

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Thermal risk assessment for the epoxidation of linseed oil by classical Prisleschajew epoxidation and by direct epoxidation by H₂O₂ on alumina

Perez Sena, Wander; Salmi, Tapio; Estel, Lionel; Leveneur, Sebastien

Published in:
Journal of Thermal Analysis and Calorimetry

DOI:
[10.1007/s10973-019-08894-2](https://doi.org/10.1007/s10973-019-08894-2)

Published: 01/01/2019

Document Version
Accepted author manuscript

Document License
CC BY-ND

[Link to publication](#)

Please cite the original version:
Perez Sena, W., Salmi, T., Estel, L., & Leveneur, S. (2019). Thermal risk assessment for the epoxidation of linseed oil by classical Prisleschajew epoxidation and by direct epoxidation by H₂O₂ on alumina. *Journal of Thermal Analysis and Calorimetry*, -. <https://doi.org/10.1007/s10973-019-08894-2>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Thermal risk assessment for the epoxidation of linseed oil by classical Prileschajew epoxidation and by direct epoxidation by H₂O₂ on alumina

*Wander Y. Pérez-Sena^{1,2}, Tapio Salmi², Lionel Estel¹, Sébastien Leveneur^{*1,2}*

¹Normandie Univ, INSA Rouen, UNIROUEN, LSPC, EA4704, 76000 Rouen, France, E-mail :
sebastien.leveneur@insa-rouen.fr

²Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland.

ABSTRACT

Substitution of fossil feedstock by vegetable oils is growing due to environmental constraints and oil depletion. Among the different valorization routes for vegetable oils, epoxidation of their unsaturation is widely used. The epoxidation is an exothermic reaction which could lead to a thermal runaway. There are different routes for the vegetable oil epoxidation: Prileschajew by performic and peracetic acid, which are the most used. Another promising alternative is the direct epoxidation by hydrogen peroxide by alumina. The goal of this manuscript is to rank the thermal risk of these three epoxidation routes by determining the safety parameter time-to-maximum rate under adiabatic condition (TMR_{ad}). The Advanced Reactive System Screening Tool (ARSST) was used to conduct these experiments. It was found that the direct epoxidation is safer than the two other routes.

KEYWORDS: liquid-liquid reactions, adiabatic calorimeter, thermal risk assessment, epoxidation, heterogeneous catalyst.

1. INTRODUCTION

The use of vegetable oils as industrial feedstock could be a promising substitute to petroleum-derived compounds. For instance, production of biodiesel from transesterification of vegetable oils is a well-developed process at the industrial level [1-5]. Vegetable oils are used in industry because they are renewable, biodegradable, non-toxic and abundant.

Epoxidized vegetable oils can be seen as platform molecules because they can be transformed into various chemicals [6]: polyols, carbonated vegetable oils [7-8], polyurethanes [9-10] or thermoset polymers [6].

Conventionally, the production of epoxidized vegetable oils is carried out by the Prileschajew method [11-16]. It is a liquid-liquid reaction system, where there are several consecutive and parallel exothermic reactions [17-19]. The first step is the formation of percarboxylic acid in the aqueous phase from the reaction between hydrogen peroxide and the corresponding carboxylic acid. Then, the percarboxylic acid diffuses in the organic phase to epoxidize the unsaturated groups of the vegetable oils. Due to the presence of several exothermic reactions, the risk of thermal runaway exists [20-26]. As mentioned in the study of Dakkoune et al. [27], thermal runaway has been one of the main reasons for accident in the French chemical industries from 1974 to 2014.

The critical issues of the Prileschajew method are:

- production of organic waste during the process;
- production of percarboxylic acid, usually performic or peracetic acid, which are thermally unstable;
- acidity of the reaction mixture, due to the presence of carboxylic acids, favoring the ring-opening as a side reaction [19];
- separation step and waste treatment are more demanding due to the presence of carboxylic and percarboxylic acids;
- formic and acetic acids are the most used oxygen carrier and can cause corrosion.

Hence, direct epoxidation of vegetable oils by oxygen and hydrogen peroxide is seen as the best option concerning thermal safety, waste treatment and selectivity. Scotti et al. [28] have shown that epoxidation of oleic acid by a cumene-O₂ system on CuO/Al₂O₃ presents good results of conversion and selectivity. Nevertheless, there is still the problem of organic waste, i.e., cumene.

Epoxidation of vegetable oil by hydrogen peroxide has been studied by some research groups.

Sepulveda et al. [29] tested different alumina catalysts for the epoxidation of methyl oleate and soybean oil methyl ester by hydrogen peroxide in different organic solvents. They reached a conversion of ca. 100%.

Di Serio et al. [30] tested $\text{Nb}_2\text{O}_5\text{-SiO}_2$ catalyst for the epoxidation of soybean oil in organic solvents, but the selectivity was quite low.

Turco et al. [31] studied the epoxidation of soybean oil and methyl oleate with hydrogen peroxide on γ -alumina in the presence of different organic solvents. They have demonstrated that the solvent plays an important role for this system. They have reported that acetonitrile was the best solvent for the epoxidation of methyl oleate.

Parada Hernandez et al. [32] have studied the system $\text{H}_2\text{O}_2/\text{alumina}/\text{ethyl acetate}$ for the epoxidation of methyl ricinoleate. They demonstrated that this system is efficient for the epoxidation of this oil.

As previously mentioned, the direct epoxidation of vegetable oils by hydrogen peroxide might be thermally safer than by the Prileschajew method. To the best of our knowledge, we did not find any study proposing such comparison. In the Prileschajew method, hydrogen peroxide might be more stable because of the acidity of the reaction mixture [33]. Whereas, during the direct epoxidation by hydrogen peroxide, the acidity of the reaction mixture is lower, thus hydrogen peroxide is less thermally stable.

The objective of this article is to compare the thermal risk for the epoxidation of linseed oil by three chemical systems: Prileschajew oxidation by using peracetic acid, Prileschajew method by using performic acid and by the direct epoxidation of hydrogen peroxide on alumina. Linseed oil is a promising vegetable oil for polymer industry due to the presence in majority of linolenic acid. This fatty acid has three unsaturation allowing several possibility of linkages. For the latter system, we did not use any solvents to avoid any side reactions, such as the interaction between hydrogen peroxide and solvent. Such a comparison is not easy because the chemical systems are different. **Fig. 1** Shows a typical reaction scheme for the Prileschajew epoxidation.

HERE Fig. 1 Prileschajew epoxidation scheme

For the evaluation of the thermal risk on the epoxidation of linseed oil, the TMR_{ad} (Time to Maximum Rate under adiabatic conditions) was chosen as a reliable safety parameter to identify the probability of hazardous scenarii [34].

The measurement of the severity is characterized by the parameter ΔT_{ad} , which is the temperature difference between the final and initial temperature under adiabatic operation. The measurement of the adiabatic temperature rise is challenging, because in the presence of several reactions its value change with the initial temperature, which is not the case for a single reaction [35]. From a technical point of view, the measurement of the final temperature is cumbersome. Indeed, even

under high pressure of an inert gas, if the energy released by the reactions is high, then the boiling point will be reached. At the boiling point, the reaction temperature cannot increase anymore.

The adiabatic calorimeter ARSST standing for Advanced Reactive System Screening Tool was used [20-21; 36-40] to determine TMR_{ad} . This calorimeter allows to conduct experiments under high pressure of inert gas, and thus limits evaporation phenomenon. The other benefits of ARSST is the use of glass cells decreasing the thermal inertia factor, which is close to one. Its use is mainly addressed to the study of thermal risk assessment for runaway scenarii including the explosion risk with the aid of monitoring the pressure rise. It can also be used for modelling reactive system, estimating thermodynamic and kinetic constants and pressure relief vent sizing design [21, 36, 41].

We have decided to use the most conservative assumption implying to determine the $TMR_{ad}(T_p)$ at the initial temperature T_p by using the zero-order approximation.

2. EXPERIMENTAL SECTION

2.1 Chemicals

The following chemicals were used: raw linseed oil (iodine value = 183.7) from MP Biomedicals, aluminum oxide (50-200 μ m, 60 A) supplied by Across Organic, sulfuric acid (95-98 wt%) purchased from AppliChem, formic acid (99-100 wt%), hydrogen peroxide (purity > 33 wt%) and acetic acid (99-100 w%) were purchased from VWR Chemicals.

2.2 Experiments performed in ARSST

The ARSST calorimeter is a pseudo-adiabatic reactor, which can reach near-adiabatic conditions following the heat loss compensation principle by using an electrical heating supply [20-21; 36-40]. The ARSST consists of a 10 mL glass test cell equipped with a heating belt and a magnetic stirrer. The heating belt allows to adjust the electrical heating. The test cell is kept well insulated by fiberglass and under pressure with an inert gas such as nitrogen to limit reaction mixture evaporation. A containment vessel equipped with thermocouples and a pressure transducer houses the test cell and the rest of the components [21-22]. A more detailed description of the calorimeter can be found in our previous work [21-22]. The term T_1 is the reaction temperature.

