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Interaction of thermal and kinetic parameters for a liquid–liquid reaction system: Application to vegetable oils epoxidation by peroxycarboxylic acid

Sébastien Leveneur [a,b,1,*], Junliu Zheng [a,c], Bechara Taouk [a], Fabrice Burel [c], Johan Wärnå [b,d], Tapio Salmi [b]

[a] LSPC – Laboratoire de Sécurité des Procédés Chimiques, INSA Rouen, 685 Avenue de l'Université, FR-76801 Saint-Etienne-du-Rouvray, France
[b] Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland
[c] Normandie Université, INSA de Rouen, CNRS UMR 6270 PBS & FR 3038, Avenue de l'Université, 76801 Saint-Etienne-du-Rouvray, France
[d] Umeå University, Chemical-Biological Center, Technical Chemistry, SE-901 87 Umeå, Sweden

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ABSTRACT

A mathematical model was developed to analyze an exothermic liquid–liquid reaction system using epoxidation of oleic acid by peroxyformic acid formed *in situ* as an example. Kinetic and thermal parameters were included, mass transfer parameters were eliminated from the model and evaporation/condensation was taken into account. A calorimetric semi-batch reactor under isoperibolic mode was used in the experimental work. Different initial aqueous-phase concentrations of H_2O_2 [6.5–8.8 mol/l], water [44–45 mol/l], molar flow rate of formic acid [0.02–0.54 mol/min], initial reaction temperature [50–70 °C] and amount of organic phase [34–46 wt.%] were studied. A non-linear regression method was used to estimate kinetic (*e.g.*, rate constant at average temperature and activation energy) and thermal parameters (*e.g.*, reaction enthalpy) of the epoxidation and ring-opening reactions. The standard reaction enthalpy changes were estimated to be -116 kJ/mol for epoxidation reaction and -50 kJ/mol for the ring opening.

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1. Introduction

The world consumption of lubricants is estimated to be 40 million tons per year, used in very different areas from car engines to office chairs. As in fuel industry, the majority of lubricants are petroleum-derived. Even though depletion of crude oil will increase the price of petroleum raw material, the reason to use bio-lubricants instead of petro-based one is mainly environmental. Indeed, several studies have shown that 30–40% of lubricants escape into the environment through such routes as spills, leaks and evaporation [1]. For these reasons, research has been focused on an inexpensive, non-toxic and renewable source of lubricants, *i.e.*, bio-based lubricants. At present, the cost of bio-based lubricant is higher than petro-based lubricants, but compared to maintenance and energy costs, it is a minor factor (Fig. 1) [2].

The production of bio-lubricant is based on the use of vegetable or animal oils, and several ways of synthesis exist: esterification or transesterification as biodiesel, selective hydrogenation, or epoxidation of the oils by peroxycarboxylic acids. The latter route of production follows the philosophy of Green Chemistry, because there is no production of waste such as glycerol or the use of explosive reactants such as hydrogen. Epoxidized vegetable oils can also be used for different purposes, such as intermediates for polymer synthesis, as plasticizers or as scavenger during the synthesis of PVC. Compared to petroleum-derived products, they present several advantages: low toxicity and biodegradability.

There are several ways of synthesis of epoxidized vegetable oils [3–6], but the use of peroxycarboxylic acids, *e.g.*, peroxyformic or peroxyacetic acids, is the most efficient and greener way [3]. It is a liquid–liquid reaction system, where the peroxycarboxylic acid is formed *in situ* from the carboxylic acid and hydrogen peroxide.

The literature review concerning the kinetics of vegetable oil epoxydation is quite vast. However, one should differentiate between the studies carried out under isothermal and

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Abbreviations: EOA, epoxidized oleic acid; FA, formic acid; OA, oleic acid; PFA, peroxyformic acid.

[*] Corresponding author at: LSPC – Laboratoire de Sécurité des Procédés Chimiques, INSA Rouen, 685 Avenue de l'Université, FR-76801 Saint-Etienne-du-Rouvray, France. Tel.: +33 232 95 66 54; fax: +33 232 95 66 52.
E-mail address: sebastien.leveneur@insa-rouen.fr (S. Leveneur).
[1] Tel.: +33 232 95 66 54; fax: +33 232 95 66 52.

