Supporting Information

Thermal safety assessment through the concept of structure-reactivity: application to vegetable oils valorization.

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SI1 Determination of TMR$_{ad}$

During ARSST experiment, an electrical heating rate is applied to the reaction mixture. Thus, the energy balance for the reaction mixture can be expressed as:[88-89]

$$m_R . \hat{C}_{PR} . \frac{dT_P}{dt} = q_r(T_P) + q_{electrical} \qquad (S1)$$

where $q_{electrical}$ is the electrical power provided by the system.

The electrical power varies with the reaction temperature to provide a constant temperature ramp to the reaction temperature until the onset temperature.

During the first part of the experiment, one can neglect the heat-flow rate due to the chemical reactions $q_r(T_P)$, because the temperature increase is mainly due to the electrical power.[89] From the initial temperature to the so-called onset temperature (T_{onset}), one can determine the value of temperature ramp due to electrical power, $\beta_{electrical}$ (Figure S1). Thus, eq S1 becomes

$$\begin{aligned}
\frac{dT_P}{dt} &= \frac{q_r(T_P)}{m_R . \hat{C}_{PR}} + \frac{q_{electrical}}{m_R . \hat{C}_{PR}} \\
&= \frac{q_r(T_P)}{m_R . \hat{C}_{PR}} + \beta_{electrical}
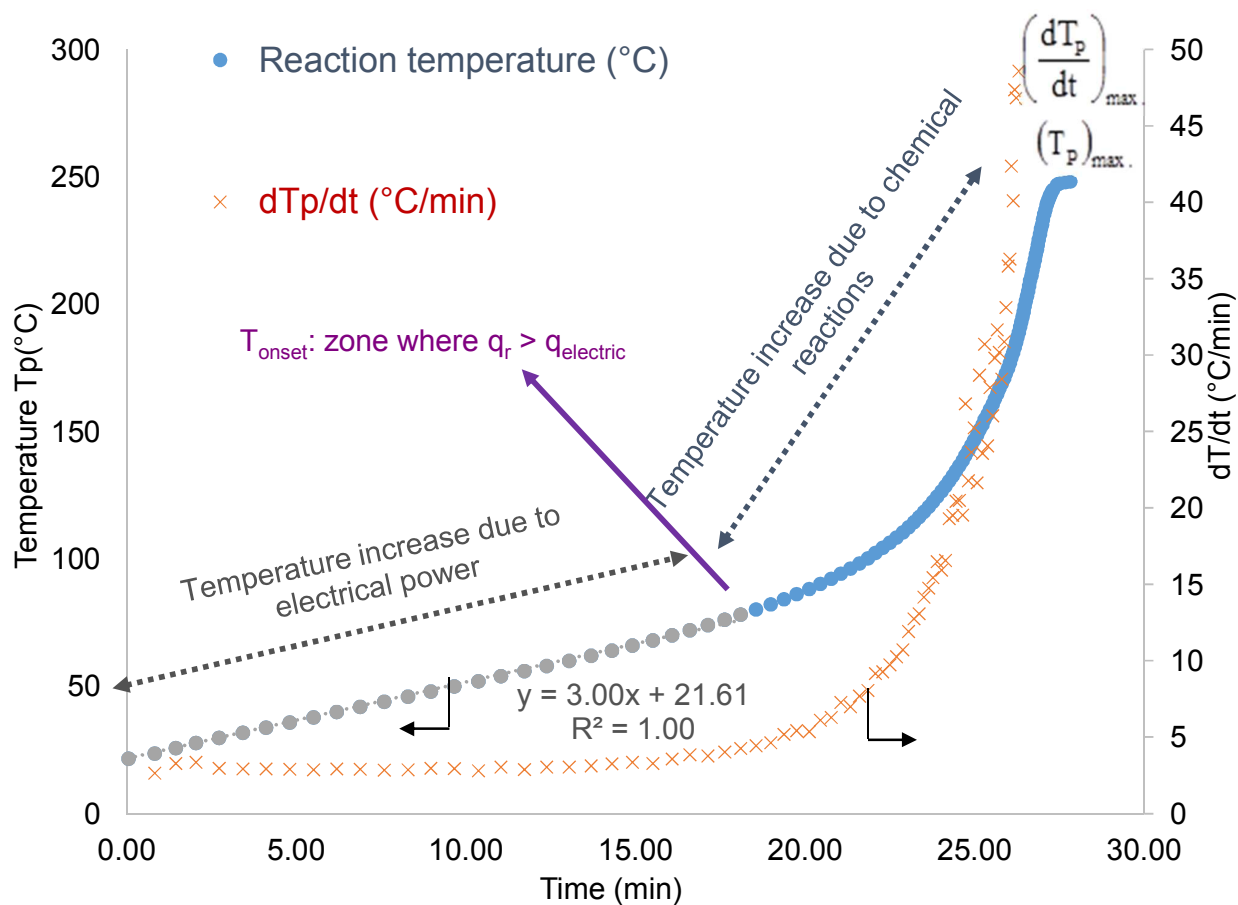\end{aligned} \qquad (S2)$$

Figure S1. Temperature profile during an ARSST experiment for the epoxidation of cottonseed oil by performic acid.

TMR_{ad} was calculated from T_{onset} to $\left(\dfrac{dT_P}{dt}\right)_{max.}$.

The heat-flow rate released by chemical reactions $q_r(T_p)$ at a temperature T_p can be expressed as

$$q_r(T_P) = -R.\Delta H_R.V_R \tag{S3}$$

where, R (mol.L^{-1}.s^{-1}) is the reaction rate, ΔH_R (kJ/mol) is the reaction enthalpy and V_R is the reaction mixture volume.

The detailed kinetics and thermodynamics of this system can be time-consuming, and then the zero-order approach was used, which is largely adopted by the process safety community.

Eq S3 becomes

$$q_r(T_P) = -k(T_P).\Delta H_R.V_R \tag{S4}$$

where, $k(T_p)$ is the rate constant for a zero-order kinetics at T_p.

The evolution of the rate constant with temperature can be expressed by a modified Arrhenius equation as:

$$k(T_P) = k(T_{ref}).exp\left(\frac{-E_a}{R}\left(\frac{1}{T_P} - \frac{1}{T_{ref}}\right)\right) \tag{S5}$$

where, $k(T_{ref}) = Ae^{-\left(\frac{Ea}{RT_{ref}}\right)}$ is the rate constant at a reference temperature T_{ref}, A is the pre-exponential factor, E_a the activation energy and R is the gas constant.

