k_4$	0.00018	$\text{L mol}^{-1} \text{min}^{-1}$	8860.000
$k_{tri,4}$	0.02810	$\text{L}^3 \text{mol}^{-3} \text{min}^{-1}$	-

## 2. Methodology

The set of equations has been set, tested and validated by an experimental system, described in details elsewhere (Santacesaria et al., 2011). The experimental tests were conducted by adding continuously the oxidizing mixture of hydrogen peroxide and formic acid ( $\text{H}_2\text{O}_2 = 36.7 \text{ g}$ , 60 % w/w; formic acid = 5.38 g, 95 % w/w purity) at the temperature of 10 °C in a 100 g of well stirred soybean oil containing 0.64 g of sulfuric acid as catalyst (Figure 2).

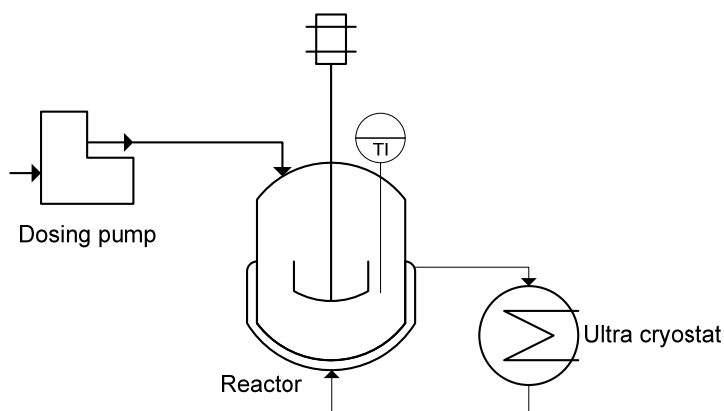


Figure 2. The lab reactor for the epoxidation of oil.

The flow rate was  $0.3 \text{ cm}^3 \text{ min}^{-1}$ ). A 30% volume excess of reactant with respect to stoichiometry was also considered. The initial temperature,  $T_{in}$ , of the reaction environment was about 65 °C. The system exchanged heat with a thermostatic fluid circulating in a jacket surrounding the reactor and regulated to obtain an approximately constant reaction temperature ( $\sim 65 \text{ °C}$ ).

Based on the model, results of the model are expressed in terms of Yields, Conversion and Selectivity, by using the iodine number:

$$\text{Conversion}(\%) = \frac{I_2^{\text{initial}} - I_2^{\text{final}}}{I_2^{\text{initial}}} \cdot 100 \quad (4)$$

$$\text{Yield}(\%) = \frac{n_{e,1,org} + n_{e,2,org} + n_{e,3,org}}{n_d^0} \cdot 100 \quad (5)$$

$$\text{Selectivity}(\%) = \frac{\text{Yield}}{\text{Conversion}} \cdot 100 \quad (6)$$

where  $I_2$  is the grams of iodine that is taken up by 100 g of oil between the initial and final phases,  $n_{e,1,org}$ ,  $n_{e,2,org}$ ,  $n_{e,3,org}$  are the moles of epoxide obtained by mono-enes, di-enes and tri-enes of the molecules of oil and  $n_d^0$  are the moles of double bond of the molecules of oil at the initial time.

For the hazard analysis, “geometry-based criteria” (Hub & Jones) and “sensitivity-based criteria” as defined in details in Varma et al. (1999) and Strozzi and Zaldivar (1994) can be adopted. It has been proved that the Hub & Jones criteria have strong limitations as, e.g. for autocatalytic reactions. Hence, more refined methodologies have been defined in the literature, based on the sensitivity criteria and more specifically on the “divergence criteria”. Bosch et al. (2004) have extensively reviewed and analysed this opportunity and reached the general conclusions that safety conditions are not respected if the following two embedded-parameters function, in particular temperature and conversion  $z$ , is always positive:

$$\frac{d^2T}{dt^2} + \frac{d^2z}{dz^2} > 0 \quad (7)$$

This criterion has been adopted in the following. However, some modifications have been adopted. If both first and second derivatives for temperature or conversion are negative, so that a false signal is due, the term is set to zero.

The procedure for QFS to the chemical system described above has been set by considering the Cooling number  $Co$  criterion as defined by Westerterp and Molga (2004):

$$Co = \frac{(UA)_o t_d}{\varepsilon (\rho c_p V)_o} \quad (8)$$

where  $t_d$  is the dosing time and  $\varepsilon$  is the relative volume increase due to the addition and the pedix means at the initial conditions.

### 3. Results and Discussion

The evaluation of the Cooling number allows the generalisation of result to any scale and the possibility of analysing the QFS conditions. Table 2 shows the reaction parameter and the ratio of maximum process temperature to the water peroxide decomposition temperature (90°C).

