

Preliminary Study of Epoxidation of Soybean Oil in Stirred Tank Reactor: the Effect of the Mixing Program

Chiara Vianello^a, Damiano Piccolo^a, Ernesto Salzano^b, Giuseppe Maschio^{*a}

^a Department of Industrial Engineering, University of Padua, 9, F. Marzolo, 35131 Padua, Italy

^b Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum - Università di Bologna, Via Terracini 28, 40131 Bologna (IT)
giuseppe.maschio@unipd.it

Epoxidated vegetable oils are largely employed as plasticizer instead of harmful phthalates and they represent a sustainable choice to produce lubricants and intermediates. In this work, the epoxidation of soybean oil is carried using hydrogen peroxide (H₂O₂) 32wt.% and acetic acid instead of the commonly used H₂O₂ at 60wt.% and formic acid to reduce the risk of detonation and corrosion. The efficacy of an acid catalyst (sulfuric acid) is tested. Particular attention is focussed on a proper mixing program.

1. Introduction

Thanks to the epoxidation processes of vegetable oils and of fatty acids, it is possible to synthesize environmental-friendly lubricants but also plasticizers, polymer stabilizers and paint and coating components. Epoxidated oils are also employed as intermediates for various products such as alcohols, alkanolamines, glycols, carbonyl or olefinic compounds and polyols for important polymers including polyurethanes and polyesters (Sepulveda et al., 2007, Li et al., 2015).

As concerns the bio-lubricants, they are a good and sustainable choice if one wants to substitute the petroleum-derived lubricants with a new, renewable and bio-degradable product. Concerning the use of vegetable epoxidated oils as additive in plastics, it is reminded that epoxidized soybean oil is largely employed as co-stabilizer and secondary plasticizer of PVC (polyvinyl chloride) and its production consists in more than 2000 kton/yr (Eierdanz, 1993).

Industrially, the epoxidation of vegetable oils is a well-known reaction, with patented applications since 1949, as demonstrates the patent of Terry and Wheeler. This technology employs acetic acid, hydrogen peroxide, sulfuric acid as acid catalyst and oil. This method, even if with some variations is still largely employed (Dinda et al., 2008, De Quadros et al., 2016, Jia et al., 2011, Santacesaria et al. 2011). As mentioned in this patent, in the early days the epoxidation was performed using perbenzoic acid, that is highly costly and difficult to separate from the oil. However, several other methods are available. For example, other authors used a solid catalyst as alumina (Sepulveda et al. 2007) or ion exchange resin as the case of Sinadinovic-Fiser (2014). Li et al. (2015) carried out epoxidation with an innovative electrochemical method. Chavan et al. (2015) intensified the process by using ultrasounds. Leveneur et al. (2014) studied the intensification by microwave heating. Several other methods can be found, using catalyst as hypohalous acids (Guenter et al., 2003).

In this article, the epoxidation is carried out according to the first approach. The hydrogen peroxide is used as a donor of oxygen to carry out the epoxidation of the oil. However, because of the neglectable solubility of H₂O₂ in the organic phase, a vector of oxygen is needed, such as a peroxy-carboxylic acid. The solution consists in the preliminary oxidation of the carboxylic acid to peroxy-carboxylic acid in the aqueous phase, thanks to the H₂O₂. The peroxy-carboxylic acid diffuses into the organic phase and epoxidises the oil, passing from peroxy-carboxylic to carboxylic acid. In the end, the carboxylic acid diffuses into the aqueous phase restarting the cycle. The process is made of two steps of reaction and two steps of mass transfer and it is well described by De Quadros *et al.* (2015).

In this work, hydrogen peroxide is chosen at 30wt.% instead of the commonly used one at 60wt.% to reduce the risk of detonation. Formic acid is replaced with acetic acid to avoid corrosion of the reactor and results

safer in the case of absence of catalyst in terms of decomposition (Vianello, 2015) Since the effect of sulfuric acid is not completely clear as reported by Sinadinovic-Fiser et al. (2014), a proper study is needed. In this way, the effect of the presence of sulfuric acid is studied. Moreover, the influence of the mixing program is examined.

2. Experimental description

2.1 Materials

The acetic acid 98%, the hydrogen peroxide 34% and the sulfuric acid are purchased from *Sigma-Aldrich*. Soybean oil in a food grade is purchased from a local supermarket.

