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Master Degree Thesis in Chemical and Process Engineering

EPOXIDATION OF SOYBEAN OIL BY CONVENTIONAL AND NON-CONVENTIONAL METHODS

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Abstract

The aim of the thesis focuses on a study of the soybean oil epoxidation using peroxyacetic acid in a calorimetric reactor, comparing conventional and non-conventional methods. The objective of this work is the study of the epoxidation of soybean oil using peroxycarboxylic acid and hydrogen peroxide in absence of any acidic catalyst (base case) or in presence of an acid liquid or solid catalyst. The case that employs a liquid catalyst (sulfuric acid) represents the classical conventional method. The use of ion exchange resins as a solid catalyst represents a non-conventional and innovative method. As a matter of fact, the traditional process does not employ a solid catalyst but in some cases a liquid one (sulphuric or phosphoric acid). This solid catalyst has been chosen for economic reason (low cost), great capability of separation by simple filtering and possibility of reuse. In both cases, a sensitivity analysis and an optimization of the operating process variables is carried out, such as the concentration of the reactants or the catalyst and the mixing program. In addition, the heat exchange coefficient of the calorimetric reactor is determined using a system designed and built *ad hoc*. Moreover, a safety study on the conditions (temperature and pressure) at which runaway reactions takes place is performed in a Thermal Screening Unit. Eventually, an estimation of the heat of reaction is performed.

It is to remind that epoxidated soybean oil (ESBO) is largely used as plasticizer and stabilizer in PVC and, after the interdiction of many phthalates, it represents an optimal sustainable non-toxic alternative. ESBO can be also an intermediate for other products as polyols for the synthesis of polyurethane and polyesters.

Index

Introduction

In this thesis, a study on the epoxidation of soybean oil is carried out using peroxyacetic acid in a calorimetric reactor, comparing conventional and non-conventional methods. The objective of this work is the study of the epoxidation of soybean oil using peroxycarboxylic acid and hydrogen peroxide in absence of any acid catalyst (base case) or in presence of an acid liquid or solid catalyst. The case that employs a liquid catalyst (sulfuric acid) represents the classical conventional method. The use of ion exchange resins as a solid catalyst represents a non-conventional and innovative method. As a matter of fact, traditional process does not employ solid catalyst but in some cases a liquid one (sulphuric or phosphoric acid). This solid catalyst has been chosen for economic reason (low cost), great capability of separation by simple filtering and possibility of reuse.

As concerns the scientific and commercial interest of this work, it is to remind thanks to the epoxidation of vegetable oils, it is possible to synthetize environmental-friendly lubricants but also plasticizers and stabilizers for polymers. Epoxidated oils are also employed as intermediates for various product such as alcohols, alkanolamines, glycols, carbonyl or olefinic compounds and polyols for important polymers including polyurethanes and polyesters ([1,2]).
As concerns the epoxidated oils as addictive in plastics, it is reminded that epoxidized soybean oil (ESBO) is largely employed as stabilizer and plasticizer of PVC (polyvinyl chloride). Its production consists in more than 2000 kton/yr ([3]) and, after the interdiction of many phthalates, it represents an optimal sustainable non-toxic alternative.
The production of epoxidated vegetable oils on industrial scale has been carried out with patented application since 1946 ([4]), using carboxylic acid as oxygen carriers. Although this route is well-established and still used nowadays and, several different routes can be found in the literature in order to carry out epoxidation. Hence, a brief overview of these techniques is reported:

1. Biphasic epoxidation: hydrogen peroxide, oil, carboxylic acid and liquid catalyst ([5,6]). This is the commonly used method and two phases are present (organic and inorganic ones). H_2O_2 is used as donor of oxygen and since it is not soluble in the organic phase, a soluble carrier of oxygen is needed such as peroxycarboxylic acid. The process is structured as follows. The carboxylic ac. is oxydized in the aqueous phase to peroxycarboxylic acid. The

peroxycarboxylic acid moves to the organic phase in which it epoxidize the oil, reducing itself to carboxylic acid. Finally, the carboxylic acid moves back to the aqueous phase, restarting the cycle. Usually, formic acid (very reactive) or acetic acid (more selective) are used as carboxylic acid. Sometimes a liquid catalyst is added, such as sulphuric or phosphoric acid.

2. Triphasic epoxidation: hydrogen peroxide, oil, carboxylic acid and solid catalyst ([7]). This technique is similar to the one at point 1, however a solid catalyst is used such as acid ion exchange resins or alumina (less effective). The time required by the process is lower than the previous case and the catalyst is reusable with minimal yield losses.
3. Multiphase epoxidation: electrochemical technique using oil, gaseous O_2, formic and hydrochloric acid ([8]). In the cathodic compartment of the reactor H_2O_2 is produced, that oxidize formic acid which in turn epoxidizes the oil, as point 1. In the anodic compartment epoxidation can take place by forming chloridrine. The huge advantages of this techniques are the weel-controlled and in situ production of H_2O_2 and the reduced time of the reaction.
4. Microwave or ultrasound enhanced epoxidation. The techniques are similar to point 1 and 2 but intensified by using microwave or ultrasound ([9,10]). These methods are very effective.
5. Other methods such as epoxidation by aloydrine and ipohalogenous acids, otherwise by cumene hydroperoxide or using many catalysts such as silver or Nb_2O_5-SiO_2.

After this concise bibliographic review, the methods that are studied in this work are the first and the seconds. Essentially, they are very similar except for the catalyst, when used. In the case of this work, acetic acid is used as a vector of oxygen, since formic acid is too aggressive towards the instrumentations. Moreover, it permits great reactivity but low selectivity. Hydrogen peroxide 60wt.%, that is traditionally used in industry, is replaced with the one at 30wt.% in order to reduce the risk of detonation

In order to reach the objective, first of all, a deep safety study on the conditions (temperature and pressure) at which runaway reactions takes place is performed. This step is necessary since the presence of hydrogen peroxide can originate high temperature and pressure that could be very dangerous. Moreover, the process of epoxidation and the effect of the presence of the two catalysts is studied using a calorimetric reactor. An optimization of the operating process variables in both cases is carried out. The heat exchange coefficient of this reactor is determined using a system designed and built *ad hoc*. The obtained product is evaluated in terms of conversion and selectivity. In conclusion a thermal study is carried out, in order to estimate the heat of reaction.

As concerns the preliminary safety study, it is carried out in a *Thermal Screening Unit* (TSU) by Hel. This piece of instrumentation is a small reactor capable to contain a couple of millilitres collocated in an electric oven. TSU permits to perform temperature ramped or isothermal tests and to collect data of pressure and temperature. This study is indispensable to know the temperature at which hydrogen peroxide decomposes in a non-controllable way (runaway) and the pressure involved in this case. Clearly, the development of high pressure could create serious safety issues for the operators if this process is applied in an industrial scale.

As concerns the study on the epoxidation, the process is carried out in a calorimetric reactor, a jacketed, stirred, batch reactor equipped with thermocouples both inside the reactor and at the inlet and at the outlet of the jacket. A pressure transducer permits the measurement of pressure. In order to determine the heat exchange coefficient (useful for the calorimetric study), a proper system is developed. A well determined amount of heat is generated inside the reactor and, elaborating the data of temperature both of the transient and the steady state, the heat exchange coefficient and the effective heat capacity are determined. The heat is generated by a ceramic heater inside the reactor. This ceramic heater is a 24V very low cost heater used in 3D printers. However, during the operation of this ceramic resistor, the internal resistance and consequently the absorbed electrical power can change. In this way, a constant well determined thermal generation (that is indispensable to solve the calculation) can result quite difficult. Moreover, the possibility of changing the generated power has been taken into account, in order to exclude its influence in the heat exchange coefficient. For both reason, a simple DC regulated power supply is not enough. In fact, in addition to it, a precise automatic power controller was designed and built. This system has been design and built *ad hoc* and it is based on ATmega 328 microcontroller. The control is achieved using a feedback controller. In fact, the measured instant power that is applied to the resistor is compared with the desired power (setpoint) and, on the base of this difference, the microcontroller adjusts the voltage applied to the resistor. The desired power is set by the user by a knob. The system is equipped with analogic interfaces based on operational amplifiers LM358 that read the value of current and voltage across the ceramic heater. These data are sampled and collected by the analogic to digital converter of the microcontroller. A dedicated actuator based on a linear voltage regulator takes the PWM control signal from the microcontroller and adjusts the voltage across the heater.

Once this preliminary part is concluded, the epoxidation process can be carried in absence of any acidic catalyst or in presence of a liquid or solid one (sulfuric acid or ion exchange resin respectively). Every process variable is studied performing a sensitivity analysis. In particular, the mixing regime and mixing program, the concentration of acetic acid, the concentration of sulfuric acid or the loading of the resin are studied. Each variable is varied and the results are evaluated in terms of selectivity and conversion. The sample are analyzed by FTIR analysis and the results are elaborated in *Matlab*.
In conclusion, since the heat exchange coefficient is well determined, the temperature profile can be integrated with respect to time with *Matlab* in order to obtain the estimated heat of reaction.