2.2.1 Epoxidation of linseed oil (LSO).

2.2.1.1 By performic acid

The epoxidation was performed with 2.21 g of LSO. The LSO, hydrogen peroxide, formic and sulfuric acids were mixed together in the test cell. A constant heating rate (β) was applied along with a starting pressure of 34.47 bar. Initial temperatures of the experiment ranged between 20-35 °C. The influence of the carboxylic acid, hydrogen peroxide and sulfuric over the TMR_{ad} was evaluated. The influence of pressure on the maximum adiabatic temperature rise and TMR_{ad} was also investigated. **Table 1** shows the experimental matrix.

HERE **Table 1** Experimental matrix for epoxidation of LSO with performic acid

2.2.1.2 By peracetic acid

For these experiments, 2.21 g of linseed oil was poured into the test cell along with acetic acid, hydrogen peroxide, water and sulfuric acid as catalyst. The electrical heating rate (β) varied in the range of 1-5 °C/min. A nitrogen pressure of 34.47 bar was applied to the system in order to diminish evaporation of the mixture. The influence of acetic acid, hydrogen peroxide and sulfuric acid on TMR_{ad} was evaluated. The details of the experiment can be found in **Table 2**.

HERE **Table 2** Experimental matrix for epoxidation of LSO with peracetic acid

2.1.3 By hydrogen peroxide catalyzed by γ -alumina

The same amount of vegetable oil was poured into the reactor along with, hydrogen peroxide, water and γ -alumina. Similar initial conditions were used from previous experiments. Experiments with only hydrogen peroxide and the catalyst were conducted to evaluate the decomposition of hydrogen peroxide by alumina. The experimental matrix is shown in **Table 3**.

HERE **Table 3** Experimental matrix for epoxidation of LSO and decomposition of hydrogen peroxide through γ alumina

3. RESULTS AND DISCUSSION

3.1 Working principle of ARSST

When the chemicals were placed and sealed in the test cell, electrical heating was applied, temperature and pressure were recorded. During the experiments, the reaction temperature reaches to a point in which the temperature increases more rapidly due to the heat generated by the reactions than the temperature rise due to electrical heating [21-22]. This point is the so-called *onset* temperature [21]. **Fig. 2** illustrates a typical temperature profile obtained from an ARSST experiment.

HERE Fig. 2 Typical temperature profile from ARSST

Once the onset temperature is determined, one can estimate TMR_{ad} at any initial temperature T_p .

3.1.1 Zero-order model

Time to maximum rate under adiabatic conditions (TMR_{ad}) at an initial process temperature T_p is defined as the elapsed time between the initial temperature and the maximum of the derivate (dT_p/dt) under adiabatic conditions. The estimation of this value for the epoxidation reaction by taking into account all the steps is cumbersome and time consuming, because it requires the knowledge of kinetic and thermodynamic constants of the main and secondary reactions, i.e., reactions producing gaseous products. Therefore, a zero-order approximation was used, which is an accepted method for the determination of thermal risk parameters [34, 42]. This is a conservative way to approximate the TMR_{ad} which results in shorter times than a model based on intrinsic kinetics [21, 34].

The following expression defines the TMR_{ad} for a zero-order reaction:

$$TMR_{ad}(T_p) = \frac{m_R \cdot \hat{C}_{PR} \cdot R \cdot T_p^2}{q_R(T_p) \cdot E_a} \quad (1)$$

where, T_P is the process temperature, i.e., initial temperature, m_R is the reaction mass, \hat{C}_{PR} the specific heat capacity of the reactional mixture, R is the gas constant, E_a is the activation energy and $q_R(T_P)$ is the heat-flow rate due to chemical reactions at the process temperature.

By taking logarithms, Eq. (1) can be rearranged as follows:

$$\begin{aligned}
 \ln(\text{TMR}_{\text{ad}}) &= \ln\left(\frac{m_R \cdot \hat{C}_{PR} \cdot R \cdot T_P^2}{E_a}\right) - \ln(q_R(T_P)) \\
 &= \ln\left(\frac{m_R \cdot \hat{C}_{PR} \cdot R \cdot T_P^2}{E_a}\right) - \ln\left(A_0 \cdot \exp\left(\frac{-E_a}{R \cdot T_P}\right) \cdot \Delta H_R \cdot V\right) \\
 &= \ln\left(\frac{m_R \cdot \hat{C}_{PR} \cdot R \cdot T_P^2}{E_a}\right) - \ln(A_0 \cdot \Delta H_R \cdot V) - \frac{E_a}{R \cdot T_P} \\
 &= \ln\left(\frac{m_R \cdot \hat{C}_{PR} \cdot R \cdot T_P^2}{E_a \cdot A_0 \cdot \Delta H_R \cdot V}\right) - \frac{E_a}{R \cdot T_P} \\
 &= \text{constant} - \frac{E_a}{R} * \frac{1}{T_P} \tag{2}
 \end{aligned}$$

By plotting $\ln(\text{TMR}_{\text{ad}})$ versus $\frac{1}{T_P}$, it is possible to estimate the numerical values of the constant and the slope $\frac{E_a}{R}$ and then extrapolate the value of TMR_{ad} at any process temperature [21].

3.2 Prisleschajew epoxidation

3.2.1 Effect of nitrogen pressure

HERE Fig. 3A Reaction temperature profiles at different initial nitrogen pressures. 3B Influence of nitrogen pressure on $\text{TMR}_{\text{ad}}(T_P)$. (Table 1: Run 12, 13 and 14)

Figs. 3 shows how the pressure limits the maximum temperature which can be achieved in the system. For this reaction system, the aqueous phase evaporates first. As the aqueous phase mainly consists of water, thus the boiling point of water should be close to the bubble of the reaction mixture, which is the maximum temperature. **Table 4** confirms this tendency.

HERE Table 4 Saturation temperature of water and bubble point of the reaction mixture at different pressures

From **Fig. 3** one can notice that evaporation plays as a safety barrier, the maximum temperature that can be reached by the system is the corresponding saturation temperature of water. After the saturation point has been reached, the temperature of the mixture decreases due to the energy consumption of the evaporation process. As the pressure decreases, the value of TMR_{ad} increases. It can be noticed that the influence of pressure on this safety parameter is less pronounced when the initial process temperature is over than 40°C.

In process safety, one should consider the worst case scenario implying the total conservation of the liquid phase. For this reason, the experiments were performed with a nitrogen pressure of 34.40 bar.

3.2.2 Influence of the concentration of carboxylic acid on TMR_{ad}

The concentration ratio of the carboxylic acid to the double bond of linseed oil varied from 1:0.5 to 1:3. The concentration of hydrogen peroxide was kept constant during the experiments. The same electrical heating ramp was applied to each runs. From Eq. (2), it is possible to extrapolate the values of TMR_{ad} at different temperatures. **Fig. 4** shows the evolution of TMR_{ad} at different process temperature for the epoxidation with formic acid. As the concentration of carboxylic acid increases, the value of TMR_{ad} decreases. Indeed, an excess of carboxylic acid leads to a faster production of percarboxylic acid [17] due to the protolysis of carboxylic acid, and thus a faster production rate of the oxirane group and faster energy release. From **Fig. 4**, one can notice that for a same process temperature, TMR_{ad} is shorter for epoxidation performed by formic acid than by acetic acid. There are two reasons to explain the higher reactivity of formic acid compared to acetic acid during the epoxidation process: formic acid is a stronger acid leading to a faster production of performic acid and performic acid is less thermally stable than peracetic acid. Nevertheless, as the process temperature increases, the influence of carboxylic acid on TMR_{ad} is less pronounced.

HERE Fig. 4 Influence of carboxylic acid concentration on TMR_{ad} at different process temperatures.

(Fig.4A Table 1: Run 1, 2, 3 and 4. Fig 4B Table 2: Run 1, 2, 3 and 4)

3.2.3 Influence of H₂O₂ concentration on TMR_{ad}.

Fig. 5A displays the evolution of TMR_{ad} for the epoxidation using formic acid at different concentration ratio of hydrogen peroxide on double bond ranging from 1:2 to 1:3. Higher concentration of hydrogen peroxide leads to lower TMR_{ad} values. Otherwise, it can be noticed that the effect of this parameter is not as important as carboxylic acid concentration. The same effect was concluded from the epoxidation with acetic acid (**Fig. 5B**).