2.2 Instrumentation

The employed reactor is a batch, stirred and jacketed tank by *BüchiGlasUster* (Figure 1). It permits to record temperatures and pressure to perform calorimetric analysis on the system. The temperature control of the reactor is ensured by the silicone oil that flows in the jacket and a thermocryostat by *Huber*. A set of transducers permits to measure the temperatures inside the reactor and at the inlet/outlet of the jacket. Pressure is also measured. As regards the stirring system, a Rushton turbine is used to create a good emulsion between the organic and the inorganic phases. The shaft of the impeller is magnetically coupled to the electric motor, in such a way that sealing is guaranteed.



Figure 1. Calorimetric reactor by BüchiGlasUster used for the experiments.

2.3 Experimental procedure

The epoxidation is carried out with 105.6 g of soybean oil, 15.85g of acetic acid and 84.15g of hydrogen peroxide 34wt.%. In this way the acetic acid:hydrogen peroxide:double bonds molar ratio is equal to 0.5:1.5:1 (base case) as suggested by Dinda et al. (2008). The temperature is chosen at 60°C because it is considered the best compromise by the same authors. In order to carry out the process, first 105.6g of soybean oil are loaded in the reactor. The reactor is closed such as the seal is ensured, and the Huber thermocryostat is set to 60°C. The acetic acid-hydrogen peroxide mixture is heated up for 10 minutes in a flask at 65°C in a thermostatic bath (by *Julabo*). Once the thermal transient in the reactor is extinguished and the acetic acid-hydrogen peroxide mixture is warmed up, the solution is loaded in the reactor by a funnel, through a top valve of the reactor. In such a way, the vacuum is created in it using a Venturi water pump and the liquid can enter the reactor. In the case that sulfuric acid is added, it is solubilized in some hydrogen peroxide. This solution is directly poured in the funnel when the hot hydrogen peroxide-acetic acid is added. The time of injection is considered as time zero.

The sample are analyzed by FTIR spectroscopy and the peaks related to glycols, epoxides and double bonds are considered. It is reminded that presence of glycols is associated to a wide peak (a band) centered on about 3500 cm^{-1} , epoxides present a peak at around 825-830 cm^{-1} whereas the peak of double bonds is around 3010 cm^{-1} (Leveneur et al., 2014, Jia et al. 2011).

3. Results

3.1 Virgin soybean oil

The FTIR spectrum of soybean oil is presented in Figure 2.

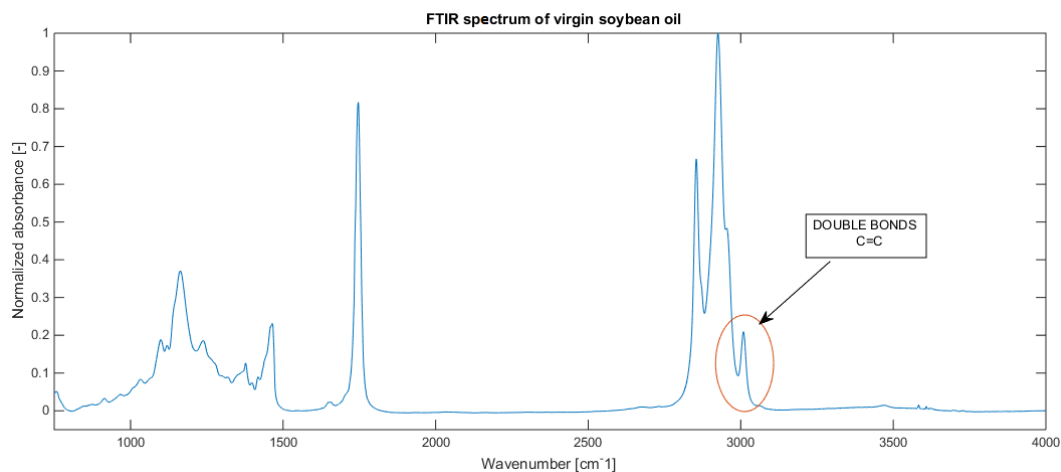


Figure 2. FTIR spectrum of virgin soybean oil.

As can be seen in Figure 2, the peak at 3010 cm^{-1} indicates the presence of double bonds C=C. The previous spectrum can be considered as a reference in order to evaluate the results.

3.2 Effect of the presence of sulfuric acid

In order to evaluate the influence of sulfuric acid, the epoxidation is carried out in presence or absence of it. Time duration of the process is 4 hours whereas impeller speed is equal to 500 rpm.