As concerns this work, it is made of five chapters. Chapter 1 deals with a wide bibliographic review of the main method used to achieve epoxidation of vegetable oils. Chapter 2 is focused on a general review of the methods used in the calorimetric studies and a short explanation of the instrumentations (TSU, calorimetric reactor and automatic power controller). Chapter 3 deals with materials and methods used to carry out experiments. Chapter 4 exposes the preliminary results of the safety study carried out by TSU and the determination of the heat exchange coefficient. Chapter 5 presents all the results obtained carrying out the epoxidation in the calorimetric reactor.

Chapter 1

Epoxidation of vegetable oils

Vegetable oils are a valuable raw material extracted from biomass, in particular form plants, fruits seeds or wood. The production of these oils is equal to 168.4 million of metric tons; the major part (80%) is absorbed by the food industry ([1,2]) and the rest is used to produce soaps and domestic products but especially lubricants and fuels. The most important sources of these oils are palm, soybean, canola and sunflower. Palm oil is commonly used and, even if its cultivation occupies only 5.5% of the lands used for the production of vegetable oils, it delivers about 32% of total amount of oils and fats thanks to its high productivity ([3]). In the case of soybean, cottonseed and sunflower the lands occupied are 40.1%, 13.8% and 10.0% respectively of the total land occupied by the cultivation of vegetable for the oil production. The production and the request of vegetable increase each year thanks to the new green technologies that attempt to substitute petroleum derivate products with new renewable ones.

Thanks to the epoxidation processes of vegetable oils and of fatty acids, it is possible to synthetize environmental-friendly lubricants but also plasticizers, polymer stabilizers and paint and coating components. Epoxidated oils are also employed as intermediates for various product such as alcohols, alkanolamines, glycols, carbonyl or olefinic compounds and polyols for important polymers including polyurethanes and polyesters ([4,5]).

As concerns the bio-lubricants, they are a good and sustainable choice if one wants to substitute the petroleum-derivate lubricants with a new, renewable and bio-degradable product. It is reminded that in 2013 the world consumption of lubricants was equal to 41.35 million metric tons and the major part derives from petroleum. It appears evident that there are good opportunities for the bio-lubricants to increase their market share.

Concerning the use of vegetable epoxidated oils as addictive 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 ([6]). The production of epoxidized soybean oil is successfully implemented at plant scale ([7,8,9]) and its use as a primary plasticizer has been growing considerably in the past years, thanks to the high quality of this material and the competiveness over the petroleum-derived ones.

In this chapter a description of the state of the art of the epoxidation processes of vegetable oils is presented both as regards the industrial applications and as the new proposal that can be found in the literature.

1.1 The reaction of epoxidation: features and possible ways

Epoxidation consists in a method of functionalizing vegetable oils and derivatives and consists in partially oxidizing the fat acids introducing an atom of oxygen where it is present an unsaturation in the chain of the molecule. It is useful to remind that vegetable oils naturally has a certain amount of unsaturations along the chain. In this way, it is possible to pass from *unsaturated oil* to *epoxidated oil* (respectively a) and b) in Figure 1.1).

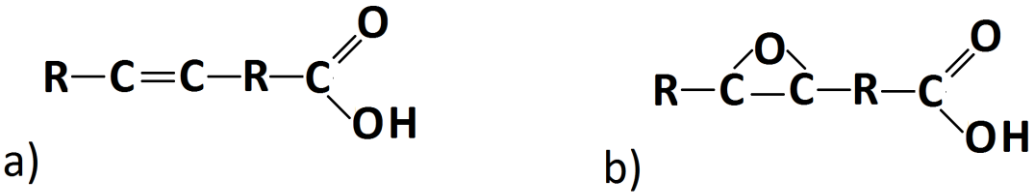


Figure 1.1. *Graphical representation of a) an unsaturated fat acid, b) an epoxidated fat acid.*

The main reaction suffers of a parallel one that cleaves the oxirane and produces α-glicol. Commercially, a product with higher content of oxirane and lower content of α-glicol is considered more valuable. At this point, it is useful to define three important quality parameter that are widely employed in the next paragraphs. They are fundamental to understand how much the oil has been epoxidized and how much by-product has been formed during the process. It appears evident that these parameters reflect their importance directly on the economical value of the product. The double bond conversion is defined as the equation (1):

$$D.B.conversion = \frac{[D.B.]_{start} - [D.B.]_{end}}{[D.B.]_{start}} \cdot 100\% \tag{1.1}$$

where *D.B.* stands for double bonds and the squared colons mean concentration, that can be volumetric or massive (mols of double bonds per unit of mass or volume of oil). The concentration of double bonds is determinable through the iodine number. This parameter permits to understand how many double bonds have react but nothing is said about how many epoxy-ring has been formed. This information is available thanks to the relative conversion to oxirane (2):

$$Relative\ conversion\ to\ oxirane = \frac{OO_{exp}}{OO_{the}} \cdot 100\% \qquad (1.2)$$

where OO_{exp} is the content of oxirane oxygen that is experimentally found and OO_{the} is the maximum oxirane oxygen that can be theoretically determined, thanks to equation (3)

$$OO_{the} = \left[\frac{IV_0/2A_i}{100+(IV_0/2A_i)\cdot A_0}\right] \cdot A_0 \cdot 100\%. \qquad (1.3)$$

A_i and A_0 are the atomic weights of iodine and oxygen respectively and IV_0 is the initial iodine number of the processed oil. Moreover, to identify how much the side reaction has affected the product, the relative conversion to α-glycol is defined as follows:

$$Relative\ conversion\ to\ \alpha\ glycol = \frac{G_{exp}}{G_{the}} \cdot 100\%. \qquad (1.4)$$

G_{exp} is the experimentally obtained content of α glycol whereas G_{the} is the maximum content that can exist and that can be calculated theoretically thanks to equation (5):

$$G_{the} = \left[\frac{IV_0/2A_i}{100+(IV_0/2A_i)\cdot 2A_{0H}}\right] \cdot 100\% \qquad (1.5)$$

where A_{OH} is the molecular weight of hydroxyl group. G_{exp} can be determined with the method reported by May (24) based on oxidation of glycol with benzyl trimethyl ammonium periodate in non aqueous medium. This method is used also by Chavan *et al.* ([21]). All these parameters are widely adopted in the literature.

Industrially, the epoxidation of vegetable oils is a well-known reaction, with patented applications since 1946 ([10]). The process was performed by a preliminary preparation of a solution of peroxyacetic acid in glacial acetic acid, obtained by the reaction between the latter and the hydrogen peroxide in the presence of a catalyst (sulfuric acid). Subsequently the solution was mixed with the oil and the epoxidation was carried-out. 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. Nowadays this technology is largely employed, even with some changes, but it suffers of some drawbacks such as the corrosiveness of the acetic acid and the fact that it is non regenerable. The process is carried out in large batch reactors in which the oil and the carboxylic acid are charged. Subsequently the hydrogen peroxide is introduced. The total time of the reaction is equal to 8 hours, so high plant investment is needed to obtain a sufficient amount of product with the target quality. It appears evident that some issues of safety are concrete. Moreover, this technology is limited by the heat removal, since the reaction is highly exothermic, especially in the early stages of the reaction.

In the literature, several ways to obtain epoxidated oils can be found. Dinda *et al.* ([11]) and Chavan *et al.* ([12]) propose a classification that consists in four main methods:

1. epoxidation with peroxycarboxilic acids. This is the most industrially used method, as previously explained. The main advantage is that this acid is non-toxic and the by-product is simply water;
2. epoxidation with organic and inorganic peroxides, which includes alkaline and nitrile hydrogen peroxide epoxidation. The reaction is catalyzed by transition metals;
3. epoxidation with halohydrines, using hypohalous acids (HOX) and their salts;
4. epoxidation with molecular oxygen using silver as catalyst. This is the simplest and cheapest route but only a very low yield can be obtained, in terms of content of oxirane towards the content of unsaturations.

This classification is useful to give an idea of the most important ways to obtain the desired product but it is too restrictive. A lot of article in the literature propose so different routes and for this reason a wider classification is needed and a more detailed description is indispensable. In this work, a new classification is presented and it comprises:

1. use of carboxylic acid (as a carrier of oxygen) and hydrogen peroxide with or without liquid homogeneous catalyst (inorganic acid). The system is bi-phasic (one inorganic and one organic liquid phases);
2. use of carboxylic acid (as a carrier of oxygen) and hydrogen peroxide with heterogeneous catalyst (solid). The system is tri-phasic (organic, inorganic and solid phases);
3. electrochemical reaction with local production of hydrogen peroxide from molecular oxygen. The system is multi-phasic (organic and inorganic liquid phases and a gaseous phase, if one does not consider the two solid electrodes and the exchange-ion membrane);
4. combined methods enhanced by ultrasound or dielectric heating, especially in the microwave range;
5. other methods.