HERE **Fig. 5** Influence of hydrogen peroxide concentration on TMR_{ad}.
(Fig. 5A Table 1: Run 6 and 7. Fig. 5B Table 2: Run 4 and 5)

3.2.4 Influence of H₂SO₄ as a catalyst

For the Prileschajew epoxidation, mineral acids like sulfuric acid are added to enhance the kinetics of the perhydrolysis reaction.

HERE **Fig. 6** Influence of sulfuric acid load on TMR_{ad}
(Fig. 6A Table 1: Run 8, 9, 10 and 11. Fig. 6B Table 2: Run 6, 7, 8 and 9)

In this section, we have studied the effect of sulfuric acid as a catalyst on the epoxidation process over TMR_{ad} for the epoxidation by using formic acid and by acetic acid. Catalyst loading was ranged between 1-3 wt%. From **Fig. 6A** it can be seen that the load of catalyst does not seem to have a strong effect on TMR_{ad} value for the epoxidation by performic acid. This is due to the fact that formic acid is a strong acid.

For the epoxidation of linseed oil by peracetic acid, the concentration of sulfuric acid has a stronger influence. This is due to the fact that acetic acid is a weaker acid, thus, as the sulfuric acid concentration increases, the TMR_{ad} is shorter.

3.3 Epoxidation by H₂O₂ catalyzed by Al₂O₃

3.3.1 Effect of catalyst loading

HERE Fig. 7 Influence of alumina loading on TMR_{ad} (Table 3: Run 1, 2, 3 and 4)

The influence of the loading of alumina on the TMR_{ad} value was studied as shown in **Fig. 7**. Higher catalyst loading shortens the TMR_{ad} as expected. The increase of catalyst amount accelerates the reaction rate, and thus the rate of energy release. Besides, the fact that the secondary reactions of hydrogen peroxide decomposition is also promoted by alumina [31, 43-44].

3.3.2 Effect of H₂O₂ concentration

HERE Fig. 8 Influence of hydrogen peroxide on TMR_{ad} with a catalyst loading of 10 wt% (Table 3: Run 5, 6 and 7)

The concentration ratio hydrogen peroxide to double bond varied from 1:1 to 1:3. A significant effect was observed when the hydrogen peroxide concentration is doubled (**Fig. 8**). Further increase of hydrogen peroxide concentration shortens the TMR_{ad} value, because of the kinetics of epoxidation and hydrogen peroxide decomposition increase [43].

3.3.3 H₂O₂ decomposition by Al₂O₃

HERE Fig. 9 Influence of the hydrogen peroxide decomposition in the presence of alumina over TMR_{ad} (Table 3: Run 8, 9, 10, 11 and 12)

The decomposition of hydrogen peroxide is a secondary reaction, which have been reported to be catalyzed by alumina in the past [31, 43-44]. For that reason, it is important to investigate the influence of this reaction on TMR_{ad} for the epoxidation process. With this aim some experiments have been performed by using only hydrogen peroxide and alumina. As it can be noticed in **Fig. 9** the loading of alumina seems to have a progressive effect on the time to maximum rate

under adiabatic mode. However, any further increase in the catalyst load over 20 wt% does not seem to affect significantly the TMR_{ad} value. These experiments confirm the presence of hydrogen peroxide decomposition by alumina.

3.4 Thermal risk comparison

In order to rank the three different epoxidation methods, TMR_{ad} was used (**Table 5**). Stoessel has defined some criteria for TMR_{ad} values [34].

HERE **Table 5** Assessment criteria for TMR_{ad}

Relying on this criterion, the probability of occurrence of a runaway reaction was evaluated for the three different epoxidation processes treated in this work.

HERE **Table 6** Probability of thermal runaway for Prileschajew epoxidation in the presence of formic acid.

The carboxylic acid concentration was found to have a strong influence on the probability of occurrence of a runaway scenario for the epoxidation by performic acid within the process temperature 40-80°C [9]. For most of the molar ratio tested, the probability of occurrence is high ranging between probable and frequent (**Table 6**). The results seem to be logical, because formic acid catalyzes the perhydrolysis reaction and performic acid is unstable. The kinetics of the system is very fast in comparison with other carboxylic acid epoxidation systems. In the case of hydrogen peroxide and sulfuric acid influence, the same tendency was found. Higher concentration of these two components will lead to shorter TMR_{ad} values. In general, the probability of runaway reaction on the epoxidation by formic acid was found to be very high.

HERE **Table 7** Probability of thermal runaway for Prileschajew epoxidation with acetic acid

The probability of occurrence of a runaway scenario for the epoxidation by peracetic acid is shown in **Table 7**. As it can be noticed the concentration of acetic acid has an important effect on TMR_{ad} . At low temperature and concentration of acetic acid the system is in the medium/low probability range. Higher temperature and concentration of acid lead to a

frequent occurrence of runaway. The hydrogen peroxide and sulfuric acid loading are less influent on the time to maximum rate. At a temperature of 20 °C, the probability of occurrence was mainly medium. Otherwise, epoxidation at this temperature is not very efficient in terms of conversion because of low reaction rates. Higher process temperatures end up on high probabilities of occurrence.

HERE **Table 8** Probability of thermal runaway for Prisleschajew epoxidation with acetic acid

Epoxidation over alumina seems to be the method with less probability of occurrence of a thermal runaway accident as it can be notice in **Table 8**. At temperatures lower than 50° C, the probability of occurrence is mostly in the low area of occurrence. Higher process temperatures lead to medium probabilities of occurrence except in the case of a high concentration of hydrogen peroxide as shown in **Table 8B**.

If one compares the three studied epoxidation methods in terms of probability of occurrence of a thermal runaway, the epoxidation by using alumina is the one with the lower values of TMR_{ad} .

4. CONCLUSIONS

Thermal risk of three different routes of epoxidation of linseed oil was studied. The two common routes of epoxidation: Prileschajew oxidation by performic and peracetic acids were tested. The promising route of direct epoxidation by hydrogen peroxide on alumina was also tested.

For that experiments in adiabatic calorimeter, namely Advanced Reactive System Screening Tool (ARSST), were carried out. Based on these experimental results, the safety parameter time-to-maximum rate under adiabatic conditions (TMR_{ad}) was determined by using the zero-order approximation. The influence of different parameters such as catalyst loading, ratio carboxylic acid on double bond, ratio hydrogen peroxide on double bond and temperature on TMR_{ad} was evaluated. A risk matrix based on the TMR_{ad} criteria defined by Stoessel was established. It was found that direct epoxidation by hydrogen peroxide on alumina present a lower thermal risk compared to the two other routes.

ACKNOWLEDGEMENTS

This study has been done in the framework of Task 2: “Green process: 2nd generation of biomass” of AMED project. The authors thank AMED project. The AMED project has been funded with the support from the European Union with the European Regional Development Fund (ERDF) and from the Regional Council of Normandie. The authors thank the Ministry of High Education, Science and Technology of Dominican Republic (MESCyT).

List of symbols

| | |
|-----------------|---|
| \hat{C}_{PR} | Specific heat-capacity [J.kg ⁻¹ .K ⁻¹] |
| E_a | Activation energy [J.mol ⁻¹] |
| ΔH | Reaction enthalpy [J.mol ⁻¹] |
| m_R | Mass of reaction mixture [kg] |
| q_{el} | Electrical heating-rate [°C.min ⁻¹] |
| q_r | Heat-flow rate due to chemical reactions [J.s ⁻¹] |
| R | Gas constant [J.K ⁻¹ .mol ⁻¹] |
| ΔT_{ad} | Adiabatic temperature rise [°C] |
| T_1 | Temperature of the reaction mixture [°C] |
| T_{Ref} | Reference temperature [°C] |
| T_i | Experimental temperature |
| T_p | Process temperature |
| V | Volume [L] |

Greek letters

| | |
|---------|---|
| β | Background heating rate [°C.min ⁻¹] |
|---------|---|

Abbreviations

| | |
|-------|---|
| AA | Acetic acid |
| ARSST | Advanced Reactive System Screening Tool |
| CA | Carboxylic Acid |
| DB | Double bond |
| FA | Formic acid |
| HP | Hydrogen peroxide |

TMR_{ad}(T_P) Time-to-maximum rate under adiabatic conditions at T_P [min]