As regards the process carried out without sulfuric acid, the result is indicated in Figure 3 (FTIR spectrum). This sample is the sample A. After 4 hours, in absence of sulfuric acid, double bonds are still present in a large amount. This means that conversion is near to 0%. Moreover, there are no peaks associated to epoxides ($820\text{--}830\text{ cm}^{-1}$). Some glycols are produced, but in very small amount. In conclusion, the process cannot be carried out without sulfuric acid, if acetic acid and diluted hydrogen peroxide (32wt.%) are used. This fact is confirmed by the total absence of overshoots in the temperature profile.

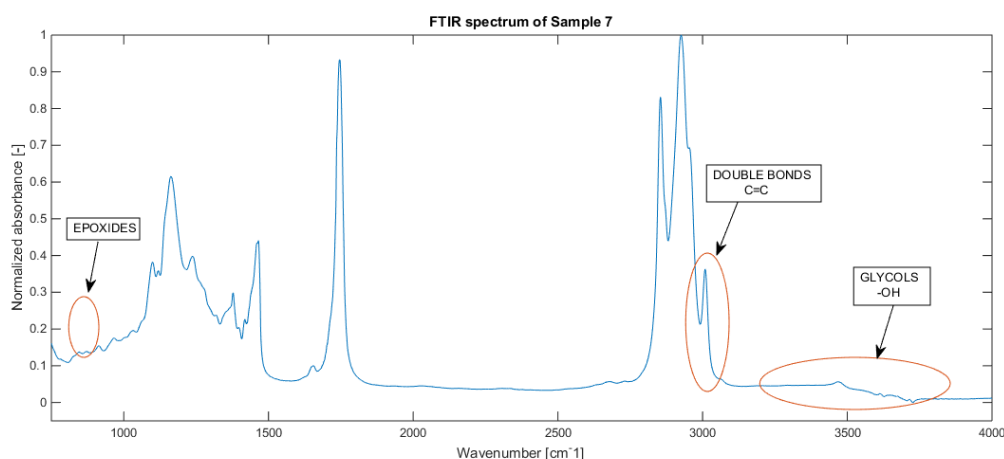


Figure 3. FTIR spectrum of Sample A. Process carried out without sulfuric acid for 4 hours. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Impeller speed 500 rpm.

At this point, the influence of sulfuric acid can be studied. The conditions are the same of the previous case but 3wt.% of sulfuric acid (with respect to oil) is added. The sample is the sample B and its FTIR spectrum is represented in Figure 4. As can be seen from the FTIR analysis, the result of sample B is totally different from

sample A. First, a noticeable peak associable to epoxides is present, so epoxidation takes place. Moreover, a peak due to the presence of glycols appears so they are surely present as by-products. The presence of the large -OH band makes difficult to understand if the C=C peak is small or totally absent.

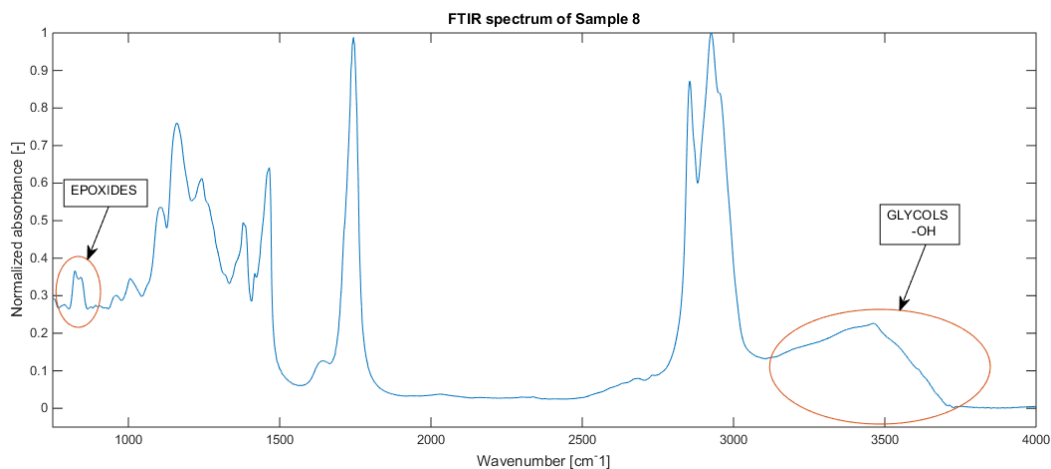


Figure 4. FTIR spectrum of Sample B. Process carried for 4 hours. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.%. Impeller speed 500 rpm.