In the ARSST system, by considering the temperature from T_{onset} to $\left(\frac{dT_P}{dt}\right)_{max.}$, one can neglect the term $\beta_{electrical}$ in eq S2. By adding eqs S4 and S5 into S2, one gets

$$
\begin{aligned}
\frac{dT_P}{dt} &= \frac{q_r(T_P)}{m_R.\hat{C}_{PR}} \\
&= \frac{-k(T_P).\Delta H_R.V_R}{m_R.\hat{C}_{PR}} \\
&= \frac{-\Delta H_R.V_R}{m_R.\hat{C}_{PR}}.k(T_{ref}).exp\left(\frac{-E_a}{R}.\left(\frac{1}{T_P} - \frac{1}{T_{ref}}\right)\right) \\
&= \frac{q_r(T_{ref})}{m_R.\hat{C}_{PR}}.exp\left(\frac{-E_a}{R}.\left(\frac{1}{T_P} - \frac{1}{T_{ref}}\right)\right)
\end{aligned}
\tag{S6}
$$

where, $q_r(T_{ref}) = k(T_{ref}).\Delta H_R.V_R$, which represents the heat-flow rate at the reference temperature by using the zero-order approach.

The integration of eq S6 from T_{onset} to the temperature T_{Pmax}, which is the temperature at

$$\left(\frac{dT_P}{dt}\right)_{max.} \text{ gives}$$

$$\frac{dT_P}{dt} = \frac{q_r(T_{ref})}{m_R.\hat{C}_{PR}}.\exp\left(\frac{-E_a}{R}.\left(\frac{1}{T_P}-\frac{1}{T_{ref}}\right)\right)$$

$$\Leftrightarrow \int_{T_{onset}}^{T_{R\max}} \frac{dT_P}{\exp\left(\frac{E_a}{R}.\left(\frac{1}{T_P}-\frac{1}{T_{ref}}\right)\right)} = \int_{t\,at\,T_{onset}}^{t\,at\,T_{Rmax}} \frac{q_r(T_{ref})}{m_R.\hat{C}_{PR}}.dt \qquad (S7)$$

For the sake of simplicity, time at T_{onset} was set at zero and time at T_{Pmax} is the time-to-maximum rate under adiabatic conditions for T_{onset}, i.e., $TMR_{ad}(T_{onset})$. Hence, eq S7 becomes

$$\left[\frac{-1}{\frac{E_a}{R.T_P^2}}.\exp\left(\frac{E_a}{R}.\left(\frac{1}{T_P}-\frac{1}{T_{ref}}\right)\right)\right]_{T_{onset}}^{T_{R\max}} = \frac{q_r(T_{ref})}{m_R.\hat{C}_{PR}}.(TMR_{ad}(T_{onset})-0)$$

$$\Leftrightarrow \frac{-1}{\frac{E_a}{R.T_{Rmax}^2}}.\exp\left(\frac{E_a}{R}.\left(\frac{1}{T_{Rmax}}-\frac{1}{T_{ref}}\right)\right) + \frac{1}{\frac{E_a}{R.T_{onset}^2}}.\exp\left(\frac{E_a}{R}.\left(\frac{1}{T_{onset}}-\frac{1}{T_{ref}}\right)\right) = \frac{q_r(T_{ref})}{m_R.\hat{C}_{PR}}.TMR_{ad}(T_{onset}) \qquad (S8)$$

In eq S8, the term $\frac{-1}{\frac{E_a}{R.T_{Rmax}^2}}.\exp\left(\frac{E_a}{R}.\left(\frac{1}{T_{Rmax}}-\frac{1}{T_{ref}}\right)\right)$ is negligible, thus eq S8 can be simplified to

$$\frac{1}{\frac{E_a}{R.T_{onset}^2}}.\exp\left(\frac{E_a}{R}.\left(\frac{1}{T_{onset}}-\frac{1}{T_{ref}}\right)\right) = \frac{q_r(T_{ref})}{m_R.\hat{C}_{PR}}.TMR_{ad}(T_{onset})$$

$$\Leftrightarrow TMR_{ad}(T_{onset}) = \frac{R.T_{onset}^2}{E_a}.\frac{m_R.\hat{C}_{PR}}{q_r(T_{ref}).\exp\left(\frac{-E_a}{R}.\left(\frac{1}{T_{onset}}-\frac{1}{T_{ref}}\right)\right)} = \frac{R.T_{onset}^2}{E_a}.\frac{m_R.\hat{C}_{PR}}{q_r(T_{onset})} \qquad (S9)$$

By using the same logic, the determination of TMR_{ad} at any temperature T_p can be expressed as:

$$TMR_{ad}(T_P) = \frac{R.T_P^2}{E_a}.\frac{m_R.\hat{C}_{P_R}}{q_r(T_P)} = \frac{R.T_P^2}{E_a}.\frac{m_R.\hat{C}_{P_R}}{k(T_P).\Delta H_R.V_R} = \frac{R.T_P^2}{E_a}.\frac{m_R.\hat{C}_{P_R}}{q_r(T_{Ref}).\exp\left(\frac{-E_a}{R}.\left(\frac{1}{T_P}-\frac{1}{T_{Ref}}\right)\right)} \qquad (S10)$$

From eq S10, it is possible to extrapolate the TMR$_{ad}$ at different temperature by using the following equation:

$$\ln\left(\text{TMR}_{ad}\left(T_P\right)\right) = \ln\left(\frac{m_R.\hat{C}_{PR}.R.T_P^2}{q_r\left(T_{Ref}\right)} * \exp\left(\frac{Ea}{R}.\left(\frac{1}{T_P} - \frac{1}{T_{Ref}}\right)\right)\right)$$

$$= \ln\left(\frac{m_R.\hat{C}_{PR}.R.T_P^2}{q_r\left(T_{Ref}\right)}\right) - \frac{Ea}{R.T_{Ref}} + \frac{Ea}{R} * \frac{1}{T_P} \qquad \text{(S11)}$$