W Water

Subscript

aq Aqueous

Ep Epoxidation

ins Insert

R, Reaction

org Organic

perh Perhydrolysis

T Total

0 Initial

References

1. Fukuda H, Kondo A, Noda H. Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*. 2001;92:405–16.
2. Körbitz W. Biodiesel production in Europe and North America, an encouraging prospect. *Renewable Energy*. 1999;16:1078–83.
3. Leung DY, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Applied Energy*. 2010;87:1083–95.
4. Santacesaria E, Vicente GM, Di Serio M, Tesser R. Main technologies in biodiesel production: State of the art and future challenges. *Catalysis Today*. 2012;195:2–13.
5. Di Serio M, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. *Energy Fuels*. 2008;22:207–17.
6. Danov SM, Kazantsev OA, Esipovich AL, Belousov AS, Rogozhin AE, Kanakov EA. Recent advances in the field of selective epoxidation of vegetable oils and their derivatives: a review and perspective. *Catal Sci Technol*. 2017;7:3659–75.
7. Cai X, Zheng JL, Wärnå J, Salmi T, Taouk B, Leveneur S. Influence of gas-liquid mass transfer on kinetic modeling: Carbonation of epoxidized vegetable oils. *Chemical Engineering Journal*. 2017;313:1168–83.
8. Zheng JL, Burel F, Salmi T, Taouk B, Leveneur S. Carbonation of vegetable oils: influence of mass transfer on reaction kinetics. *Ind Eng Chem Res*. 2015;54:10935–44.
9. Pérez-Sena WY, Cai X, Kebir N, Vernières-Hassimi L, Serra C, Salmi T, et al. Aminolysis of cyclic-carbonate vegetable oils as a non-isocyanate route for the synthesis of polyurethane: A kinetic and thermal study. *Chemical Engineering Journal*. 2018;346:271–80.
10. Sawpan MA. Polyurethanes from vegetable oils and applications: a review. *J Polym Res*. 2018;25:184.
11. Köckritz A, Martin A. Oxidation of unsaturated fatty acid derivatives and vegetable oils. *European Journal of Lipid*

Science and Technology. 2008;110:812–24.

12. Abraham ME, Benenati RF. Kinetics and mechanism of the epoxidation of unsaturated fatty acids. *AIChE Journal*. 1972;18:807–11.

13. Prileschajew N. Oxydation ungesättigter Verbindungen mittels organischer Superoxyde. *Berichte der deutschen chemischen Gesellschaft*. 1909;42:4811–5.

14. Rangarajan B, Havey A, Grulke EA, Culnan PD. Kinetic parameters of a two-phase model for in situ epoxidation of soybean oil. *J Am Oil Chem Soc*. 1995;72:1161–9.

15. Wisniak J, Navarrete E. Epoxidation of fish oil, kinetic and optimization model. *Product R&D*. 1970;9:33–41.

16. Wisniak J, Cancino A, Vega JC. Epoxidation of anchovy oils. a study of variables. *I&EC Product Research and Development*. 1964;3:306–11.

17. Zheng JL, Wärnå J, Salmi T, Burel F, Taouk B, Leveneur S. Kinetic modeling strategy for an exothermic multiphase reactor system: Application to vegetable oils epoxidation using Prileschajew method. *AIChE Journal*. 2016;62:726–41.

18. Santacesaria E, Tesser R, Di Serio M, Turco R, Russo V, Verde D. A biphasic model describing soybean oil epoxidation with H₂O₂ in a fed-batch reactor. *Chemical Engineering Journal*. 2011;173:198–209.

19. Cai X, Zheng JL, Aguilera AF, Vernières-Hassimi L, Tolvanen P, Salmi T, et al. Influence of ring-opening reactions on the kinetics of cottonseed oil epoxidation. *International Journal of Chemical Kinetics*. 2018;50:726–41.

20. Leveneur S. Thermal safety assessment through the concept of structure–reactivity: application to vegetable oil valorization. *Org Process Res Dev*. 2017;21:543–50.

21. Leveneur S, Pinchard M, Rimbault A, Safdari Shadloo M, Meyer T. Parameters affecting thermal risk through a kinetic model under adiabatic condition: Application to liquid-liquid reaction system. *Thermochimica Acta*. 2018;666:10–7.

22. Leveneur S, Estel L, Crua C. Thermal risk assessment of vegetable oil epoxidation. *J Therm Anal Calorim*.

2015;122:795–804.

23. de Quadros Jr. JV, Giudici R. Epoxidation of soybean oil at maximum heat removal and single addition of all reactants. *Chemical Engineering and Processing: Process Intensification*. 2016;100:87–93.

24. Vianello C, Piccolo D, Lorenzetti A, Salzano E, Maschio G. Study of Soybean Oil Epoxidation: Effects of Sulfuric Acid and the Mixing Program. *Ind Eng Chem Res*. 2018;57:11517–25.

25. Vianello C, Salzano E, Maschio G. Thermal behaviour of Peracetic Acid for the epoxydation of vegetable oils in the presence of catalyst. *Process Safety and Environmental Protection*. 2018;116:718–26.

26. Casson Moreno V, Russo V, Tesser R, Di Serio M, Salzano E. Thermal risk in semi-batch reactors: The epoxidation of soybean oil. *Process Safety and Environmental Protection*. 2017;109:529–37.

27. Dakkoune A, Vernières-Hassimi L, Leveneur S, Lefebvre D, Estel L. Risk analysis of French chemical industry. *Safety Science*. 2018;105:77–85.

28. Scotti N, Ravasio N, Psaro R, Evangelisti C, Dworakowska S, Bogdal D, et al. Copper mediated epoxidation of high oleic natural oils with a cumene–O₂ system. *Catalysis Communications*. 2015;64:80–5.

29. Sepulveda J, Teixeira S, Schuchardt U. Alumina-catalyzed epoxidation of unsaturated fatty esters with hydrogen peroxide. *Applied Catalysis A: General*. 2007;318:213–7.

30. Di Serio M, Turco R, Pernice P, Aronne A, Sannino F, Santacesaria E. Valuation of Nb₂O₅–SiO₂ catalysts in soybean oil epoxidation. *Catalysis Today*. 2012;192:112–6.

31. Turco R, Pischetola C, Tesser R, Andini S, Serio MD. New findings on soybean and methylester epoxidation with alumina as the catalyst. *RSC Adv*. 2016;6:31647–52.

32. Parada Hernandez NL, Bonon AJ, Bahú JO, Barbosa MIR, Wolf Maciel MR, Filho RM. Epoxy monomers obtained from castor oil using a toxicity-free catalytic system. *Journal of Molecular Catalysis A: Chemical*. 2017;426:550–6.

33. Koskinen H, Leveneur S, Sundquist A, Musakka N, Salmi T, Renvall I. Functionality of Poly(α -hydroxyacrylic acid)

as H₂O₂ stabilizing agent. *Oxidation Communication*. 2010;2:258-74.

34. Stoessel F. *Thermal safety of chemical processes*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2008.

35. Leveneur S, Vernieres-Hassimi L, Salmi T. Mass & energy balances coupling in chemical reactors for a better understanding of thermal safety. *Education for Chemical Engineers*. 2016;16:17–28.

36. Marco E, Cuartielles S, Peña JA, Santamaria J. Simulation of the decomposition of di-cumyl peroxide in an ARSST unit. *Thermochimica Acta*. 2000;362:49–58.

37. Fauske HK. Managing chemical reactivity—Minimum best practice. *Process Safety Progress*. 2006;25:120–9.

38. Burelbach, J.P. Advanced Reactive System Screening Tool (ARSST) (2000) North American Thermal Analysis Society (NATAS), 28th Annual Conference Orlando, Oct. 4-6

39. Zhu W, Papadaki MI, Han Z, Mashuga CV. Effect of temperature and selected additives on the decomposition “onset” of 2-nitrotoluene using Advanced Reactive System Screening Tool. *Journal of Loss Prevention in the Process Industries*. 2017;49:630–5.

40. Tang W, Sarvestani M, Wei X, Nummy LJ, Patel N, Narayanan B, et al. Formation of 2-Trifluoromethylphenyl Grignard Reagent via Magnesium–Halogen Exchange: Process Safety Evaluation and Concentration Effect. *Org Process Res Dev*. 2009;13:1426–30.

41. Fogler, H. S. *Elements of Chemical Reaction Engineering*. Prentice Hall Inc.; 1999.

42. G KJ, Srikanth S, Ratnaparkhi V, B R, ichhora. Reaction calorimetry as a tool for thermal risk assessment and improvement of safe scalable chemical processes. *Inorganic Chemistry: An Indian Journal*. 2017;12:1–14.

43. Sepulveda J, Teixeira S, Schuchardt U. Alumina-catalyzed epoxidation of unsaturated fatty esters with hydrogen peroxide. *Applied Catalysis A: General*. 2007;318:213–7.

44. Salem IA, Salem MA, Gemeay AH. Kinetics of heterogeneous decomposition of hydrogen peroxide with some transition metal complexes supported on silica-alumina in aqueous medium. *J. Molecular Catalysis*. 1993;84:67–75.