In conclusion, both main and secondary reactions take place, epoxides and glycols are surely present and that double bonds surely react. The fact that the reaction of epoxidation takes place is confirmed by the temperature profiles. Two great thermal overshoot are noticeable (62.17°C). This confirm that epoxidation reaction takes place, since it is an exothermic reaction. Moreover, sulfuric acid demonstrates a strong catalytic activity towards the epoxidation. Another information is given by this thermal profile. In fact, after two hours, a strong mixing at 1500 rpm is carried out for 1 minute and then 500 rpm is set again. After that, another thermal peak occurs, as can be seen in Figure 5. This lead to serious mixing issues, since this second peak indicates that segregation occurs in the reactor. In fact, after strong mixing at 1500 rpm, segregated virgin reactants can react. Another good result is that after 4 hours, there is no temperature overshoots and temperature is equal to about 59.6°C, as in the case no reactions take place. Even if another strong mixing period is carried out, temperature does not increase. This is a good proof that all the reactants have reacted after 4 hours and the conversion is near to 100%. However, the evidence that segregation occurs lead to the necessity of a proper study of the correct mixing regime, and this is the focus of the next paragraph.

After comparison with the spectrum of a soybean oil spectrum, the selectivity can be estimated equal to 77%.

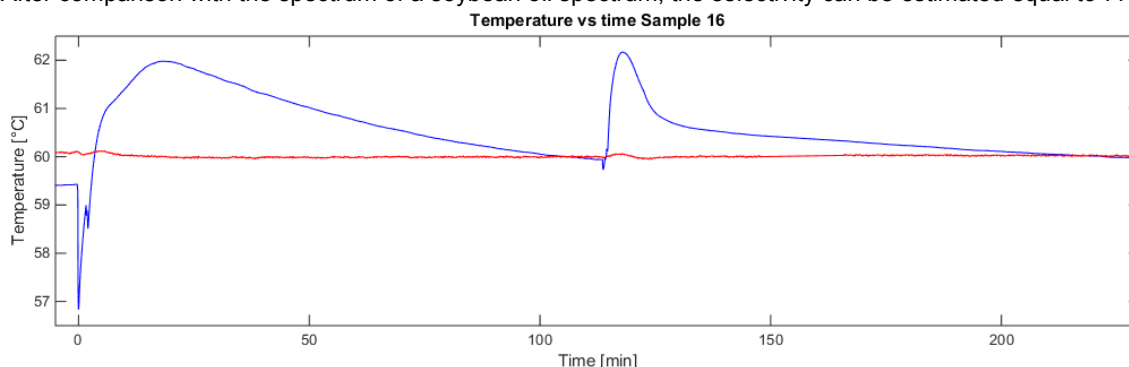


Figure 5. Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample B. Sulfuric acid 3wt.% with respect to oil. Remixing at 1500 rpm for 1 minute after 2 hours.

In conclusion, the presence of sulfuric acid is indispensable in order to carry out the process since it has a great catalytic activity towards the process.

5.3 Effect of mixing regime and mixing program

From the previous paragraph, it is evident that the agitation does not involve the whole mass. It is reminded that, dealing with a by-phasic system, mixing and mass transfer between phases is crucial. The effects of the speed of the impeller on the oil conversion are well studied by Aguilera *et al* (2016). In addition to what can be

found in literature, there is another experimental evidence. In fact, the impeller speed has a great relevance also on the degradation of oil. At 60°C, oil degrades rapidly if the impeller rotates at 1500 rpm for 4h. In this case the colour of the oil turns to orange and at 70°C the colour is nearly orange-brownish. This situation must be totally avoided. An increase of the impeller speed helps the mixing but lead to degradation.

The solution is to set up a proper mixing program, maintaining the speed at 500 rpm and every 20 minutes (including the injection instant), the speed is increased to 1500 rpm for 30 seconds. This phase will be indicated with the term *remix*. Remix implies several beneficial effects:

- the reacted epoxidized oil is taken away from the region in which the reaction takes place and in this way the product is less exposed to the acid aqueous phase, that causes the formation of glycols;
- unreacted oil is drawn by the impeller and exposed to the aqueous phase. In this way in the region where the impeller acts, there is meanly more unreacted oil than the case without remix. The result is that the rate of reaction is meanly higher.