In the next paragraphs a detailed description of these methods is reported.

1.2 Bi-phasic epoxidation: carboxylic acid, H_2O_2 and liquid catalyst.

This route is followed by the patent ([10]) that was previously mentioned and it is applied at plant scale. In that patent the peroxycarboylic acid was prepared in preliminary phase and successively it was added to the oil to carry out the reaction. However, it can be seen in the literature that this method cannot be found in the last research, since the process is performed in a batch reactor in which two liquid phase are present and a vigorous stirring is applied. In the inorganic phase hydrogen peroxide reacts with carboxylic producing the peroxycarboxylic acid (Figure 1.2). The latter has a good solubility in the organic phase and so it is used as an oxygen carrier. At the contrary, hydrogen peroxide is not soluble in the oil. In fact, thanks to the mass transfer between the two phases, the peroxycarboxylic acid is transferred to the organic phase and the epoxidation of the oil can be realized (Figure 1.3). A graphical representation of the process can be delivered by Quadros *et al.* ([13]) in Figures 1.2, 1.3, who use formic acid as the carboxylic acid.

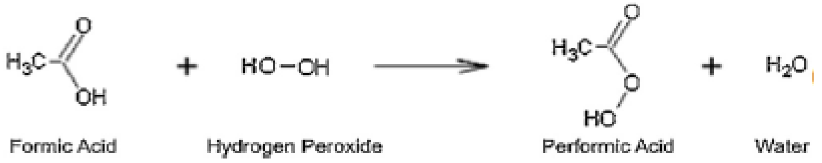


Figure 1.2. *Graphical representation of the formation of the peroxycarboxylic acid from hydrogen peroxide and carboxylic acid ([13]).*

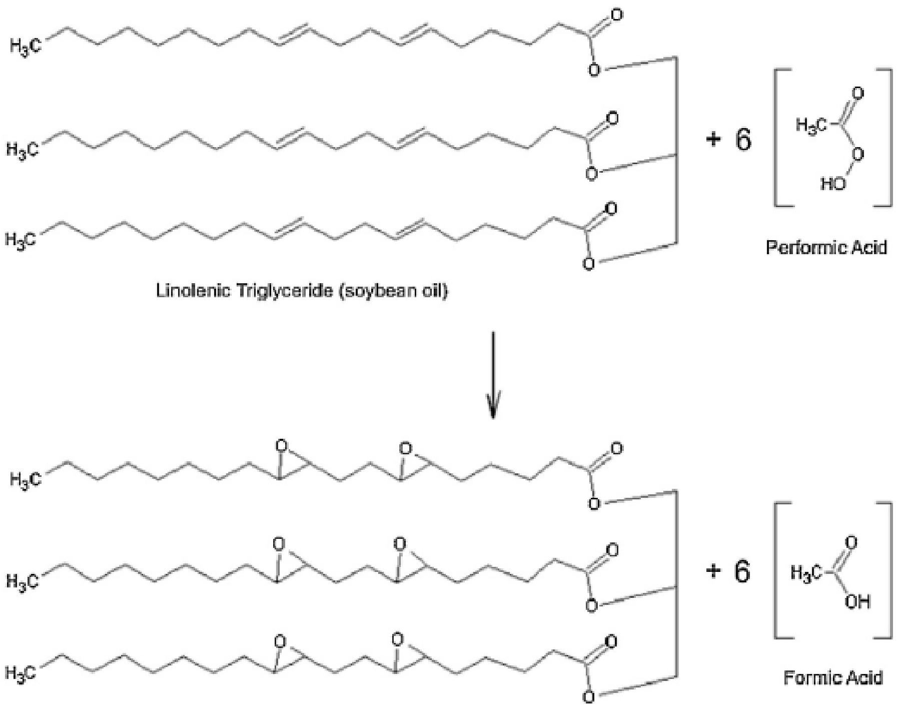


Figure 1.3. *Graphical representation of the epoxidation of a vegetable oil using a peroxycarboxylic acid as a carrier of oxygen ([13]).*

During the reaction, the oxirane is created whereas the peroxycarboxylic acid comes back at carboxylic acid (since it has transferred an oxygen to the unsaturation). This acid is transferred back to the inorganic phase where it is peroxidated again. It can be seen than the global process is made of four stages, two of reactions and two of mass transfer. This idea is well represented again by Quadros *et al.* (13) in Figure 1.4.

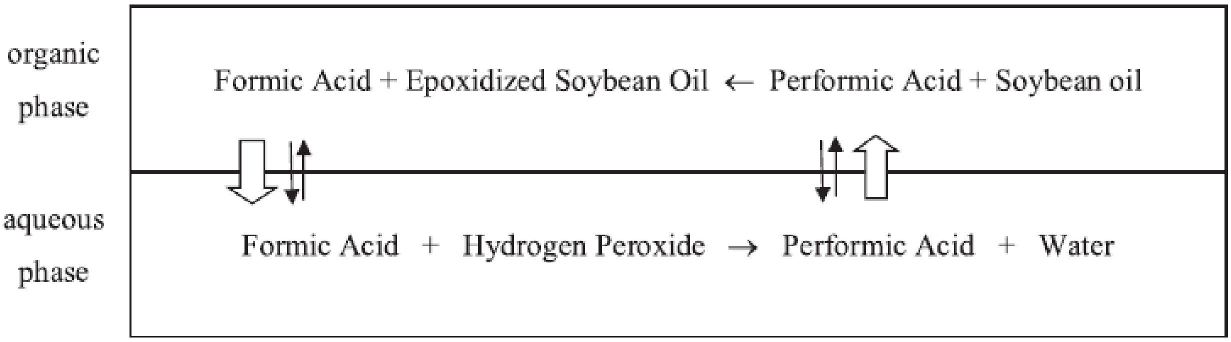


Figure 1.4. *Graphical representation of the global process of epoxidation of vegetable oil. The two mass transfer stages can be seen vertically whereas the two stages of reaction can be seen horizontally.*

As earlier mentioned, the formation of some by-products is possible, due to the cleavage of the oxirane. These by-products are hydroxyl acetate and diols. The epoxy ring opening is due to a complex system of reactions but for the sake of simplicity often only the most important reaction is considered, *i.e.* the cleavage of the oxirane by the oxonium ion (14). For this reason, this side reaction is largely promoted by acids. Moreover, the formation of the peroxycarboxylic acid is often considered the rate determining step (13,21) even if according to Santacesaria *et al.* (17) the epoxidation in the oil phase is five time slower than it. An overall first order kinetic considering a pseudo-homogeneous phase is always adopted with good results despite the rough approximation (13) whereas for the side reaction a second order kinetic is often considered.

1.2.1 Presence and concentration of the inorganic acid catalyst

As regards the presence of liquid acid catalyst, it can be added or not and the effect of this is not completely clear. Firstly, the presence of an inorganic acid surely prevents the spontaneous decomposition of the peroxycarboxylic acid: this is both an experimental and theoretical evidence according to Zhao *et al.* (15,16). This aspect surely helps the global process. Secondly, the presence of an acid prevents the dissociation of the acetic acid. This dissociation should be detrimental for the formation of peroxycarboxylic acid and the oxirane even if this aspect is in contrast what it is said in by Li *et al.* (15). Anyway, a lot of literature discusses about the beneficial effect of acid conditions, generally with pH between 3.5 and 6.5. In fact, according to Dinda e*t al* ([11]). it is an evidence that phosphoric and sulfuric acid do have a great catalytic activity on the process (especially the latter) and both boost the formation of the oxirane. In this way the conversion of oxygen to oxirane could extent to 67.5% in 10 hours and to 70% in 6 hours for the two acids respectively (mass fraction of acid equal to 2%).

It is reminded that not all the acids are catalyst for this reaction, in fact nitric and hydrochloric acid do not have a good catalytic activity according the same authors. Moreover, the beneficial effect of sulfuric and phosphoric acid is also proved by Santacesaria *et al.* ([17]), that demonstrate a huge difference in the catalytic activity between the first one with respect to the second one. In fact, when hydrogen peroxide is injected in the reactor filled with oil and catalyst, a peak of temperature of 65°C was determined in the case of the sulfuric acid, whereas a rise of only 13°C in the case of the phosphoric acid.