$$= \text{constant} + \frac{Ea}{R} * \frac{1}{T_P}$$
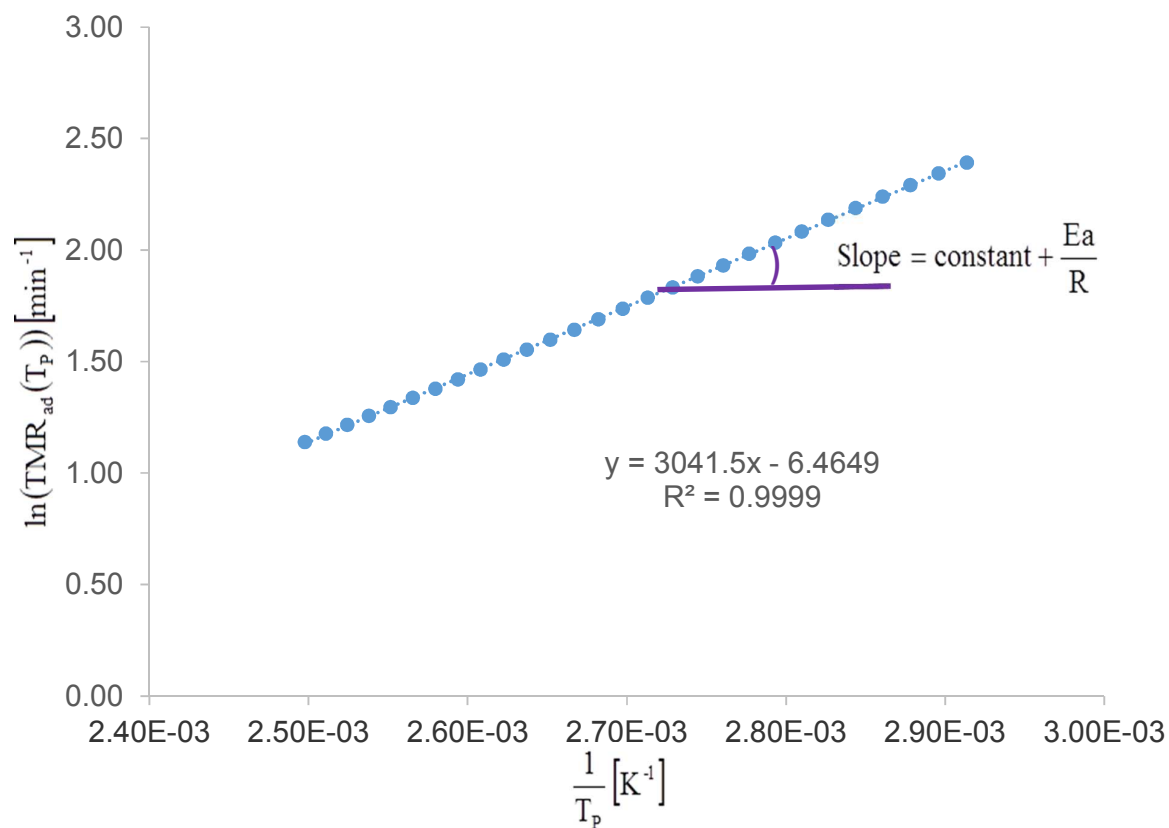
Figure S2 Linear relationships between $\ln\left(\text{TMR}_{ad}\left(T_P\right)\right)$ and $\dfrac{1}{T_P}$.

Based on eq S11, it is possible to extrapolate the value of TMR_{ad} at different process temperature (Figure S2). At industrial scale, the process of epoxidation is carried out within the temperature range 60-80°C. The values of $TMR_{ad}(T_P)$ at 60 and 80°C were determined by using eq S11. The onset temperature can be higher than 60 or 80°C, for that reason $TMR_{ad}(T_P=60°C)$ and $TMR_{ad}(T_P=80°C)$ were determined by extrapolation.

-SI2 Effect of stirring and electrical heating

There is a possibility to tune the stirring speed on the ARSST equipment. A first step was to determine the influence of the stirring on the value of TMR_{ad}.
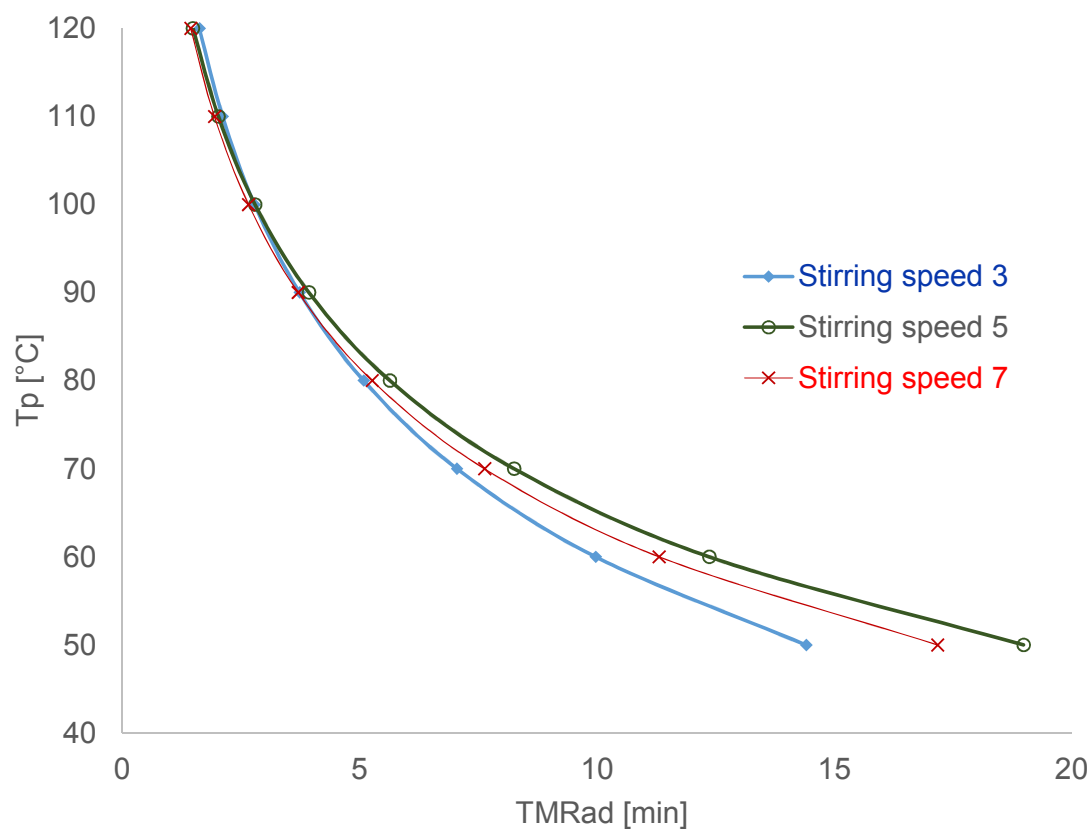
Figure S3. Effect of stirring on the epoxidation of cottonseed oil by performic acid at ca. 3.4°C/min.

When the stirring speed is higher than 5, one can consider that its effect on TMR_{ad} is negligible (Figure S3). From Figure S3, one can neglect mass transfer limitation when the stirring speed is between 5 and 7. Thus, all the experiments were performed at a stirring speed of 7.

For ARSST experiments, one should tune the value of the temperature ramp by calibrate the electrical heating rate. To record reliable safety criteria, one should test different temperature ramps.

Figure S4. Effect of electrical heating rate on the epoxidation of cottonseed oil by performic acid.