The sensitivity of different parameters in the experimental tests described above has been assessed. Input data and results are reported in the following tables, starting from the initial conditions of Test 1 as reported in Table 2, which show the maximum temperature and the yield by varying the reactant flow rate.

*Table 2: Test conditions and modelling results for epoxidation reaction.  $T_w$  (°C) = 70 °C.  $T_{in}$  = 65 °C. 30 % volume excess of reactant.*

Test	1	2	3	4	5
Q, flow rate (cm <sup>3</sup> min <sup>-1</sup> )	0.30	0.50	1.00	2.00	3.00
$T_{MAX}$ (°C)	78.42	82.28	90.93	103.23	181.90
Yield (% w/w)	80.26	85.40	89.75	92.24	93.05

Quite clearly, the onset of a runaway reaction can be seen for test 3, which shows a maximum temperature higher than the decomposition temperature of hydrogen peroxide. Tests 4 and 5 are totally out of control as the temperature is higher than the boiling temperature of water. For the first three tests, the following Table 3 reports the same data but stoichiometric reaction (hence no excess). It is easy to see that the cold excess of reactant is useful for safety reason, however with a small decrease of yield.

*Table 3. Modelling results for epoxidation reaction with stoichiometric ratio and 30% volume excess, by varying inlet flow rate.  $T_w$  (°C) = 70 °C.  $T_{in}$  = 65 °C.*

Test	6	7	8
Q, flow rate (cm <sup>3</sup> min <sup>-1</sup> )	0.30	0.50	1.00
$T_{MAX}$ (°C)	95.41	85.79	171.19
Yield (% w/w)	78.12	83.76	92.02

Test 2 has been also modified for the inlet temperature. Results are reported in Table 4, which shows the low effect of this parameter.

*Table 4. Modelling results for epoxidation reaction with 30% excess of reactant with respect to stoichiometric ratio by varying wall temperature and inlet flow rate.  $T_{in}$  = 65 °C.*

Test	9	10	11	12
Q, flow rate (cm <sup>3</sup> min <sup>-1</sup> )	0.50	0.50	1.00	1.00
$T_{MAX}$ (°C)	60.00	65.00	60.00	65.00
Yield (% w/w)	72.76	78.97	84.09	94.15

By considering the given results, both in terms of yield and maximum temperature, Tests 9 and 10 seem the optimal choice for both yield and safety, so that the same input conditions have been adopted for the test of heat transfer coefficient, which may vary due to several effects: viscosity, fouling and others, but also the effects of modified materials for the vessel system. Results are reported in Tables 5 and 6.

Table 5. Modelling results for epoxidation reaction by varying the heat transfer coefficient for Test 11.

Test	13	14	15	16
U % variation	-20.00	-10.00	+10.00	+20.00
T <sub>MAX</sub> (°C)	95.63	80.20	69.86	69.09
Yield (% w/w)	87.88	84.49	82.12	81.51

Table 6. Modelling results for epoxidation reaction by varying the heat transfer coefficient for Test 12.

Test	17	18	19	20
U % variation	-20.00	-10.00	+10.00	+20.00
T <sub>MAX</sub> (°C)	118.89	85.82	82.82	81.39
Yield (% w/w)	89.53	85.71	83.15	82.62

Finally, the Figure 3 reports the time to maximum epoxidation, and the selectivity for the given test.