However, in the case of the castor oil, Sinadinovic-Fiser *et al* ([18]) have not found a great catalyst activity of the sulfuric acid. Moreover, there are some works in which no sulfuric/phosphoric acid at all is used, *i.e.* Jia *et al* ([19]) or Quadros *et al.* ([11])

Finally, it is to remind that also the fraction of the inorganic acid is crucial. In fact, if on a hand a low content of acid does not permit a good catalysis of the reaction, on the other hand a large content of acid causes the cleavage of the oxirane, producing a large amount of by-products (α-glycol) that decrease the commercial value of the product. According to Aguilera *et al*. pH lower than 3.5 permits the protonation of oxirane and, consequently, the cleavage of it ([1]). Similarly, Dinda *et al.* ([11]) refer that a mass fraction of sulfuric acid (98%) greater than 3% promotes this side-reaction so they choose an optimum value of 2%.

1.2.2 Choice and concentration of the carboxylic acid

As concerns percarboxylic acid, both formic and acetic acid are largely used. The main difference is that the first one is more reactive and permits a fast conversion of the double bond of the oil, whereas the latter is less reactive. Propionic acid presents a weak reactivity and for this reason it is seldom used ([20]). Nevertheless, formic acid is highly corrosive, it largely promotes the cleavage of the oxirane ([11]) and, because of its high reactivity, it could give an excessive rise of temperature with risk of runaway reactions: for these reasons acetic acid is often preferable. This aspect is well highlighted by Dinda *et al.* ([11]) and acetic acid is largely employed in several others cases ([1,12,18,20,21]). However, formic acid is still employed by Santacesaria *et al.* (^{17}) and in other few cases (^{13,17,19}). Moreover, it is to remind that acetic acid promotes the cleavage of the oxirane less than formic acid. In addition, the molar ratio between the acid and the double-bond is crucial because a low concentration of acetic acid does not permit a good transfer of oxygen to the oil, but a large amount of acid rapidly promotes the formation of by-product. This proportion has been well studied by Dinda *et al.* (^{11}) and Chavan *et al.* (^{21}) according to which the optimum value is 0.5:1, whereas other ratios (0.25 or 0.75) conduct to the cases earlier explained. This value is also adopted by Sniadinovic-Fiser *et al.* (^{18}) and corroborate the fact that this is a good value.

1.2.3 Concentration of the hydrogen peroxide

Hydrogen peroxide is employed at a high concentration in order to have a great reactivity. Dinda *et al.* (^{11}) use hydrogen peroxide at 50% wt., Santacesaria *et al*. (^{17}) and De Quadros *et al.* (^{13}) use hydrogen peroxide at 60%. Sepulveda *et al.* (^{4}) try hydrogen peroxide both at 70% and 100% (anhydrous) to demonstrate that the first case is the most effective and some water is necessary to the reaction. However, at such a high concentration the danger of explosion is not negligible and for this reason it is more reasonable to use hydrogen peroxide at lower concentration. In this case Jia, Gong *et al*. (^{19}), Sinadinovic-Fiser *et al.* (^{18}) uses hydrogen peroxide at 30% wt.

Moreover, like in the previous case, there is an optimum molar ratio between the hydrogen peroxide and the double-bond of the oil. The optimum molar ratio is between 1.5:1 and 2:1, as demonstrated by Dinda *et al* (^{11}). A greater amount of hydrogen peroxide makes the desiderate product less stable beacause of the cleavage of the oxirane. A lower molar ratio does not guarantee a sufficient amount of oxygen for the epoxidation. This value is adopted also by Sinadonivic-Fiser *et al.* (18) and by Chavan *et al.* (^{21}).

1.2.4 Effect of temperature, enthalpy of reaction and kinetic parameters

The process is usually carried out at a temperature within the range of 50°C and 70°C. Industrially, the temperature of 80°C is generally adopted as a threshold above of which emergency procedure are taken (^{13}). Because of the presence of the side reaction, the temperature cannot increase too much otherwise the kinetics of both reactions are so accelerated that the degradation of the oxirane is remarkable. In this case, fast conversion is obtainable but a low selectivity affects the process. At the contrary, if the temperature is too low, high selectivity with a low velocity of conversion characterize the process. For these reason according Dinda *et al.* ([11]) the optimum is at 60°C, that is adopted also by Santacesaria *et al.* ([17]), Leveneur *et al.* ([20]), Chavan *et al.* ([21]) and De Quadros *et al.* ([13]). Similarly, according to Sinadinovic-Fiser *et al.* (18) the optimum is at 50°C

A rigorous study of the enthalpy both of the main reaction and the side one was carried out by Leveneur *et al.* ([14]) using formic acid. According to them, the enthalpy of the main reaction is equal to -116 kJ/mol whereas the one of the side reaction was determined equal to -50 kJ/mol. To calculate these results they neglect the mass transfer because they suppose being in kinetic control and so they do not use the mass transfer coefficient. However, there is no great clarity about the enthalpy of the main reaction. In fact, according to De Quadros *et al.* ([13]) the enthalpy of the main reaction is equal to -196 kJ/mol, using formic acid. These data is within the range of the previous result and those delivered by Santacesaria *et al.* ([17]) that is equal to -230kJ/mol, using formic acid.

As concerns the kinetic parameters, i.e. the activation energies of both reactions, according to Leveneur *et al.* ([14]) they are equal to 99 kJ/mol and 34 kJ/mol for the main and the side reactions respectively. Similarly, according to Rangarajan *et al.* they are equal to76 and 66 kJ/mol for the main and the side reaction. The first data are obtained with formic acid whereas the second one are obtained with acetic acid.

This data set is well explained by Table 1.1.

Table 1.1. *Thermodynamic and kinetic data of the main and side reactions.*

	Rangarajan *et al* ([22]) (acetic acid)	De Quadros *et al* ([13]) (formic acid)	Leveneur *et al* ([14]) (formic acid)	Santacesaria *et al.* ([17]) (formic acid)
Enthalpy of main reaction		-196 kJ/mol	-116 kJ/mol	-230 kJ/mol
Enthalpy of side reaction		-	-50 kJ/mol	-
Activation energy of main reaction	76 kJ/mol	-	99 kJ/mol	-
Activation energy of side reaction	66 kJ/mol	-	34 kJ/mol	-

In conclusion, in order to summarize the route explained in this paragraph, the principal data useful to the process are reported in Table 1.2.

Table 1.2. *Recapitulatory table of the typical process conditions of the two-phase process.*

Temperature	H_2O_2 concentration	H_2O_2/double bond molar ratio	Formic-acetic acid/double bond molar ratio	Sulfuric-phosphoric acid concentration	Time required to maximum yield
50-70°C	30-60% wt.	1.5:1-2:1	0.5:1	0-2% wt	6-10h

1.3 Tri-phasic epoxidation: carboxylic acid, H_2O_2 and solid catalyst.

The process and the reactions are similar to what it was explained in the paragraph 1.2. This route consists in adding a solid acid catalyst instead of the liquid inorganic one. The idea is not so different from the previous route, but it is more complex because of the presence of third, solid phase. The catalysts that are used could be ion exchange sulfonated acid resins or alumina (that is in fact acid). This route is only experimental and it is not so wide-spread as the previous one.

1.3.1 Solid catalyst: ion exchange resin

This case is well studied Sinadinovic-Fiser *et al.* ([18]) and the method that is explained in this paragraph is based on their work. The process is carried out at 50°C using castor oil, acetic acid and hydrogen peroxide at 30% wt. of concentration and strong cationic exchange resin *Amberlite IR-120*. The castor oil is diluted with benzene (1:1 mass ratio) in order to decrease the viscosity especially when the conversion is high and to promote the diffusion of the oil in the resin. In addition, the dilution of the organic phase reduces the side reaction of epoxy ring opening. Moreover, the use of a resin as a catalyst instead of the inorganic acid prevents possible polymerization of the acid.

The acid chosen as carrier of oxygen is acetic acid instead of formic acid, for the reason about selectivity explained in the previous paragraph. The molar ratio between acetic acid and double bond is chosen equal to 0.5, as the previous method.

1.3.1.1 Effect of hydrogen peroxide/double bond molar ratio

Hydrogen peroxide at 30% wt. is utilized, with a molar ratio in respect to the double bond of the oil equal to 1.5. The authors have studied a lower molar ratio (to 1.1) and it was found that increasing the molar ratio from 1.1 to 1.5 increases the selectivity too. In fact, hydrogen peroxide boosts both the reactions, but especially the first one, with these molar ratios. If molar ratio is greater than 1.5 then selectivity gets worse because of the epoxy ring opening can easily occur.

1.3.1.2 Effect of the catalyst concentration

The formation of peroxyacetic acid is catalyzed by ion exchange resin, as confirmed also by Saha *et al* ([23]), and the more the catalyst is concentrated the faster is the reaction. The authors have tried different loading of resin (5, 10, 15% wt.) and the they have found that the maximum yield in epoxy content is obtainable in shorter time with greater loading of resin and that this maximum yield increases with the loading (Figure 1.5).