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Nomenclature

A	heat transfer area [m^2]
C_p	constant-pressure heat capacity [J/K]
$\bar{C}_P$	constant-pressure heat capacity per mol [J/mol/K]
$\hat{C}_P$	constant-pressure heat capacity per mass [J/kg/K]
E_a	activation energy [J/mol]
H	enthalpy [J]
$\bar{H}$	molar enthalpy [J/mol]
ΔH_r^o	standard reaction enthalpy [kJ/mol]
ΔH_v	heat of vaporization [J/mol]
K^c	equilibrium constant, based on concentrations
K^T	thermodynamic equilibrium constant, based on activities
K_{WATER}	equilibrium molar ratio of water
K_{FA}	equilibrium molar ratio of formic acid
K_{PFA}	equilibrium molar ratio of peroxyformic acid
k	rate constant [l^2/mol/s]
k_{decomp}	decomposition rate constant [s]
m	mass [kg]
$\dot{n}$	flow of the amount of substance [mol/s]
P	pressure
Q_f	volumetric flow rate [l/s]
$\dot{Q}_c$	electrical calibration [W]
$\dot{Q}$	heat transfer rate [W]
$\dot{Q}_{ex}$	heat flux exchanged with the reactor jacket [W]
$\dot{Q}_{loss}$	heat flux lost through the top of the reactor [W]
R	gas constant [J/K/mol]
R^2	coefficient of explanation [%]
r_i	reaction rate [mol/l/s]
T	temperature
U	overall heat transfer coefficient [W/m/K]
Q_{HCOOH}	volumetric flow rate of formic acid [l/s]
V_R	reaction volume [l]
X	conversion

Greek letters

β	proportionality factor [J/s/atm]
ν_{ij}	stoichiometric coefficient
ρ	mass density [kg/l]
ω	objective function
τ	residence time

Subscripts and superscripts

add	addition
ave	average
aq	aqueous phase
decomp	decomposition
eq	equilibrium state
f	feed flow
FAD	formic acid dissociation
het	heterogeneous
hom	homogeneous
in	input
j	component j
org	organic phase
out	output
perh	perhydrolysis
ref	reference state
R.O.	ring opening
O	initial
*	interfacial value

non-isothermal conditions. To the best of our knowledge, only the group of Santacesaria et al. [7,8] has proposed a complete model coupling the energy and mass balances for this system.

A kinetic model was developed by coupling mass and energy balances, but avoiding the use of mass transfer parameters and taking into account the evaporation/condensation of aqueous phase. A calorimetric reactor was designed and operated in semi-batch under isoperibolic mode. A model molecule representing vegetable oils was used: oleic acid. Indeed, the structure of this free fatty acid is present in several vegetable oils.

2. Experimental

2.1. Apparatus and experimental procedures

The experiments were carried out in the experimental apparatus described in a previous article of our group, Leveneur et al. [9]. The reactor set-up is shown in Fig. 2.

In a first step, water, hydrogen peroxide and oleic acid were added together into the reactor. As the desired temperature was reached, a first calibration step, *i.e.*, by the Joule effect, was carried out to measure the heat capacity of the reaction mixture and the overall heat transfer coefficient through the jacket. Then, a preheated solution of formic acid was added through a dosing pump. A last calibration was made at the end of the reaction.

To prevent any contamination, which initiate the catalytic decomposition of peroxide species, all parts of the reactor system being in contact with the reaction solution were washed with hydrochloric acid, followed by another washing, with a phosphate-free detergent solution.

Table 1 introduces the experimental matrix

Different reaction enthalpies are involved in the system. To take into account all the thermal effects, even the lowest one, a micro-calorimeter was used. An isothermal micro-calorimeter, namely C80 SETARAM, was used. This calorimeter uses the Calvet design detector in which a sample and reference cells are totally surrounded by an array of thermocouple detectors allowing for

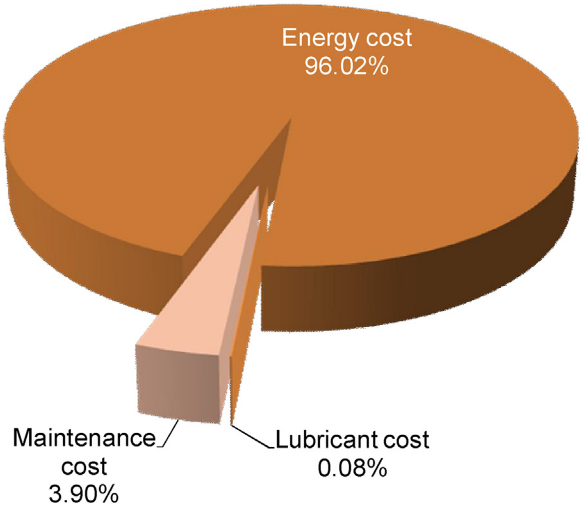

Fig. 1. Relative lubricant, energy and maintenance costs.

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