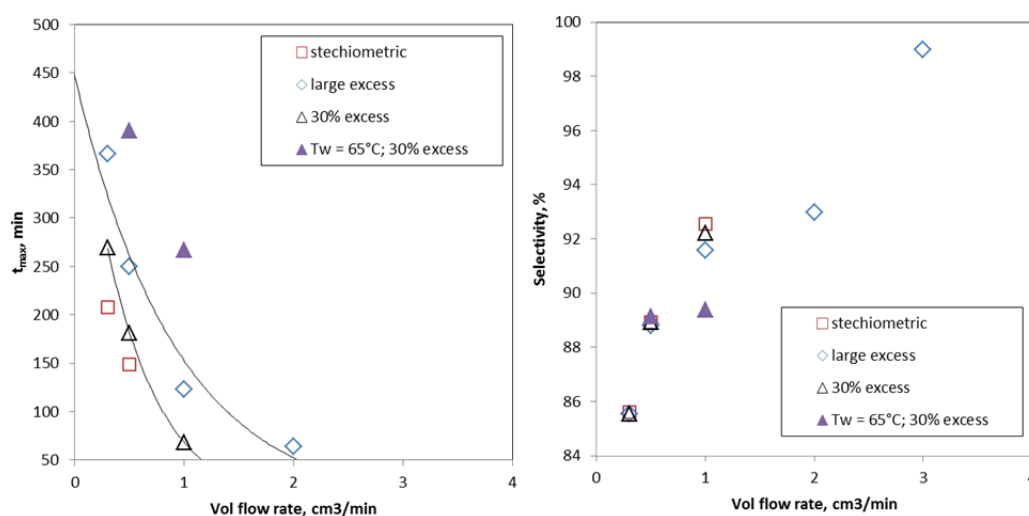


Figure 3. Time to maximum epoxidation number  $t_{max}$ , and Selectivity (bottom) vs feed flow rate. Wall temperature = 70 °C unless specified.

Results show the net decrease in the  $t_{max}$  and selectivity (and yield) when increasing the flow rate, which however represents a hazardous condition from the point of view of decomposition reaction and runaway behaviour.

In conclusion, the best option for conversion, yield and selectivity, together with very low reaction time and safety conditions (Quick, Safe reaction and Fair conversion), are obtained for reactant flow rate and jacket temperature between 0.5 and 1 cm<sup>3</sup>/min, wall temperature higher than 65°C and excess of reactant higher than 30%. In these conditions, the process is still able to prevent runaway conditions for any decrease of the heat transfer coefficient to a maximum of 10%, e.g. due to changes in the viscosity or fouling. Higher volume flow rates or wall temperature, or lower excess, result in un-safe conditions. On the contrary, lower volume flow rate and very large excess result in high reaction times and increased costs.

Results of the calculation for tests reported above are then shown in Figure 4 in terms of Cooling number  $Co$ . In the plot, the yield and the time to maximum selectivity ( $t_{max, Nepox}$ ) are reported for the QFS definition.

#### 4. Conclusion

Values of  $Co$  around 200 represents the QFS process condition. Values lower than 150 results to be inherently un-safe, whereas higher values (>250) increases the reaction time and decreases the yield and selectivity dramatically. These results must be tested further for safety but can be considered a first approach for large-scale design and future experimental applications.

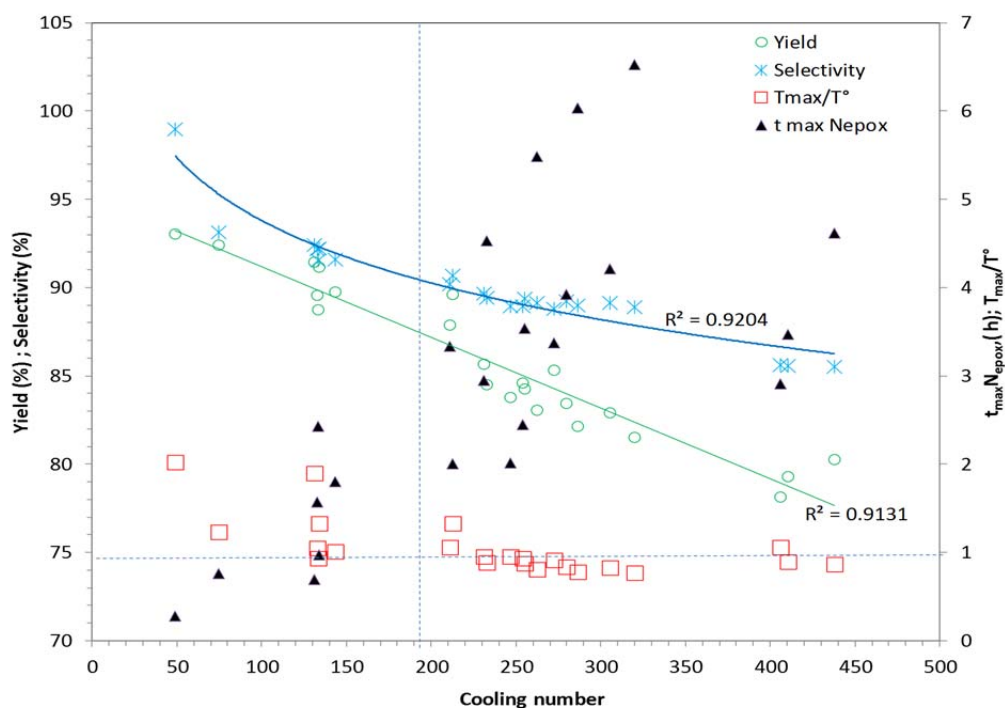


Figure 4. Time to maximum epoxidation number (Cross), Yield (Continuous line), and the ratio of process Temperature with hydrogen decomposition temperature for hydrogen peroxide (90°C) (Square) for the tests reported in this work as a function of Cooling number.

## References

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