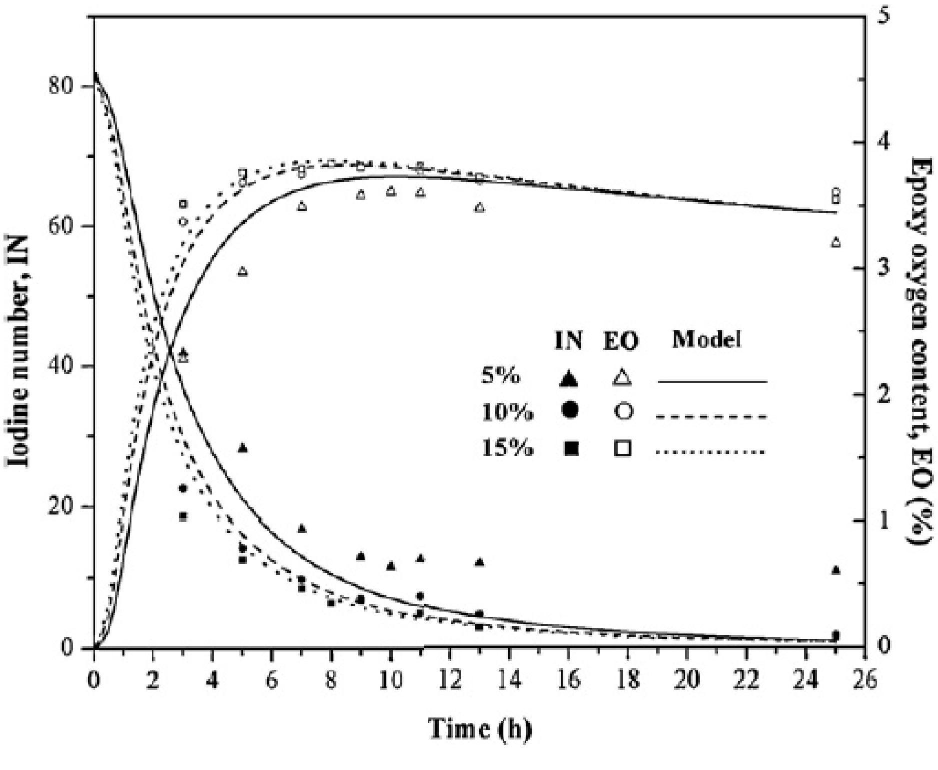


Figure 1.5. *Time dependency of experimentally determined (points) and calculated (curves) iodine number (IN) and epoxy oxygen content (EO) for in situ epoxidation of castor oil in benzene with peracetic acid, when molar ratio of double bond in oil:acetic acid:(30 wt%) hydrogen peroxide was 1:0.5:1.5, at 323 K in the presence of 5, 10 and 15 wt% of Amberlite IR-120.* ([18])

However, if there is a considerable difference between 5 and 10% of loading, there is a negligible difference between 10 and 15 %, so the optimum is considered 10 % because otherwise a greater cost of the catalyst is not payed back by a greater yield. Moreover, if the loading is larger than 15% it is possible to promote the cleavage of the oxirane.

1.3.1.3 Effect of the temperature

The temperature boosts both the main reaction and the side one. In this way, if in a hand the higher the temperature the lower is the time required to reach the maximum yield of oxirane, on the other hand the selectivity and the quality of the product decreases with it. The authors have tried three different temperatures, 30, 50, 75 °C and the optimum has been found at 50°C.

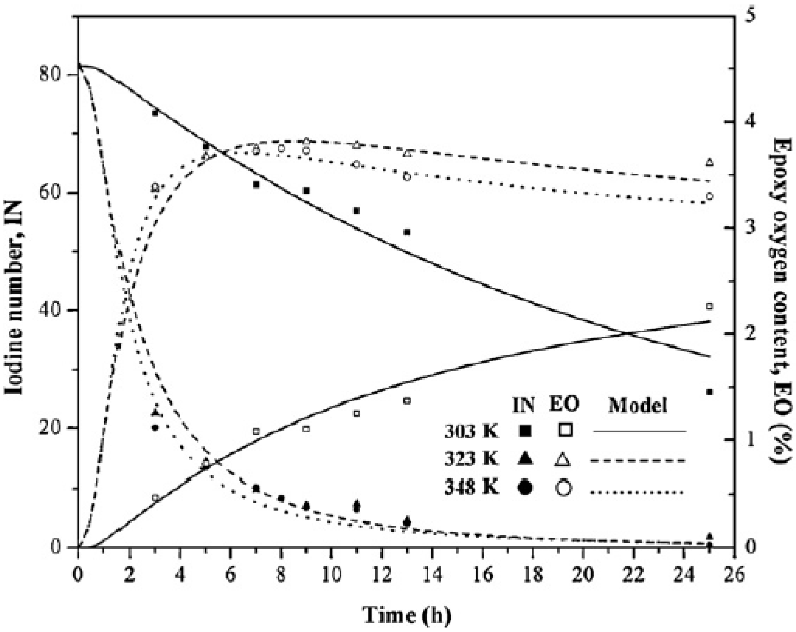


Figure 1.6. *Time dependency of experimentally determined (points) and calculated (curves) iodine number (IN) and epoxy oxygen content (EO) for in situ epoxidation of castor oil in benzene with peracetic acid, when molar ratio of double bond in oil:acetic acid:(30 wt%) hydrogen peroxide was 1:0.5:1.5, in the presence of 10 wt% of Amberlite IR-120 at 303, 323 and 348 K (18)*

The maximum conversion to epoxide that has been obtained was equal to 77.91% at 50°C in 9 hours. The quality obtained at 30°C has been slightly better but the optimum appears at 50°C.

1.3.1.4 Reusability of the catalyst

The catalyst can be reutilized with a little decrease on the rate of conversion and on selectivity. In this way, the maximum yield decrease with the number of runs of the catalyst and a greater time to obtain this maximum is needed. This aspect has been studied by the same authors (Figure 1.7).

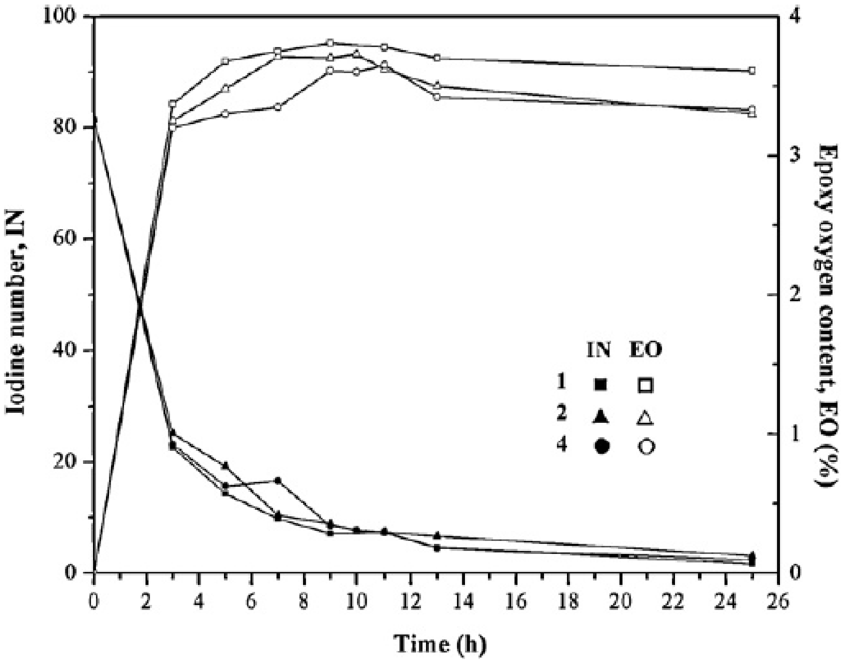


Figure 1.7. *Effect of the catalyst's recycling (1, 2 and 4 times used) on the epoxidation of castor oil in benzene with peracetic acid, when molar ratio of double bond in oil:acetic acid:(30 wt%) hydrogen peroxide was 1:0.5:1.5, in the presence of 10 wt% of Amberlite IR-120 at 323 K (*[18]*)*

After four times, the yield in the epoxide is only 4% lower and can be reached with a time shift of 2 hours. In conclusion, the quality of the product is not affected very much but the conduction of the product changes a lot.

In conclusion, in order to summarize the main variable of the process, the Table 1.3 is reported.