The thermal profile that results in this case is the one exposed in Figure 6 The sample is the sample C. The temperature profile indicates an exponential decrease as the time increase. In occasion of each remixing the temperature suddenly decreases because the heat exchange coefficient increases. The first temperature peak is equal to 62.07 °C, similarly to sample B. The fact that the rate of reaction is meanly higher than the case of sample B is demonstrated by the fact that after about 3.5 hours no thermal overshoots are appreciable. This is a very important result, since sample B requires 4 hours to extinguish the thermal transient. It can be concluded that remixing speed up the process and about 30 minutes on 4 can be saved.

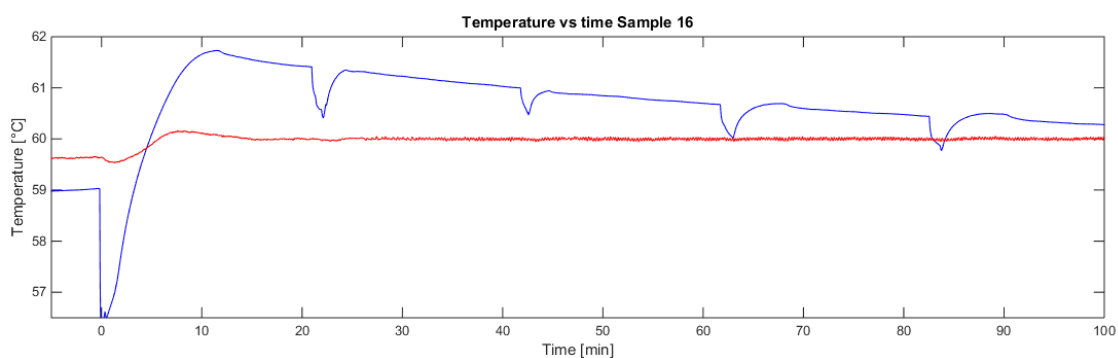


Figure 6. Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of sample C. Sulfuric acid 3wt.% with respect to oil. Remixing at 1500 rpm for 30s at interval of 20 mins.

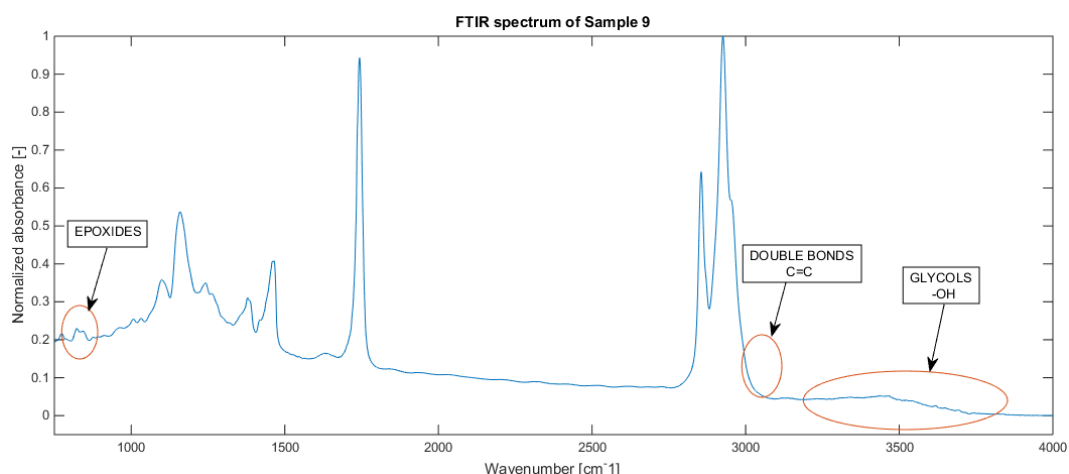


Figure 7. FTIR spectrum of sample C. Process carried out for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 minutes. Sulfuric acid 3wt.% with respect to oil.

The FTIR analysis of sample C is exposed in Figure 7. The duration of the process is 4 hours. The result is evident. The peak at 820 cm^{-1} indicates the presence of epoxides. Moreover, glycols are present in traces. The double bonds peak is totally absent, that confirms that conversion is nearly total ($\sim 100\%$) and the

products are nearly totally epoxides. The selectivity can be calculated similarly to sample B and it is equal to better than 97%. Selectivity is very good and the improvement with respect to sample B is excellent. In this way, both the increase in the rate of reaction and the improvement in selectivity can be achieved. As regard the physical properties of the epoxidized oil, it appears to be intense yellow when the conversion is low and turns to white-yellowish when the conversion is complete. The product is very viscous with respect to the virgin soybean oil. In conclusion, remixing reaches both the objectives previously exposed. This evidence is very important because a proper mixing program is fundamental to obtain a good product and this fact represent a good no-cost innovation that is not described in the literature.