From Figure S4, one can notice that TMR_{ad} values differ significantly for process temperature lower than 60°C. This differenc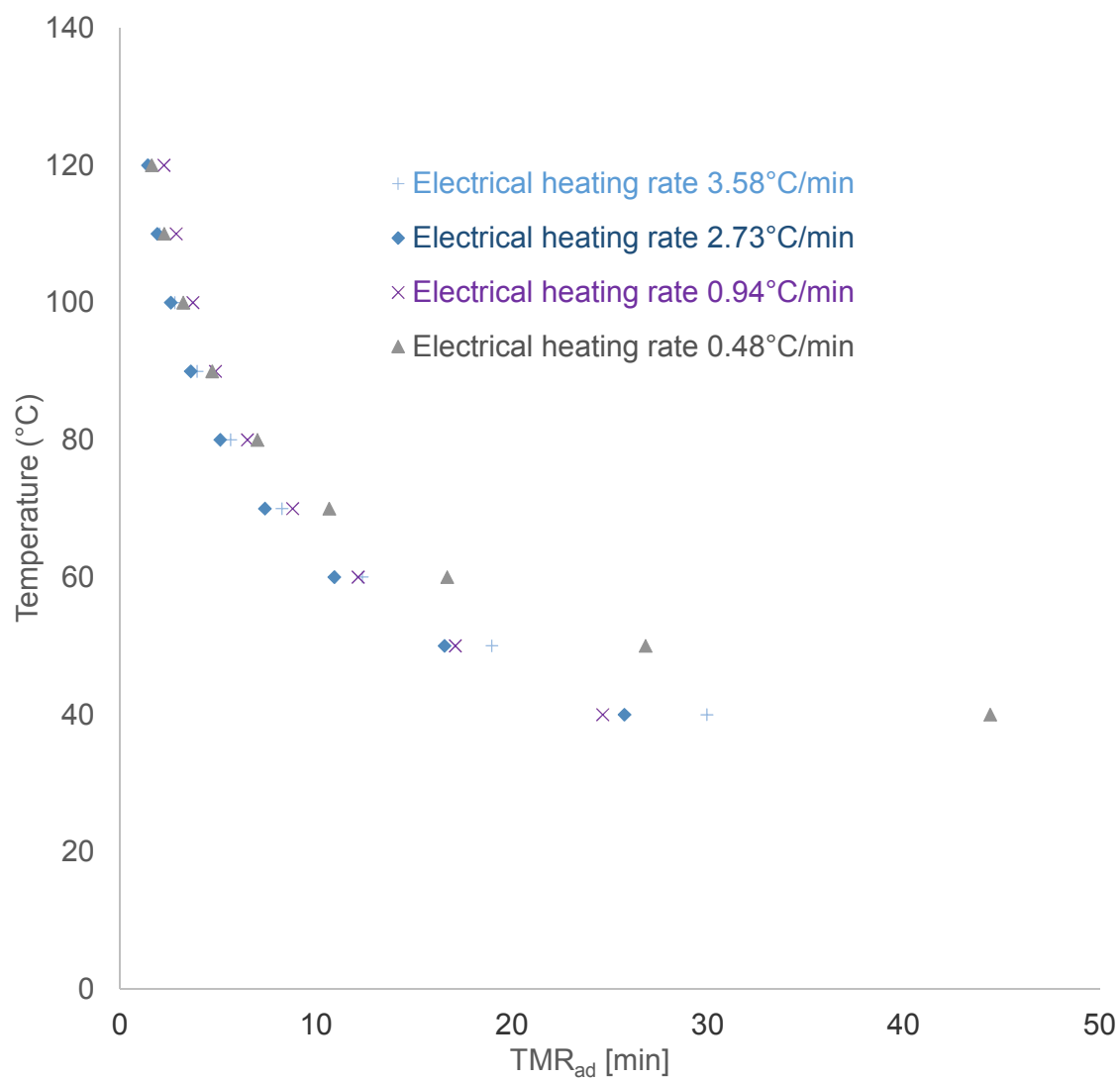e is lower when the process temperature is higher than 60°C. For the ARSST experiments, the value of the temperature ramp was between 2 and 3°C/min.

-SI3 Long reaction time

As illustrated by Figure S1, several exothermic reactions occur during the epoxidation process. A previous work of our group[38] has shown that one can segregate the exothermicity due to the epoxidation process (perhydrolysis, epoxidation and ring-opening reactions) from the exothermicity due to the decomposition of hydrogen peroxide.
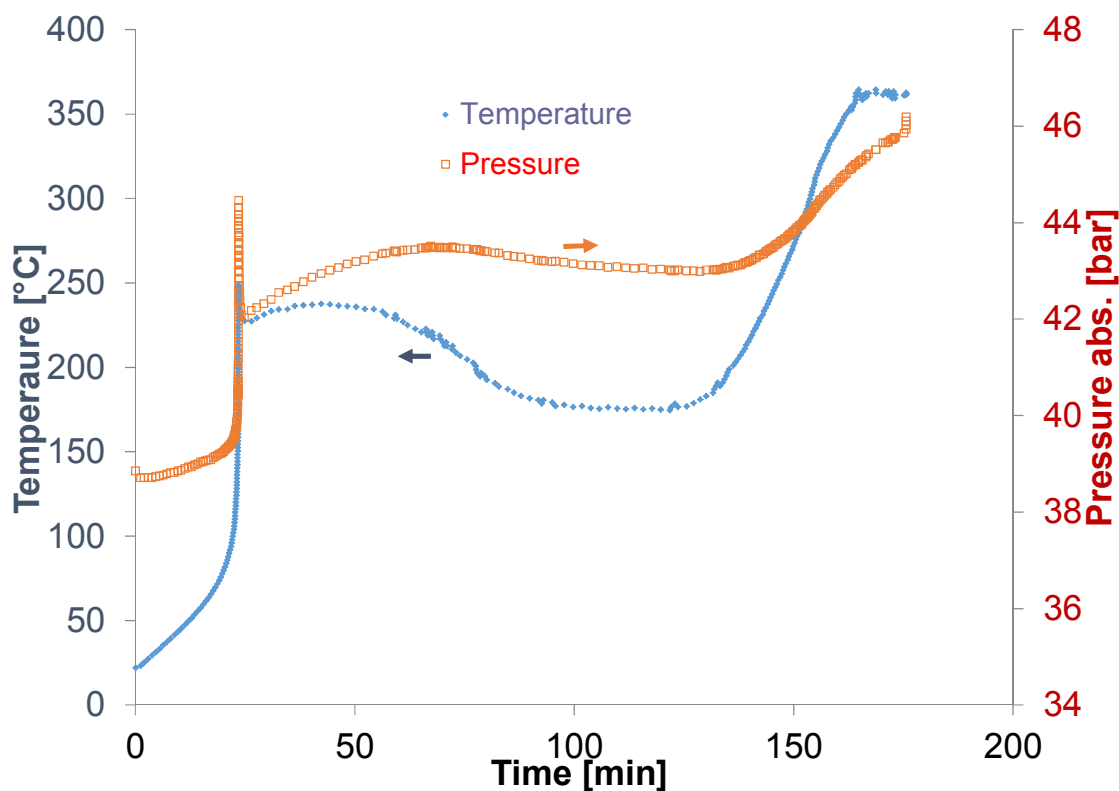
Figure S5. Temperature and pressure behaviour under long reaction time for the epoxidation of cottonseed oil by performic acid at temperature ramp of 2.33°C/min.