Table 1.3. *Recapitulatory table of the optimal values of the process variables. Three-phases process carried out in presence of ion exchange resin as catalyst.*

Oil	Temperature	H_2O_2 concentration	H_2O_2/double bond molar ratio	Formic-acetic acid/double bond molar ratio	Massive ratio catalyst/oil	Time required to maximum yield
Castor oil	50°C	30% wt.	1.1:1-1.5:1 (better 1.5)	0.5:1	5-15% (better 15)	6h

1.3.2 Solid catalyst: alumina

This method has been studied by Sepulveda *et al.* (4) and it uses alumina as a solid catalyst thanks to its acid behavior. This process is slightly different from the previous one because it does not employ a carboxylic acid but ethyl-acetate. Moreover, it uses methyl-esters after esterification of the oil and not virgin vegetable oil. However, this route is reported because it represents an interesting way to obtain the desiderate product. The vegetable compounds taken in account by the authors are methyl oleate and methyl esters of soybean oil; the hydrogen peroxide is at 70% wt. of concentration. The process is carried out at 80°C and the massive ratio between oil and catalyst is 5.

1.3.2.1 Effect of different alumina catalysts

In the case of the epoxidation of methyl oleate, the authors have tried different kinds of alumina (Sol-gel, Acros and Fluka) with aqueous hydrogen peroxide. As earlier mentioned, acidic sites are responsible of the catalysis and different catalytic activities has been observed for each kind of alumina. In Figure 1.8, a plot is reported representing the conversion versus time.

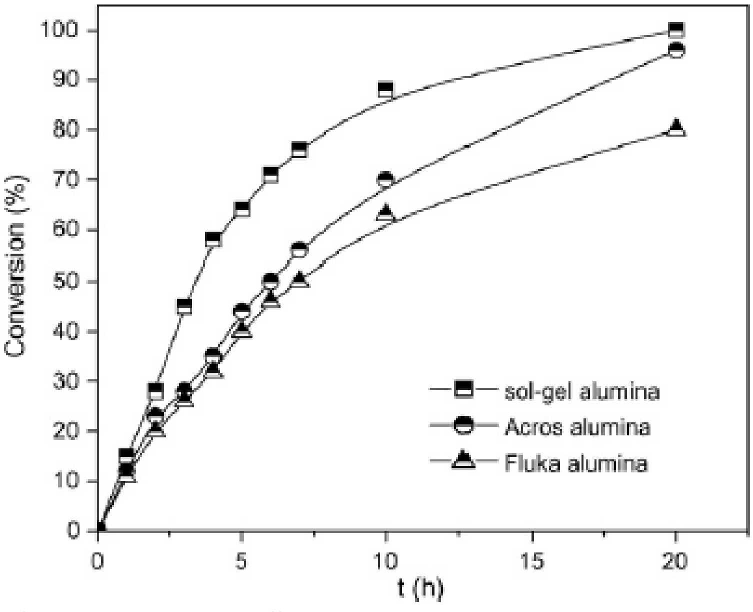


Fig. 1.8. *Epoxidation of methyl oleate using different aluminas. Conditions:aqueous H_2O_2/oleate = 2 (mol/mol); methyl oleate/catalyst = 5 (w/w);80°C (4)*

The different activities can be explained carrying out a BET analysis, and the main difference that is responsible of this fact is the different surface area per unit of mass (Table 1.4)

Table 1.4. *BET surface of the aluminas (sol-gel, Acros and Fluka) used in the expoxidation of methyl oleate.*

Alumina	BET surface area [$m^2\ g^{-1}$]
Sol-gel	280
Acros	200
Fluka	195

1.3.2.2 Effect of methyl oleate/hydrogen peroxide molar ratio

The authors have studied different molar ratios between methyl oleate and hydrogen peroxide. This study is reported in Figure 1.9.

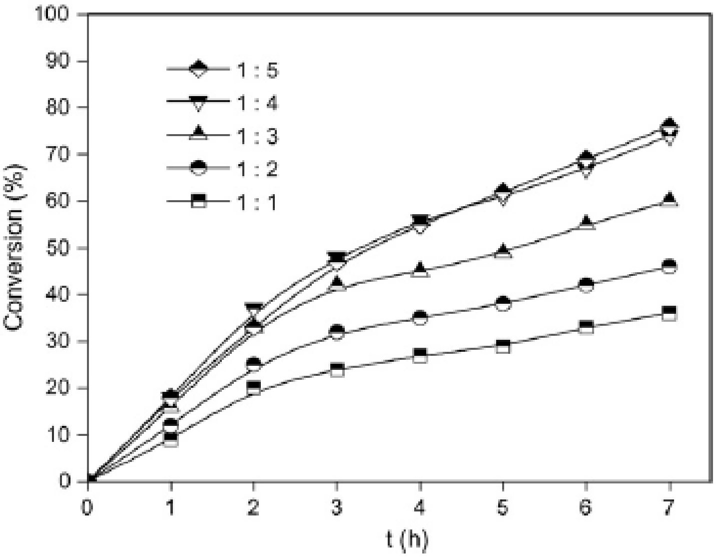


Figure 1.9. *Effect of methyl oleate/H_2O_2 molar ratio in the epoxidation of methyl oleate with Acros alumina. Conditions: methyl oleate/catalyst = 5 (w/w); 80°C ([4]).*

A molar ratio of 1:4 is sufficient to guarantee an appropriate conversion. The excess of hydrogen peroxide is needed because of the partial decomposition of it that is catalyzed by the alumina.

1.3.2.3 Epoxidation of methyl esters of soybean oil

In the case of epoxidation of methyl esters of soybean oil, Acros alumina is used. The methyl linolenate was totally epoxidized after 6 hours whereas the methyl linoleate was converted at 87% after 9 hours. These data are reported in Figure 1.10, referring to results obtained with methyl oleate. The selectivity was better than 97% for the esters.

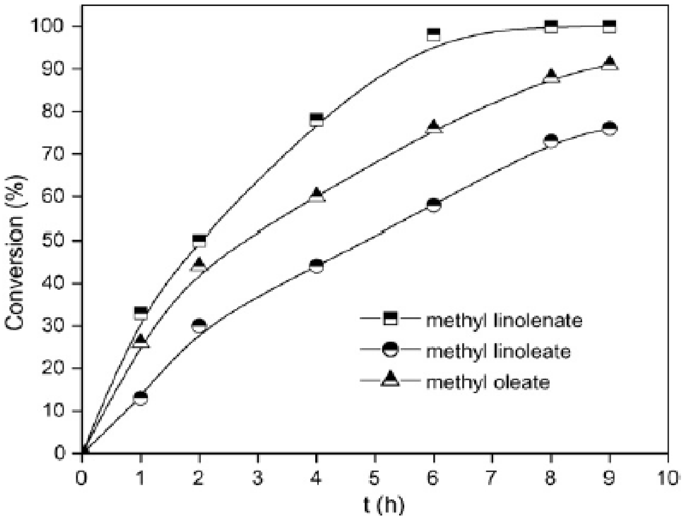


Figure 1.10. *Epoxidation of methyl esters of soybean oil with Acros alumina. Conditions: H_2O_2/soybean methyl esters = 4 (mol/mol); 2.5 g of methyl esters; substrate/catalyst = 8 (w/w); 80°C (^{4}).*

1.3.2.4 Reusability of the catalyst

The authors have carried out different tests to evaluate the reusability of the catalyst in the case of Acros and sol-gels aluminas. Epoxidizing methyl oleate, sol-gel alumina presents a small loss in conversion (Figure 1.11 a) and negligible difference in selectivity. As concerns the Acros alumina, a more rapid deactivation is observed, reaching 50% of conversion after three runs. (Figure 1.11 b).

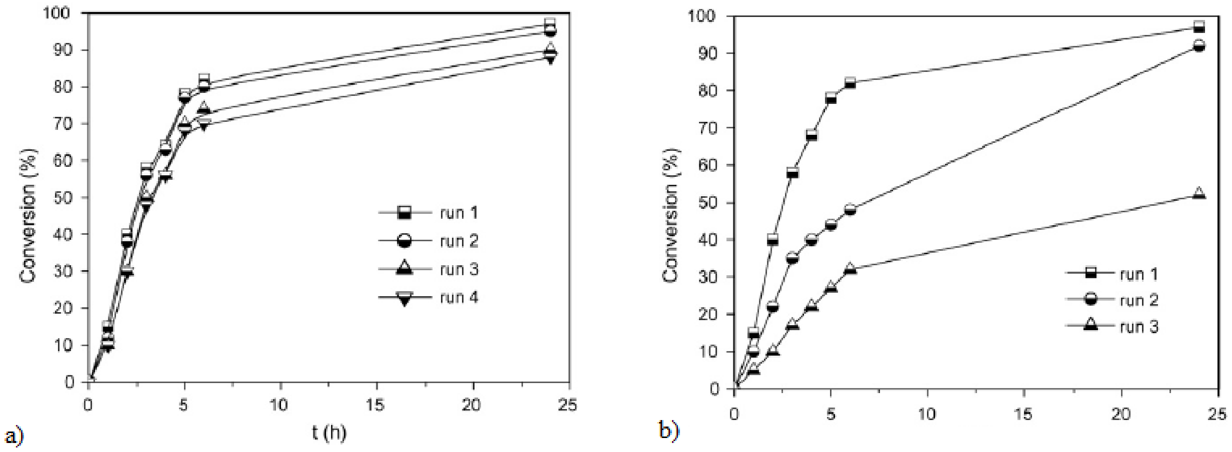


Figure 1.11 *Recycling of the sol–gel alumina (a) and Acros alumina (b) in the epoxidation of methyl oleate. Conditions: substrate/catalyst = 5 (w/w); aqueous H_2O_2/oleate = 4 (mol/mol); 80°C (^{4})*

In conclusion, in order to summarize the main variable of the process, the Table 1.5 is reported.