Table 1 Experimental matrix for epoxidation of LSO with performic acid

| RUN | Initial concentration (mol.L ⁻¹) | | | | | V _{org} (L) | V _{aq} (L) | β (°C.min ⁻¹) | Initial T1 (°C) | Initial P (bar) |
|-----|--|------------|--------------------|-------------------|---|----------------------|---------------------|------------------------------------|--------------------|--------------------|
| | [DB] org | [HP] aq | [CA] _{aq} | [W] _{aq} | [H ₂ SO ₄] _{aq} | | | | | |
| 1 | 6.45 | 5.4 | 1.69 | 44.84 | 0.00 | 0.00238 | 0.00456 | 1.26 | 25.5 | 34.94 |
| 2 | 6.45 | 5.35 | 3.39 | 40.12 | 0.00 | 0.00240 | 0.00457 | 1.46 | 21.4 | 34.98 |
| 3 | 6.45 | 5.35 | 4.45 | 37.52 | 0.00 | 0.00239 | 0.00460 | 1.80 | 22.4 | 34.75 |
| 4 | 6.45 | 5.39 | 5.5 | 34.88 | 0.00 | 0.00240 | 0.00458 | 2.27 | 22.8 | 35.02 |
| 5 | 6.45 | 4.01 | 6.07 | 36.56 | 0.00 | 0.00237 | 0.00382 | 1.24 | 27.6 | 34.47 |
| 6 | 6.45 | 5.07 | 6.21 | 35.55 | 0.00 | 0.00238 | 0.00394 | 1.03 | 29.7 | 34.61 |
| 7 | 6.45 | 6.05 | 6.13 | 34.37 | 0.00 | 0.00238 | 0.00409 | 1.12 | 29.0 | 34.39 |
| 8 | 6.45 | 5.26 | 5.23 | 36.92 | 0.00 | 0.00237 | 0.00378 | 2.63 | 27.7 | 34.40 |
| 9 | 6.45 | 5.25 | 5.27 | 36.87 | 0.23 | 0.00237 | 0.00380 | 2.47 | 27.3 | 34.74 |
| 10 | 6.45 | 5.25 | 5.29 | 36.82 | 0.35 | 0.00238 | 0.00378 | 3.76 | 29.5 | 33.85 |
| 11 | 6.45 | 5.29 | 5.21 | 36.92 | 0.51 | 0.00237 | 0.00380 | 3.01 | 29.5 | 34.45 |
| 12 | 6.45 | 5.24 | 5.23 | 36.97 | 0.00 | 0.00238 | 0.00378 | 3.41 | 23.7 | 7.51 |
| 13 | 6.45 | 5.25 | 5.25 | 36.89 | 0.00 | 0.00237 | 0.00380 | 3.05 | 24.9 | 21.37 |
| 14 | 6.45 | 5.27 | 5.21 | 36.96 | 0.00 | 0.00238 | 0.00370 | 2.63 | 27.7 | 34.40 |

Table 2 Experimental matrix for epoxidation of LSO with peracetic acid

| RUN | Initial concentration (mol.L ⁻¹) | | | | | V _{org} (L) | V _{aq} (L) | β (°C.min ⁻¹) | Initial T1 (°C) | Initial P (bar) |
|-----|--|--------------------|--------------------|-------------------|---|----------------------|---------------------|------------------------------------|--------------------|--------------------|
| | [DB] _{org} | [HP] _{aq} | [CA] _{aq} | [W] _{aq} | [H ₂ SO ₄] _{aq} | | | | | |
| 1 | 6.45 | 5.79 | 1.65 | 42.43 | 0.00 | 0.00238 | 0.00460 | 3.76 | 31.2 | 35.23 |
| 2 | 6.45 | 5.80 | 3.26 | 37.24 | 0.00 | 0.00238 | 0.00467 | 4.33 | 35.8 | 34.74 |
| 3 | 6.45 | 5.50 | 4.51 | 33.2 | 0.00 | 0.00237 | 0.00464 | 4.03 | 33.9 | 34.95 |
| 4 | 6.45 | 5.81 | 5.84 | 28.93 | 0.00 | 0.00239 | 0.00463 | 4.71 | 32.1 | 34.47 |
| 5 | 6.45 | 4.55 | 5.79 | 30.96 | 0.00 | 0.00238 | 0.00463 | 1.45 | 33.7 | 35.30 |
| 6 | 6.45 | 4.27 | 4.28 | 36.16 | 0.00 | 0.00238 | 0.00471 | 1.70 | 22.9 | 34.54 |
| 7 | 6.45 | 4.28 | 4.28 | 36.17 | 0.15 | 0.00239 | 0.00467 | 1.68 | 27.5 | 34.88 |
| 8 | 6.45 | 4.28 | 4.28 | 36.14 | 0.29 | 0.00238 | 0.00468 | 2.05 | 28.4 | 35.01 |
| 9 | 6.45 | 4.29 | 4.30 | 36.1 | 0.46 | 0.00241 | 0.00465 | 1.89 | 28.1 | 35.09 |

Table 3 Experimental matrix for epoxidation of LSO and decomposition of hydrogen peroxide through γ alumina

| RUN | Initial concentration (mol.L ⁻¹) | | | | | V _{org} (L) | V _{aq} (L) | β (°C.min ⁻¹) | Initial T1 (°C) | Initial P (bar) |
|-----|--|--------------------|--------------------|-------------------|------------------------------------|----------------------|---------------------|------------------------------------|--------------------|--------------------|
| | [DB] _{org} | [HP] _{aq} | [CA] _{aq} | [W] _{aq} | Al ₂ O ₃ (g) | | | | | |
| 1 | 6.45 | 7.34 | 0 | 45.84 | 0.00 | 0.00261 | 0.00441 | 3.88 | 25.0 | 34.55 |
| 2 | 6.45 | 7.35 | 0 | 45.82 | 0.70 | 0.00259 | 0.00439 | 3.42 | 26.9 | 35.03 |
| 3 | 6.45 | 7.16 | 0 | 46.08 | 1.41 | 0.00259 | 0.00448 | 3.23 | 26.7 | 35.00 |
| 4 | 6.45 | 7.32 | 0 | 45.87 | 2.11 | 0.00261 | 0.00438 | 3.75 | 22.0 | 34.51 |
| 5 | 6.45 | 3.425 | 0 | 51.02 | 0.77 | 0.00262 | 0.00460 | 2.87 | 26.2 | 34.50 |
| 6 | 6.45 | 7.27 | 0 | 45.94 | 0.74 | 0.00259 | 0.00434 | 3.42 | 22.5 | 34.69 |
| 7 | 6.45 | 10.77 | 0 | 41.32 | 0.73 | 0.00259 | 0.00440 | 4.20 | 26.8 | 35.00 |
| 8 | 0 | 10.77 | 0 | 41.31 | 0.00 | 0.00000 | 0.00631 | 3.42 | 24.8 | 34.79 |
| 9 | 0 | 10.77 | 0 | 41.31 | 0.37 | 0.00000 | 0.00631 | 3.92 | 25.6 | 34.64 |
| 10 | 0 | 10.77 | 0 | 41.31 | 0.72 | 0.00000 | 0.00632 | 4.20 | 26.3 | 34.63 |
| 11 | 0 | 10.77 | 0 | 41.31 | 1.41 | 0.00000 | 0.00631 | 4.30 | 28.0 | 34.77 |
| 12 | 0 | 10.77 | 0 | 41.31 | 2.14 | 0.00000 | 0.00631 | 4.27 | 28.0 | 34.68 |

Table 4 Boiling point of water and bubble point of the reaction mixture at different pressures

| Initial Pressure (bar) | Saturation temperature of water (°C) | Maximum temperature (°C) |
|---------------------------------------|---|---|
| 7.51 | 170 | 177 |
| 21.37 | 198 | 217 |
| 34.40 | 243 | 243 |

Table 5 Assessment criteria for TMR_{ad}

| Simplified | Extended | TMR_{ad} (h) |
|-------------------|-------------------|-----------------------------|
| High | Frequent | < 1 |
| | Probable | 4-8 |
| Medium | Occasional | 8-24 |
| Low | Seldom | 24-50 |
| | Remote | 50-100 |
| | Almost Impossible | >100 |

Table 6 Probability of thermal runaway for Prisleschajew epoxidation in the presence of formic acid

A.

| Probability of occurrence | DB:CA molar ratio | | | |
|---------------------------|-------------------|----------|----------|----------|
| | T_p (°C) | 1:0.5 | 1:1 | 1:1.3 |
| 20 | probable | probable | probable | frequent |
| 30 | probable | frequent | frequent | frequent |
| 40 | probable | frequent | frequent | frequent |
| 50 | frequent | frequent | frequent | frequent |
| 60 | frequent | frequent | frequent | frequent |
| 70 | frequent | frequent | frequent | frequent |
| 80 | frequent | frequent | frequent | frequent |