By performing reaction on a long time, one can notice the presence of a second decomposition due to the excess of hydrogen peroxide (Figure S5). The first peak is linked to the reactivity of the produced percarboxylic acids. When the first exothermic peak appeared, the electrical heater was switched off.

-SI4 Values of TMR$_{ad}$ at 60 and 80°C

Cottonseed oil epoxidation

Carboxylic acid	Temperature 60 TMR$_{ad}$ [min]	Temperature 80 TMR$_{ad}$ [min]
Formic acid	14.36	8.56
Acetic acid	255.86	66.92
Propionic acid	471.81	102.02
nButyric acid	171.51	53.49
Valeric acid	797.59	147.43
iButyric acid	1053.77	180.54
Lactic acid	75.77	25.42
Hexanoic acid	2889.02	468.28
2-Ethylbutyric acid	1512.52	275.63

Olive oil epoxidation

Carboxylic acid	Temperature 60 TMR$_{ad}$ [min]	Temperature 80 TMR$_{ad}$ [min]
Formic acid	11.54	4.66
Acetic acid	181.05	49.67
Propionic acid	1621.66	248.81
nButyric acid	979.07	177.24
Valeric acid	944.96	161.73
iButyric acid	827.27	152.28
Lactic acid	153.31	50.20
Hexanoic acid	5992.14	609.09
2-Ethylbutyric acid	929.26	155.14

Linseed oil epoxidation

	Temperature 60	Temperature 80
Carboxylic acid	TMR$_{ad}$ [min]	TMR$_{ad}$ [min]
Formic acid	8.48	3.82
Acetic acid	216.69	55.82
Propionic acid	743.76	158.35
nButyric acid	x	x
Valeric acid	784.52	180.44
iButyric acid	x	x
Lactic acid	192.00	65.31
Hexanoic acid	x	x
2-Ethylbutyric acid	621.25	137.78

Oleic acid epoxidation

	Temperature 60	Temperature 80
Carboxylic acid	TMR$_{ad}$ [min]	TMR$_{ad}$ [min]
Formic acid	8.78	3.72
Acetic acid	386.30	79.75
Propionic acid	766.57	134.22
nButyric acid	1338.94	177.34
Valeric acid	x	x
iButyric acid	1857.91	231.98
Lactic acid	80.83	34.12
Hexanoic acid	961.25	163.04
2-Ethylbutyric acid	2163.31	293.58

Linoleic acid epoxidation

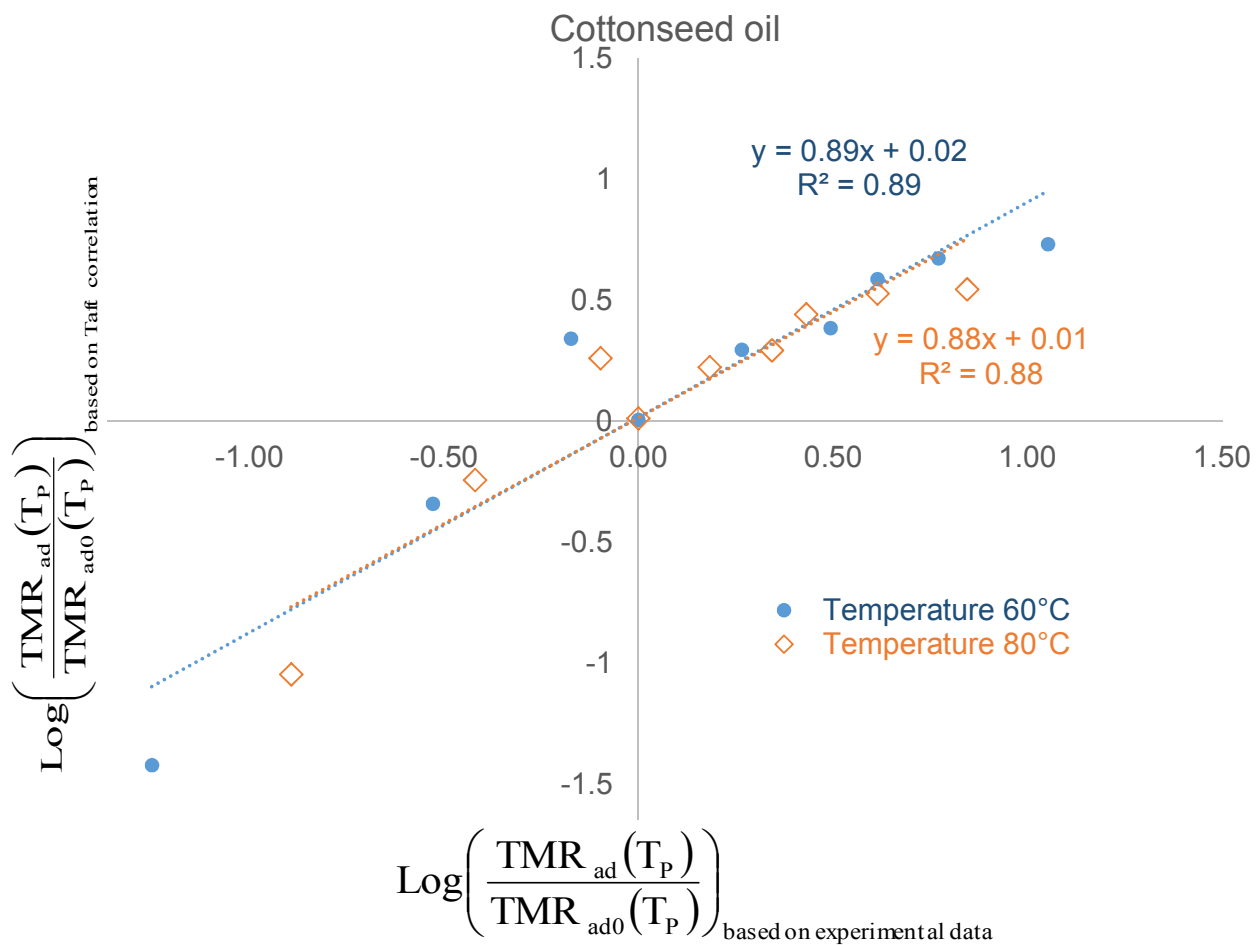| Carboxylic acid	Temperature 60 TMR_{ad} [min]	Temperature 80 TMR_{ad} [min]
Formic acid	8.30	3.39
Acetic acid	162.90	41.79
Propionic acid	522.88	105.47
nButyric acid	x	x
Valeric acid	x	x
iButyric acid	x	x
Lactic acid	98.44	39.07
Hexanoic acid	680.93	163.31
2-Ethylbutyric acid	1131.37	156.89

Figure S6. Parity plot for the epoxidation of cottonseed oil by using formic, acetic, propionic, n-butyric, valeric, i-butyric, lactic, hexanoic and 2-ethylbutyric acids.