Table 1.5. *Recapitulatory table of the optimal values of the process variable. The process is carried out in presence of alumina as catalyst.*

Oil (methyl esters)	Temperature	H_2O_2 concentration	H_2O_2/double bond molar ratio	Massive ratio oil/catalyst	Time required to maximum yield
Soybean oil	80°C	70% wt.	4:1	5:1	6-10 hours

1.4 Multi-phase electrochemical epoxidation

The multi-phase electrochemical epoxidation is completely different from the other methods and it has been deeply studied with by Li *et al.* (^{15}). All the explanation and the figures are made by these authors and are taken from their work. The oil taken in account is castor oil. This method is based on an electrochemical synthesis and it presents the great vantage that the reaction is completely and easily controllable by controlling the current flowing in the cell. The equipment is made of an electrochemical cell, an oxygen bubbler, a temperature control device and a DC regulated 30V-10A power supply (not a potentiostat / galvanostat but simply a DC supply). The cell contains two compartments, divided by an ion exchange membrane. The electrodes are made in graphite for the cathode and in $Ti/SnO_2 + Sb_2O_4/PbO_2$ for the anode. Each compartment has a volume of 300mL and both of them has been filled with 40g of oil, formic acid and 3mL of hydrochloric acid. The molar ratio between castor oil double bonds and formic acid is in the range of 6 and 10. The pH is adjusted in the range 5-7 by adding $NaHCO_3$ (sodium bicarbonate). The temperature at which the process is carried out is between 20 and 40°C and the power supply is controlled by current, in order to have a current density between 0.1 and 0.5 Acm^{-2}. The oxygen is bubbled at a constant rate of 1 to 5 cm^3/s. After the reaction, the oil is washed with distilled water and vacuum distilled.

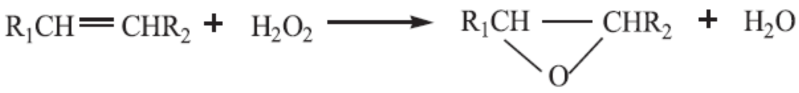
1.4.1 – Mechanism of reaction

The process is made of several steps and the synthesis of the epoxide can occur in both of the compartments. As concerns the cathodic compartment, the route hypothesized by the authors is as follows.

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \qquad (1.6)$$

$$HCOOH + H_2O_2 \xrightarrow{H^+} HCOOOH + H_2O \tag{1.7}$$

(1.8)

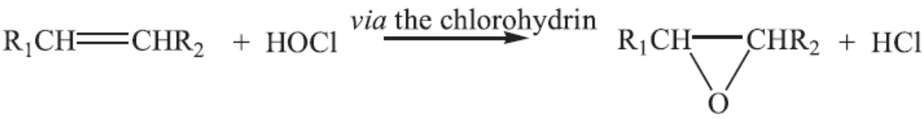


(1.9)

As concerns the anodic compartment, the route hypothesized by the authors is as follows.

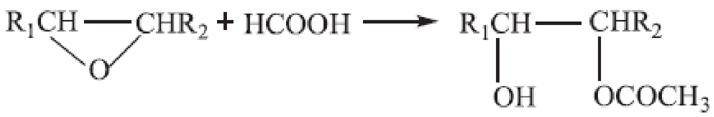
$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1.10}$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \tag{1.11}$$

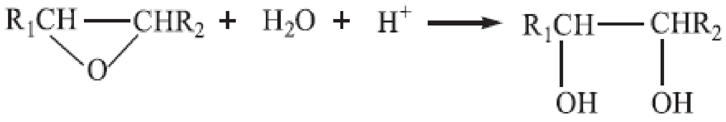


(1.12)

As concerns the side reaction (epoxy ring opening) the reactions are as follows.



(1.13)



(1.14)

The same mechanism is graphically represented by the authors by the Figure 1.12.

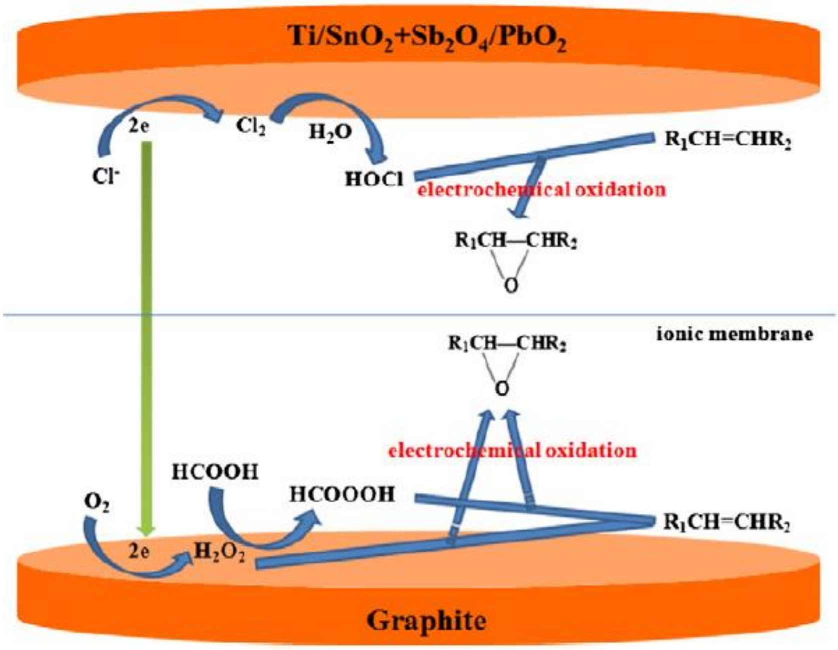


Figure 1.12. *Schematic representation of the electrochemical epoxidation of unsaturated fatty acids (* [5] *).*

In this way, the hydrogen peroxide is not introduced but it is formed in situ by electrochemical synthesis. This is a huge advantage because handling hydrogen peroxide always introduces a danger of explosion because of its decomposition. In this case the production of this chemical is precisely controlled by controlling the current. Hydrogen peroxide reacts with formic acid generating peroxyformic acid, under acid catalysis. At this point, peroxyformic acid reacts with the double bond forming the epoxy ring and returning formic acid. The epoxidation can occur at the anodic compartment too. In fact, thanks to the presence of hydrochloric acid, the electrochemical formation of molecular chlorine from chlorine ion is possible. Molecular chlorine can react with an equilibrium reaction with water, forming hypochlorous acid and chloric acid. Hypochlorous acid can react with the double bond of the oil and via chlorohydrin the epoxy ring and chloric acid. This route is similar to the one used for epoxidation of ethylene by forming chlorohydrin; this method was exploited in the past in order to obtain ethylene oxide.

1.4.2 – Effect of pH

The influence of the pH is remarkable and the optimum is at 6.5 as it can be seen in Figure 1.13.

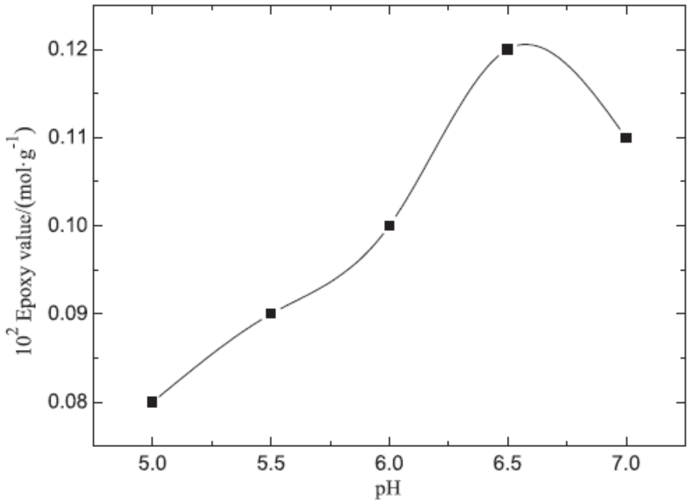


Figure 1.13. *Effect of pH on electrochemical epoxidation of castor oil. (25 °C temperature, 3 h reaction time, 3 cm3 s−1 passing oxygen rate, 8Mratio of castor oil double bonds to HCOOH and 0.3 A cm−2 current density).(*[15]*)*

As concerns the pH in the catholyte, the authors explain that this effect probably results from the influence on the production of hydrogen peroxide and formic acid in the catholyte. It is to remind that the pH regulates the dissociation of formic acid $HCOOH$ to $HCOO^-$ and H^+. If pH is too low, below 6.5, $HCOOH$ is predominant and it does not lead to epoxy formation. At the contrary, $HCOO^-$ is predominant at pH higher than 7 and it is detrimental to the formation of hydrogen peroxide. In this way, increasing the pH means to speed up the epoxidation but makes more difficult the generation of H_2O_2. In consequence, a compromise must be found. However, as concerns the epoxy formation, this explanation does not agree with what said in the previous methods. It could depend on the so different methods of synthesis of the oxirane (chemical vs electrochemical).