B.

| Probability of occurrence | DB:HP molar ratio | | |
|---------------------------|-------------------|----------|----------|
| | T_p (°C) | 1:1 | 1:1.4 |
| 20 | probable | frequent | frequent |
| 30 | frequent | frequent | frequent |
| 40 | frequent | frequent | frequent |
| 50 | frequent | frequent | frequent |
| 60 | frequent | frequent | frequent |
| 70 | frequent | frequent | frequent |
| 80 | frequent | frequent | frequent |

C.

| Probability of occurrence | Sulfuric acid loading (wt %) | | | |
|---------------------------|------------------------------|----------|----------|----------|
| | 0 | 1 | 2 | 3 |
| T_p (°C) | | | | |
| 20 | probable | probable | probable | probable |
| 30 | frequent | frequent | frequent | frequent |
| 40 | frequent | frequent | frequent | frequent |
| 50 | frequent | frequent | frequent | frequent |
| 60 | frequent | frequent | frequent | frequent |
| 70 | frequent | frequent | frequent | frequent |
| 80 | frequent | frequent | frequent | frequent |

Table 7 Probability of thermal runaway for Prisleschajew epoxidation with acetic acid

A.

| Probability of occurrence | DB:CA molar ratio | | | |
|---------------------------|-------------------|------------|------------|------------|
| | T_p (°C) | 1:0.5 | 1:1 | 1:1.4 |
| 20 | Impossible | occasional | occasional | occasional |
| 30 | remote | probable | probable | probable |
| 40 | seldom | probable | probable | probable |
| 50 | occasional | probable | probable | probable |
| 60 | probable | probable | probable | probable |
| 70 | probable | probable | frequent | frequent |
| 80 | probable | frequent | frequent | frequent |

B.

| Probability of occurrence | DB:HP molar ratio | |
|---------------------------|-------------------|------------|
| | T_p (°C) | 1:1.4 |
| 20 | occasional | occasional |
| 30 | probable | probable |
| 40 | probable | probable |
| 50 | probable | probable |
| 60 | probable | probable |
| 70 | frequent | frequent |
| 80 | frequent | frequent |

C.

| Probability of occurrence | Sulfuric acid loading (wt %) | | | |
|---------------------------|------------------------------|------------|----------|----------|
| | 0 | 1 | 2 | 3 |
| T _p (°C) | | | | |
| 20 | occasional | occasional | probable | probable |
| 30 | probable | probable | probable | frequent |
| 40 | probable | probable | probable | frequent |
| 50 | probable | probable | frequent | frequent |
| 60 | probable | frequent | frequent | frequent |
| 70 | frequent | frequent | frequent | frequent |
| 80 | frequent | frequent | frequent | frequent |

Table 8 Probability of thermal runaway for Prisleschajew epoxidation with acetic acid

A.

| Probability of occurrence | Catalyst loading (wt %) | | | |
|---------------------------|-------------------------|------------|------------|------------|
| | T_p (°C) | 0 | 10 | 20 |
| 20 | impossible | impossible | impossible | seldom |
| 30 | impossible | remote | seldom | occasional |
| 40 | impossible | seldom | occasional | occasional |
| 50 | remote | occasional | occasional | probable |
| 60 | seldom | probable | probable | probable |
| 70 | occasional | probable | probable | probable |
| 80 | probable | probable | probable | probable |

B.

| Probability of occurrence | DB:HP molar ratio | | |
|---------------------------|-------------------|------------|------------|
| | T_p (°C) | 1:1 | 1:2 |
| 20 | impossible | seldom | occasional |
| 30 | impossible | seldom | occasional |
| 40 | remote | occasional | probable |
| 50 | seldom | probable | probable |
| 60 | occasional | probable | probable |
| 70 | probable | probable | probable |
| 80 | probable | probable | frequent |