Figure S7. Parity plot for the epoxidation of olive oil by using formic, acetic, propionic, n-butyric, valeric, i-butyric, lactic, hexanoic and 2-ethylbutyric acids.

Linseed oil

$y = 0.97x + 0.00$
$R^2 = 0.97$

$y = 0.95x + 0.00$
$R^2 = 0.95$

$\text{Log}\left(\dfrac{\text{TMR}_{ad}(T_P)}{\text{TMR}_{ad0}(T_P)}\right)_{\text{based on Taft correlation}}$

$\text{Log}\left(\dfrac{\text{TMR}_{ad}(T_P)}{\text{TMR}_{ad0}(T_P)}\right)_{\text{based on experimental data}}$

1

0.5

0

-0.5

-1

-1.50   -1.00   -0.50   0.00   0.50   1.00

● Temperature 60

◇ Temperature 80

Figure S8. Parity plot for the epoxidation of linseed oi by using formic, acetic, propionic,
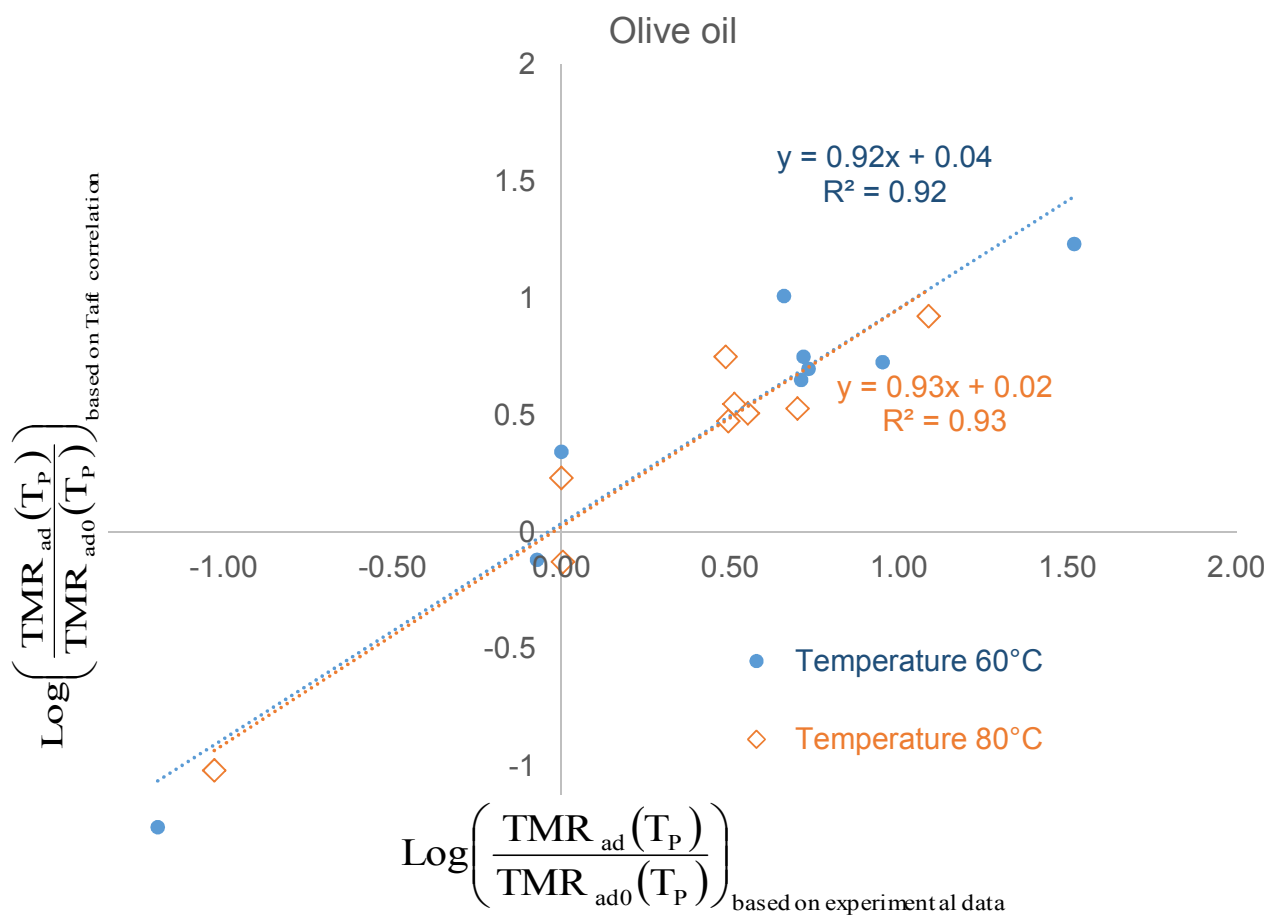
valeric, lactic and 2-ethylbutyric acids.

Figure S9. Parity plot for the epoxidation of oleic acid by using formic, acetic, propionic, n-butyric, i-butyric, lactic, hexanoic and 2-ethylbutyric acids.