Table 1. Main results of this work. Red colour highlights the most effective condition.

Remixing	Yes	Not
Sample	C	B
Conversion after 4h (estimated)	~100%	~100%
Selectivity after 4h (estimated)	97%	77%
Time required to complete conversion (estimated)	3.5	4

4. Conclusions

In conclusion, is demonstrated that the process can be carried out with diluted hydrogen peroxide and weaker carboxylic acid (acetic one) to improve safety. The process must be carried out in presence of an acid catalyst (sulfuric acid). In fact, it demonstrates a very intense catalytic activity. The importance of the mixing program is relevant because it permits to better control and speed up the process and to increase the selectivity from 77% up to 97%. This is a great improvement that can be obtained in a simple way and with no economical effort.

References

- Aguilera A.F., Tolvanen P., Eränen K., Leveneur S., Salmi T., 2016, "Epoxidation of oleic acid under conventional heating and microwave radiation," *Chem. Eng. Process. Process Intensif.*, vol.102, pp.70–87.
- Chavan A. P. and Gogate P. R., 2015, "Ultrasound assisted synthesis of epoxidized sunflower oil and application as plasticizer," *J. Ind. Eng. Chem.*, vol. 21, pp. 842–850.
- de Quadros J. V. and Giudici, R., 2016, "Epoxidation of soybean oil at maximum heat removal and single addition of all reactants," *Chem. Eng. Process. Process Intensif.*, vol. 100, pp. 87–93.
- Dinda S., Patwardhan A. V., Goud V. V., Pradhan N. C., 2008, "Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids," *Bioresour. Technol.*, vol. 99, no. 9, pp. 3737–3744.
- Eierdanz H., 1993, *Industrial fatty chemical raw materials, processes, products*. Weinheim.
- Guenter S., Rieth R., Rowbottom K. T., 2003, *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., vol. 12. John Wiley and Sons.
- Janković M. R., Sinadinović-Fišer S. V., Govedarica O. M., 2014, "Kinetics of the epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion-exchange resin," *Ind. Eng. Chem. Res.*, vol. 53, no. 22, pp. 9357–9364.
- Jia L. K., Gong L. X., Ji W. J., Kan C. Y., 2011, "Synthesis of vegetable oil based polyol with cottonseed oil and sorbitol derived from natural source," *Chinese Chem. Lett.*, vol. 22, no. 11, pp. 1289–1292, 2011.
- Leveneur S., Ledoux A., Estel L., Taouk B., Salmi T., 2014, "Epoxidation of vegetable oils under microwave irradiation," *Chem. Eng. Res. Des.*, vol. 92, no. 8, pp. 1495–1502.
- Li W., Tian M., Du H., Liang Z., 2015, "A new approach for epoxidation of fatty acids by a paired electrosynthesis," *Electrochem. commun.*, vol. 54, pp. 46–50.
- Santacesaria E., Tesser R., Di Serio M., Turco R., Russo V., Verde D., 2011, "A biphasic model describing soybean oil epoxidation with H₂O₂ in a fed-batch reactor," *Chem. Eng. J.*, vol. 173, 1, pp. 198–209.
- Sepulveda J., Teixeira S., Schuchardt U., 2007, "Alumina-catalyzed epoxidation of unsaturated fatty esters with hydrogen peroxide," *Appl. Catal. A Gen.*, vol. 318, pp. 213–217.
- Terry D. E. and Wheeler D. H., 1949, "Process of preparing epoxy derivatives form unsaturated aliphatic compounds.," 4,458,484.
- Vianello C., Salzano E., Maschio G., 2015, Safety Parameters and Preliminary Decomposition Kinetic of Organo-Peroxy Acids in Aqueous Phase, *Chemical Engineering Transaction*, vol 43, pp. 2371-2376.
- Vianello C., Salzano E., Maschio G., 2016, Kinetics and safety analysis of peracetic acid, *Chemical Engineering Transaction*, vol 48, pp. 559-564.