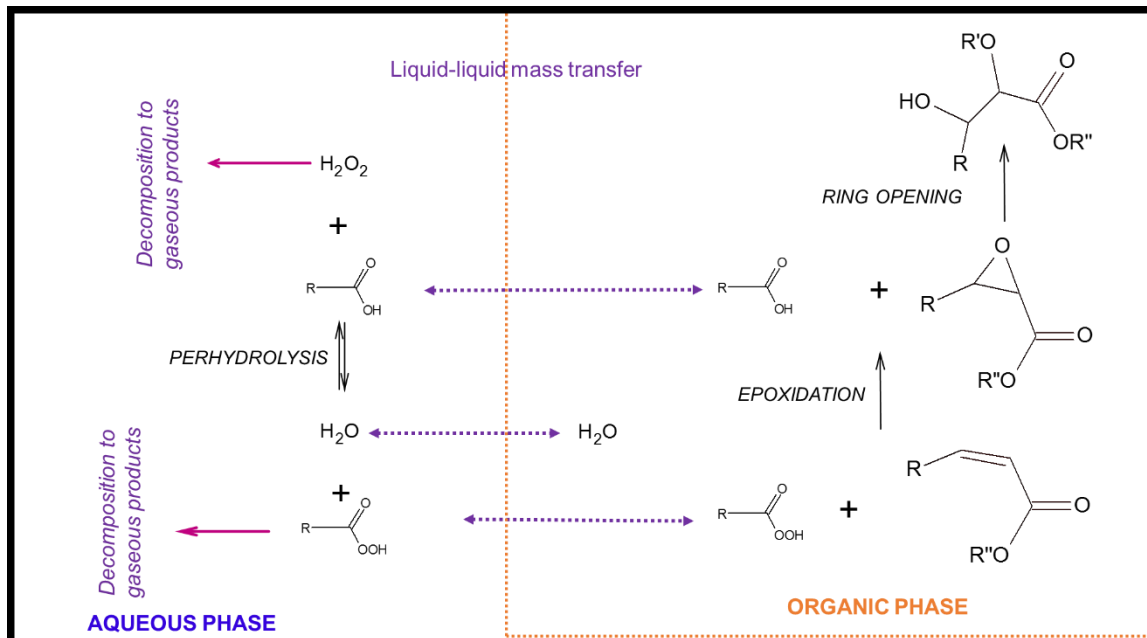


Fig. 1 Prileschajew epoxidation scheme

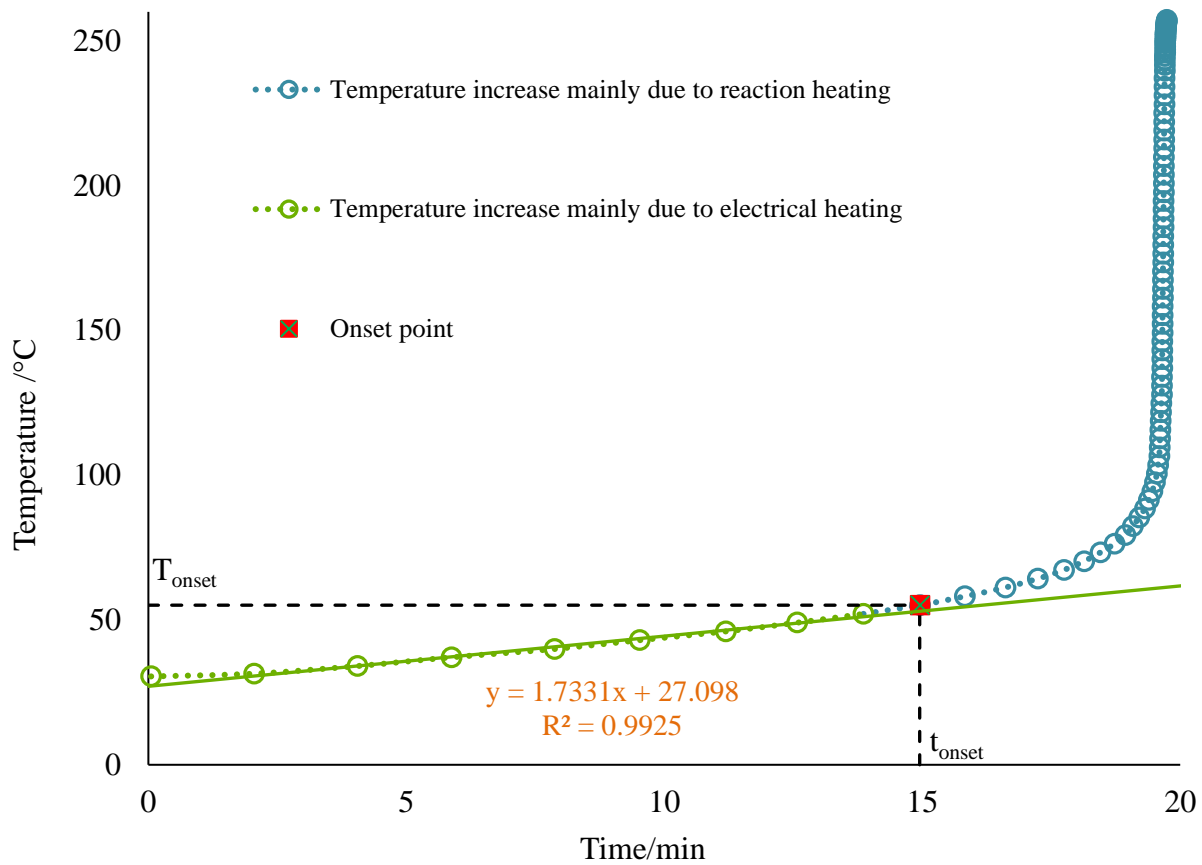


Fig. 2 Typical temperature profile from ARSST

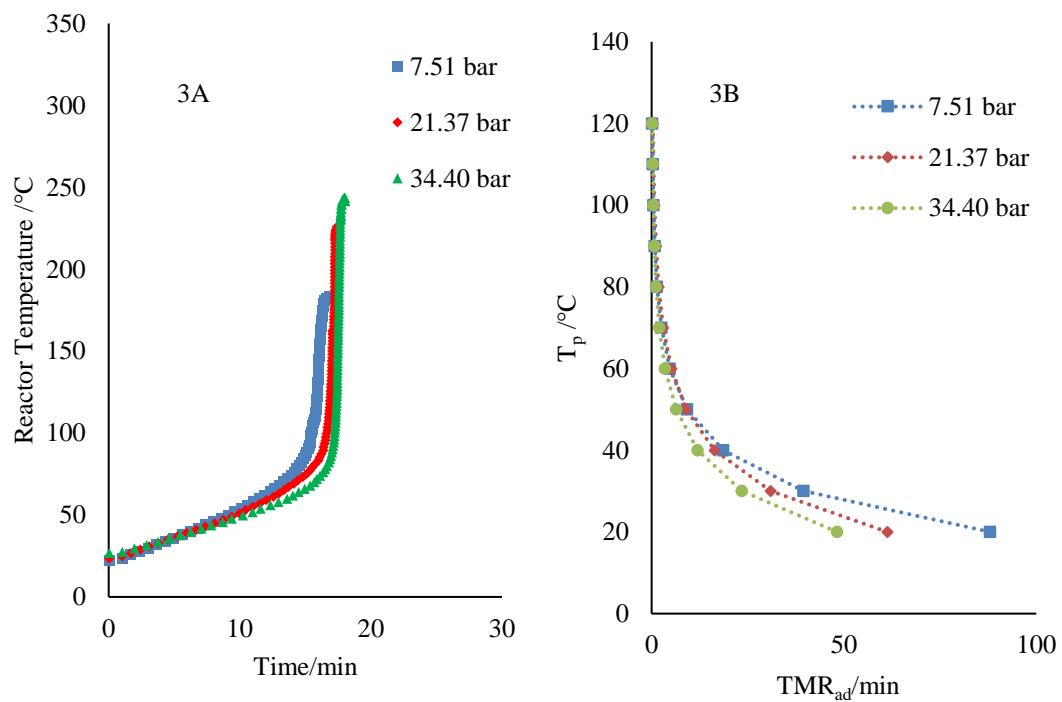


Fig. 3A Reaction temperature profiles at different initial nitrogen pressures. **3B** Influence of nitrogen pressure on TMR_{ad} (T_p). (Table 1: Run 12, 13 and 14)

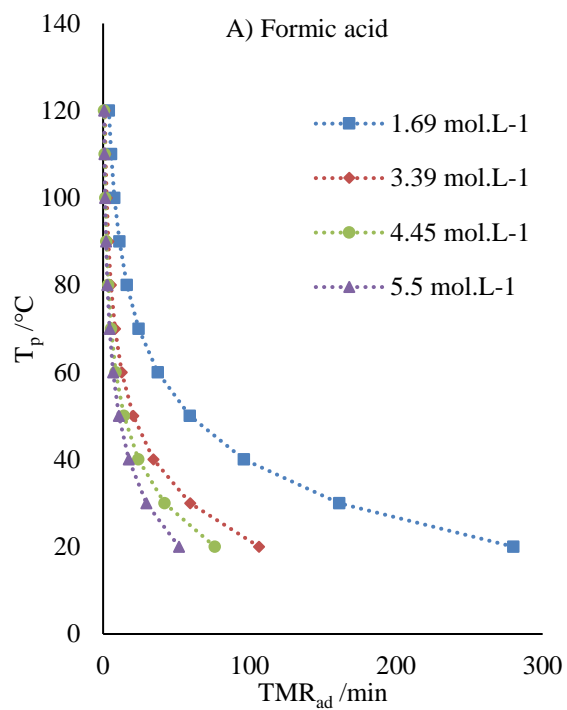


Fig. 4 Influence of carboxylic acid concentration on TMR_{ad} at different process temperatures.
 (Fig.4A Table 1: Run 1, 2, 3 and 4. Fig 4B Table 2: Run 1, 2, 3 and 4)

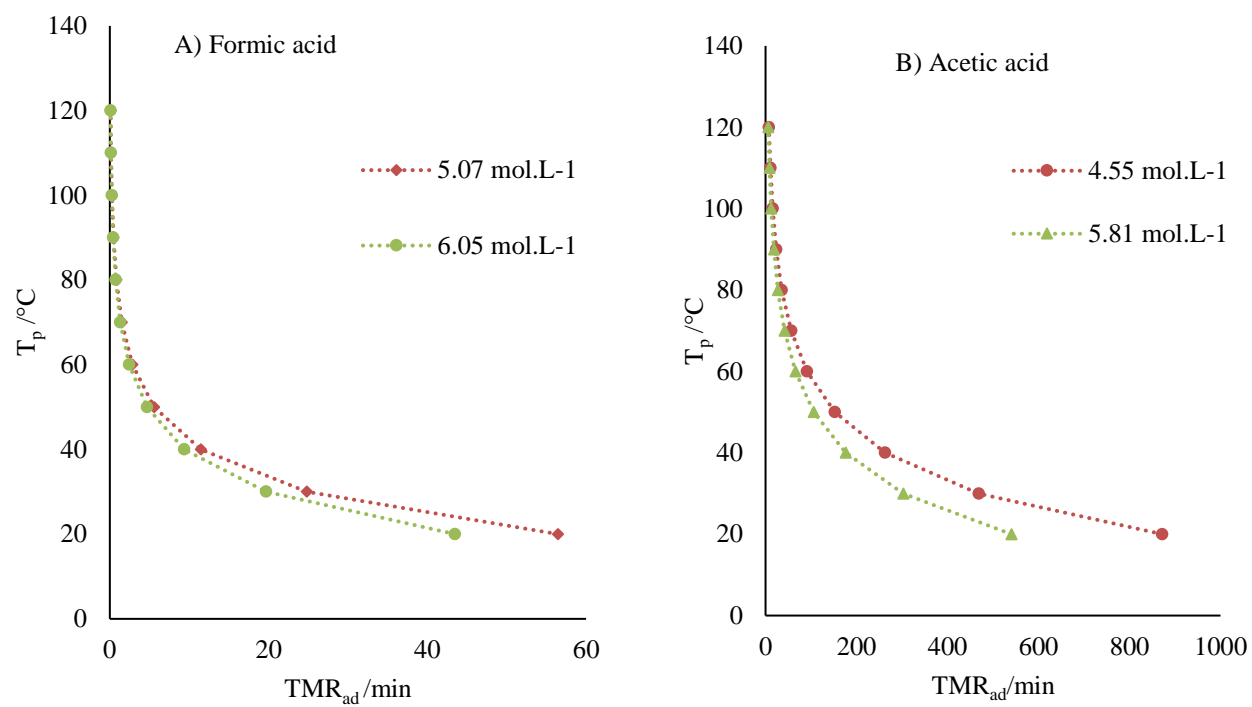


Fig. 5 Influence of hydrogen peroxide concentration on TMR_{ad}.
 (Fig. 5A Table 1: Run 6 and 7. Fig. 5B Table 2: Run 4 and 5)