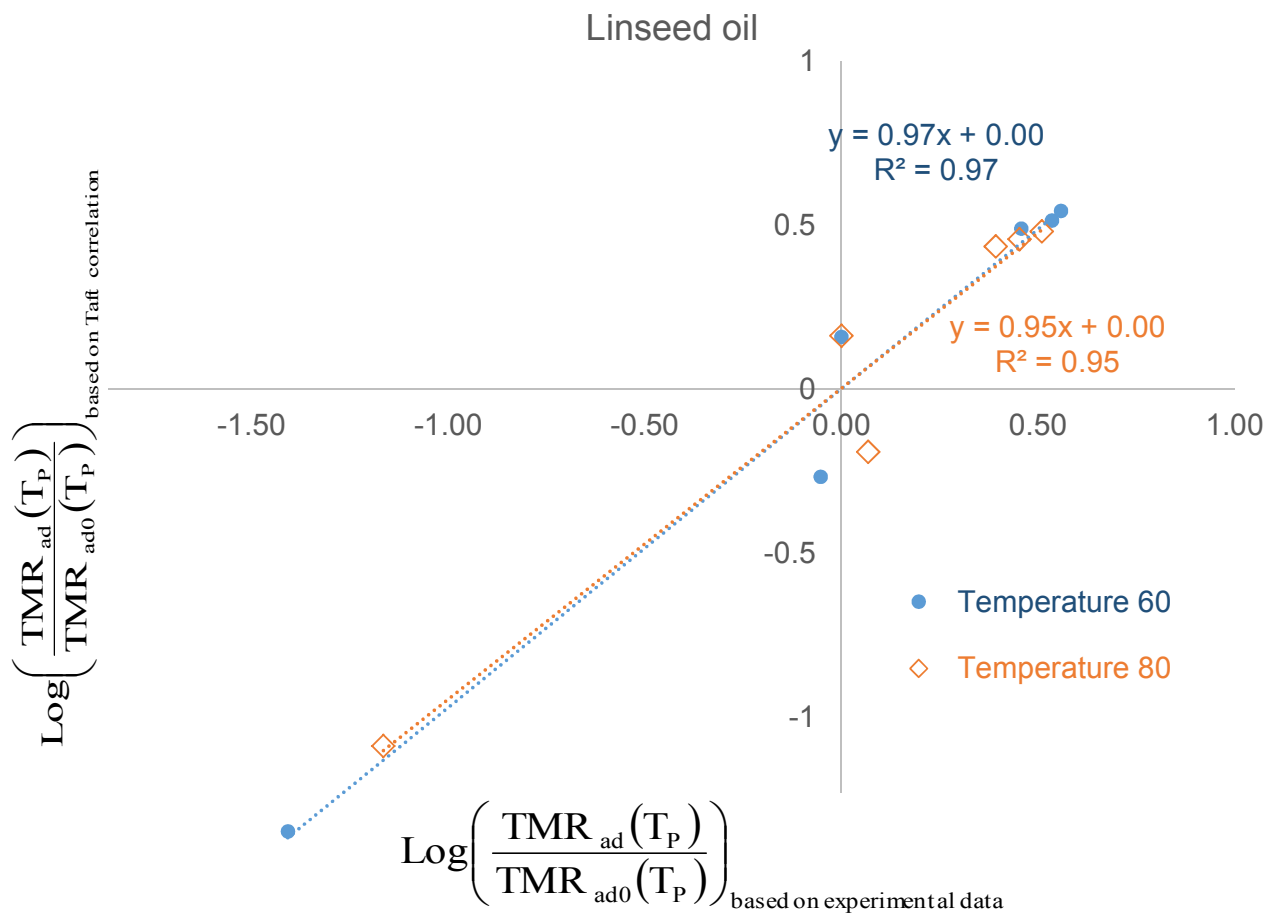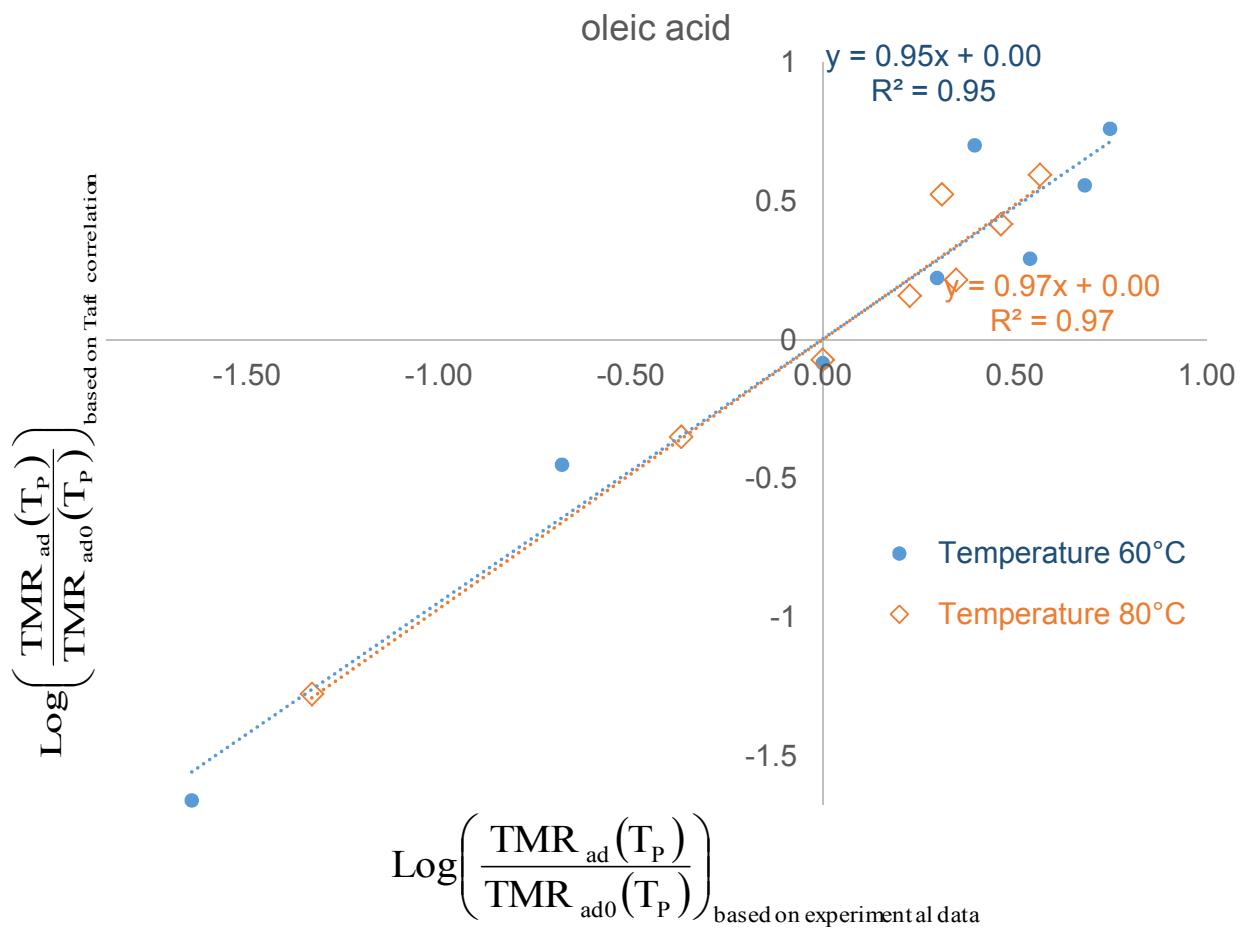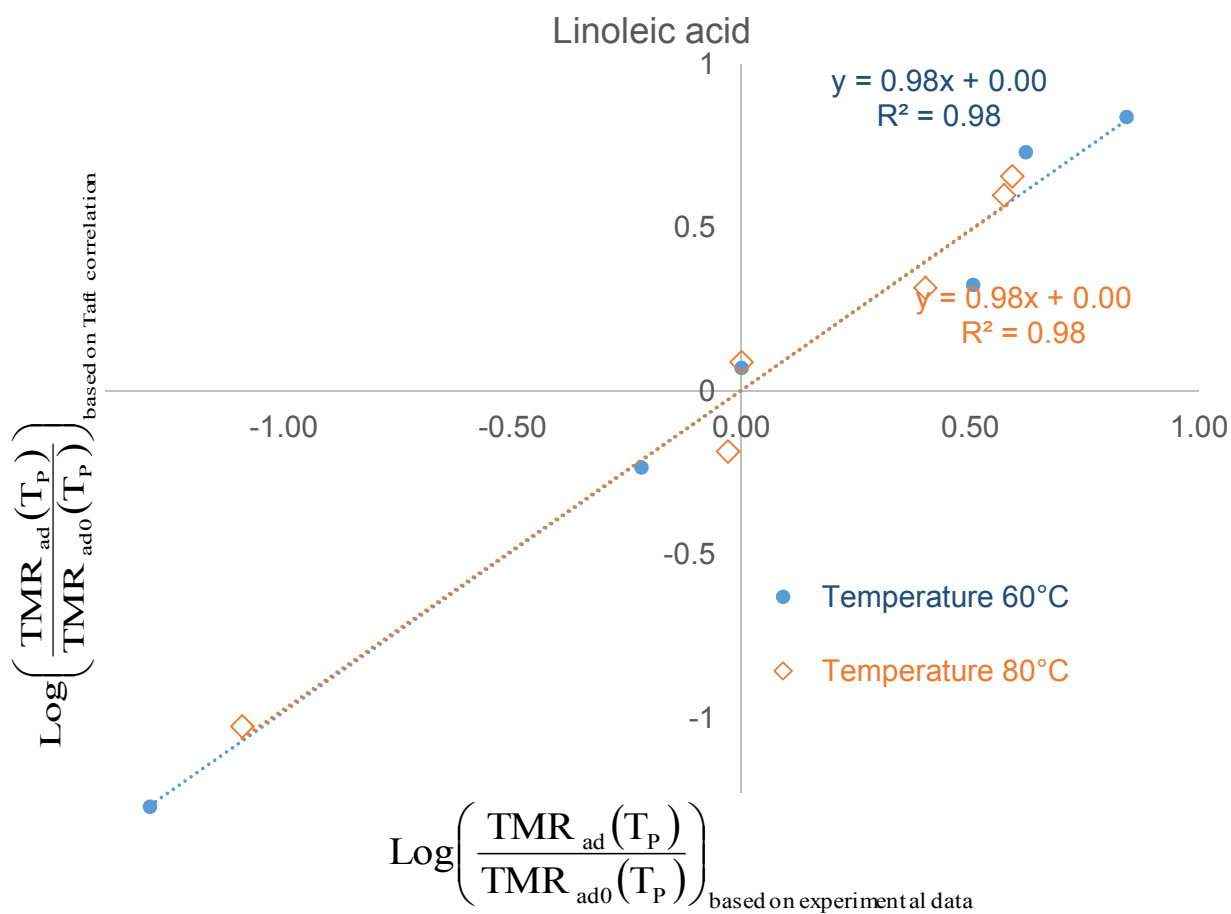Figure S10. Parity plot for the epoxidation of linoleic acid by using formic, acetic, propionic, lactic, hexanoic and 2-ethylbutyric acids.

-SI6 Experimental matrix for the different experiments

	Nature of carboxylic acid	Amount of carboxylic acid (mol)	Amount of hydrogen peroxide (mol)	Amount of water (mol)	Mass of oil (gram)	Temperature ramp (°C/min)
COTTONSEED OIL	Formic acid	0.02	0.03	0.21	3.16	3.00
	Acetic acid	0.02	0.03	0.21	3.12	2.95
	Propionic acid	0.02	0.03	0.21	3.13	2.65
	n-Butyric acid	0.02	0.03	0.21	3.16	2.90
	Valeric acid	0.02	0.03	0.21	3.18	2.37
	iso-Butyric acid	0.02	0.03	0.21	3.18	2.37
	Lactic acid	0.02	0.03	0.22	3.14	2.88
	Hexanoic acid	0.02	0.03	0.21	3.20	2.38
	2-ethyl butyric acid	0.02	0.03	0.21	3.19	2.43
COTTONSEED OIL	Formic acid	0.03	0.03	0.22	3.16	2.98
	Acetic acid	0.03	0.03	0.20	3.24	2.77
	Propionic acid	0.03	0.03	0.22	3.20	2.39
	n-Butyric acid	0.03	0.03	0.21	3.20	2.30
	Valeric acid	0.02	0.03	0.22	3.19	2.29
	iso-Butyric acid	0.03	0.03	0.21	3.18	2.26
	Lactic acid	0.03	0.03	0.23	3.19	2.12
	Hexanoic acid	0.03	0.03	0.21	3.19	2.39
	2-ethyl butyric acid	0.02	0.03	0.21	3.18	2.32

	Formic acid	0.03	0.03	0.21	3.34	3.22
	Acetic acid	0.03	0.03	0.21	3.32	2.68
	Propionic acid	0.03	0.03	0.21	3.33	2.27
	n-Butyric acid	X	X	X	X	X
LINSEED OIL	Valeric acid	0.02	0.03	0.21	3.28	3.38
	iso-Butyric acid	X	X	X	X	X
	Lactic acid	0.03	0.03	0.21	3.28	2.76
	Hexanoic acid	X	X	X	X	X
	2-ethyl butyric acid	0.03	0.03	0.22	3.30	2.93
	Formic acid	0.03	0.03	0.22	3.29	2.66
	Acetic acid	0.03	0.03	0.20	3.27	2.19
	Propionic acid	0.03	0.03	0.21	3.31	1.52
	n-Butyric acid	0.03	0.03	0.22	3.31	2.08
OLEIC ACID	Valeric acid	X	X	X	X	X
	iso-Butyric acid	0.03	0.03	0.21	3.30	1.43
	Lactic acid	0.03	0.03	0.22	3.31	2.16
	Hexanoic acid	0.03	0.03	0.22	3.29	2.36
	2-ethyl butyric acid	0.03	0.03	0.21	3.30	2.64

	Formic acid	0.03	0.03	0.21	3.29	2.66
	Acetic acid	0.03	0.03	0.20	3.28	2.48
	Propionic acid	0.03	0.03	0.21	3.31	2.09
	n-Butyric acid	X	X	X	X	X
LINOLEIC ACID	Valeric acid	X	X	X	X	X
	iso-Butyric acid	X	X	X	X	X
	Lactic acid	0.03	0.03	0.22	3.26	2.10
	Hexanoic acid	0.03	0.03	0.22	3.33	2.16
	2-ethyl butyric acid	0.03	0.03	0.21	3.28	2.40