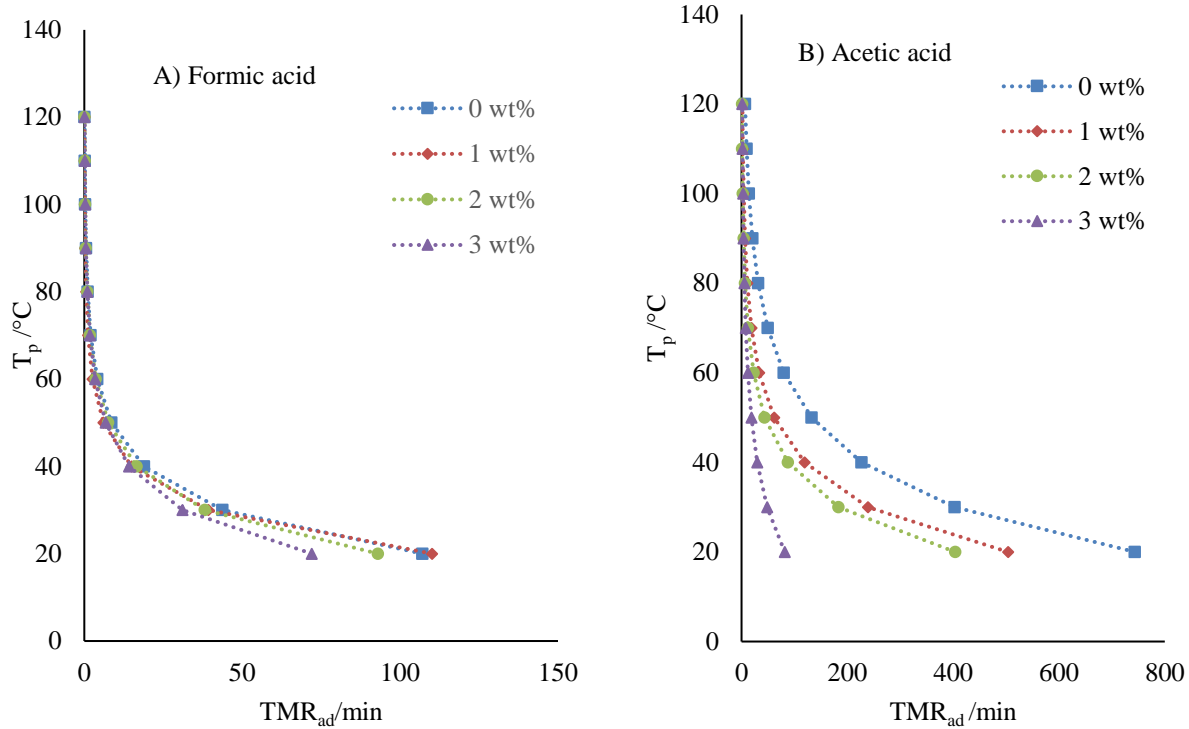


Fig. 6 Influence of sulfuric acid load on TMR_{ad}
 (Fig. 6A Table 1: Run 8, 9, 10 and 11. Fig. 6B Table 2: Run 6, 7, 8 and 9)

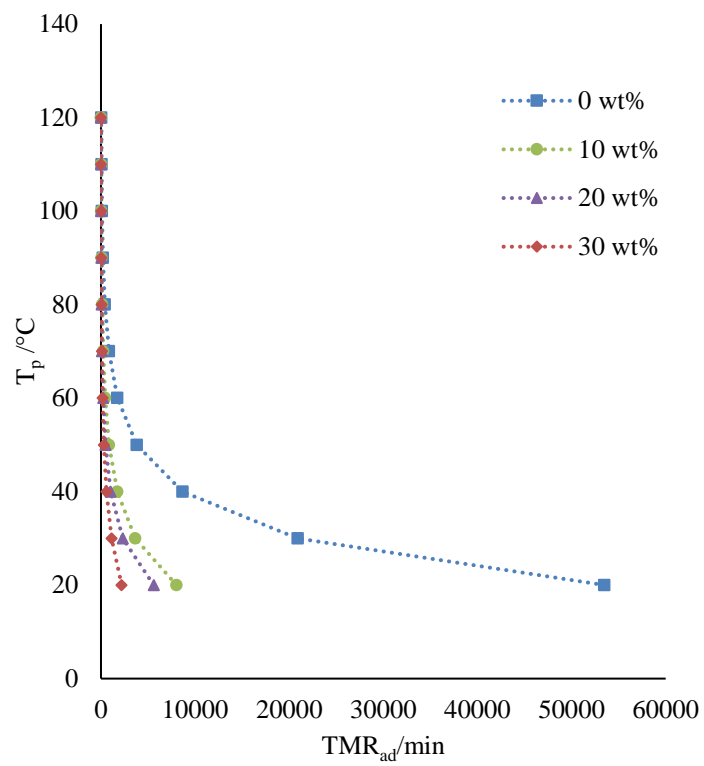


Fig. 7 Influence of alumina loading on TMR_{ad} (Table 3: Run 1, 2, 3 and 4)

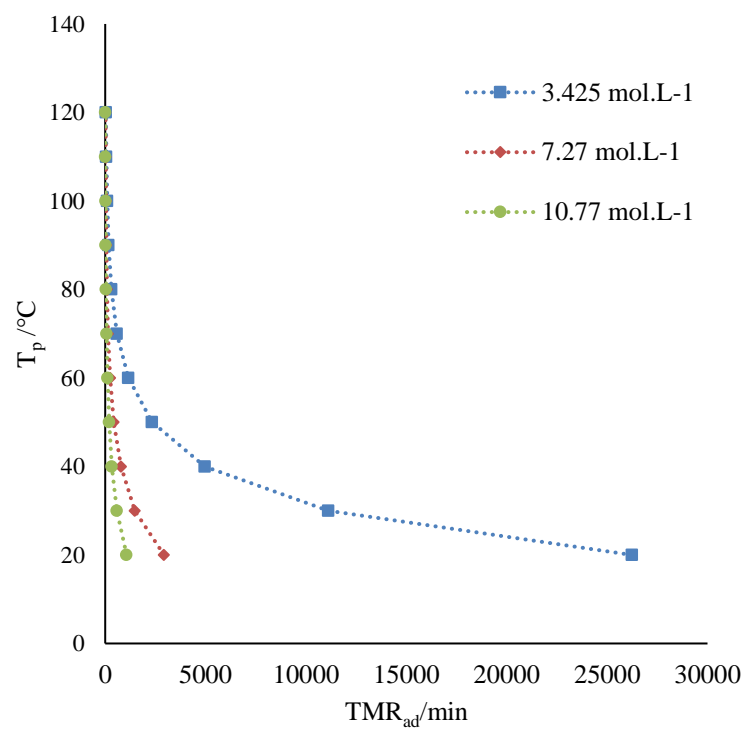


Fig. 8 Influence of hydrogen peroxide on TMR_{ad} with a catalyst loading of 10 wt% (Table 3: Run 5, 6 and 7)

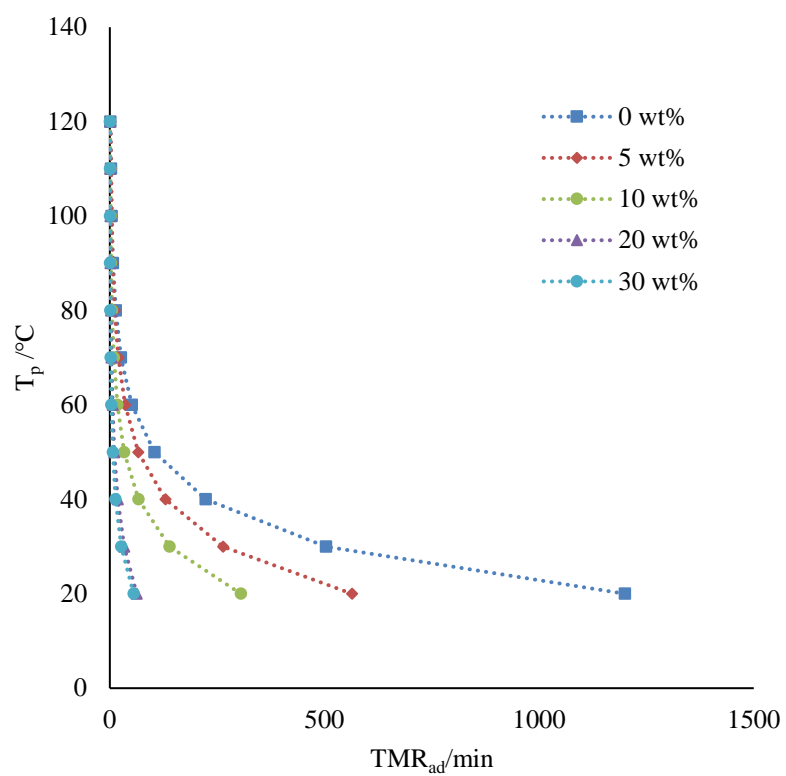


Fig. 9 Influence of the hydrogen peroxide decomposition in the presence of alumina over TMR_{ad} (Table 3: Run 8, 9, 10, 11 and 12)