As concerns the anolyte, the pH has the reverse effect, i.e. the epoxidation is faster in presence of HOCl, thus with a low pH.

1.4.3 – Effect of time

The influence of time is remarkable as concerns the cleavage of epoxy ring (reactions (13) and (14)). As can be seen in Figure 1.14, according the authors, the maximum epoxy value can be obtained at a reaction time of 3 hours.

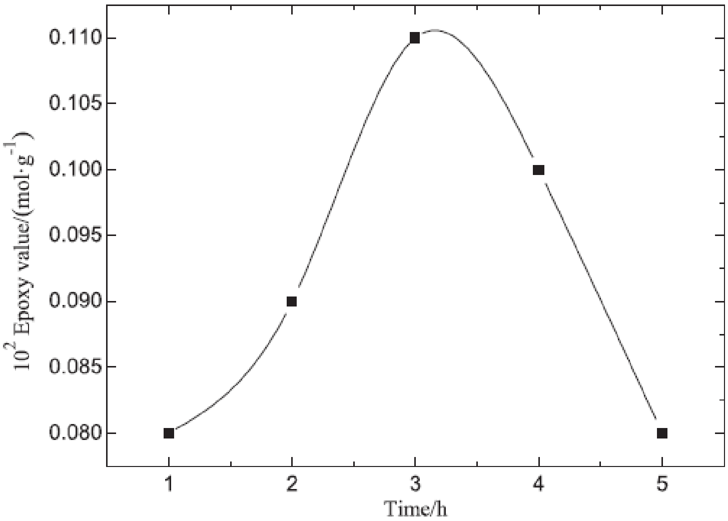


Figure 1.14. *Effect of the reaction time on electrochemical epoxidation of castor oil (pH 6.5, 25 °C temperature, 3 cm3 s−1 passing oxygen rate, 8 M ratio of castor oil double bonds to HCOOH and 0.3 A cm−2 currentdensity).*

This evidence can be explained with the fact that the concentration of epoxide increases with time whereas the concentration of double bond decreases. In this way the main reaction becomes slower whereas the opening epoxy ring accelerates.

1.4.4 – Effect of temperature

The effect of the temperature on the epoxy content can be seen in Figure 1.15, the maximum is obtained at 25°C. This value is considered the optimum.

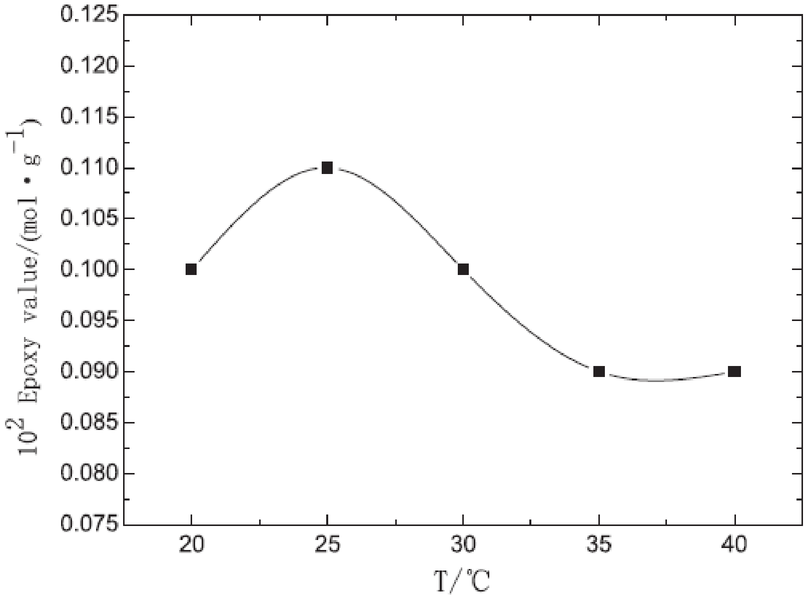


Figure 1.15. *Effect of reaction temperature on electrochemical epoxidation of castor oil (pH 6.5, 3 h reaction time, 3 cm3 s−1 passing oxygen rate, 8 M ratio of castor oil double bonds to HCOOH and 0.3 A cm−2 current density).(*[15]*)*

A lower value of epoxy content with respect to the maximum can occur both at temperatures lower or higher than 25°C (optimum) for different reasons. At low temperature (20°C) the rate of all the reactions is lower. Hence, the lower value is mainly due to the lower rate of epoxidation. Whereas, with temperature higher than 25°C the unwanted reactions become faster than the epoxidation one.

1.4.5 – Effect of oxygen bubbling rate

The effect of the volumetric rate of oxygen is represented in Figure 1.16.

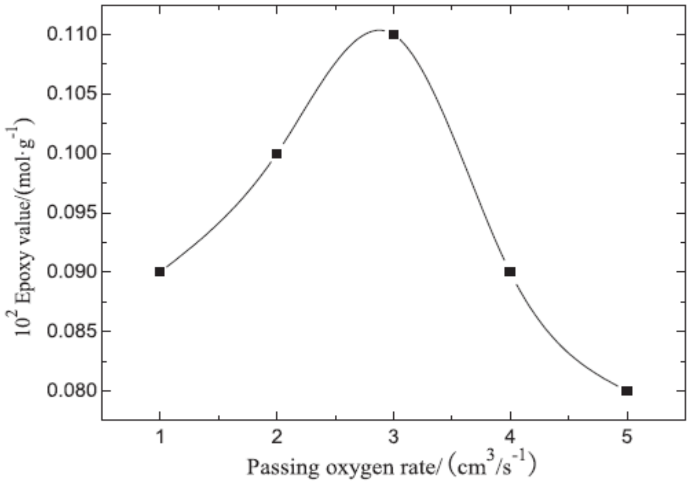


Figure 16. *Effect of passing oxygen rate on electrochemical epoxidation of castor oil (pH 6.5, 25 °C temperature, 3 h time, 8Mratio of castor oil double bonds to HCOOH and 0.3 A cm−2 current density). ([15])*

The epoxy value has a maximum when 3 cm^{3}s^{-1} of oxygen are bubbled in the cell. At lower rate, the amount of H_2O_2 and, in consequence, of $HCOOOH$ formed in the catholyte is lower. At higher volumetric rates, the hydrogen peroxide that is produced is so abundant that the formation of diols is promoted.

1.4.6 – Effect of double bonds / formic acid molar ratio

This effect of double bonds / formic acid molar ratio is graphically represented in Figure 1.17.

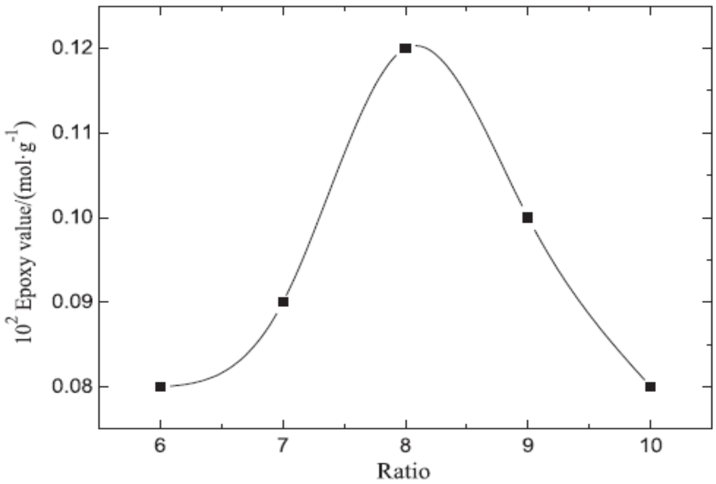


Figure 1.17. *Effect of molar ratio of castor oil double bonds to HCOOH on electrochemical epoxidation o castor oil (pH 6.5, 25 °C temperature, 3 h reaction time, 3 cm3 s−1 passing oxygen rate and 0.3 A cm−2 current density). ([15])*

The molar ratio between the oil and the formic acid influences the epoxy content a lot. The optimum can be found at molar ratio equal to 8. As in the case of two-phase chemical epoxidation, a lower amount of HCOOH does not permit a good rate of epoxidation. At the contrary, a higher amount of formic acid promotes the side reactions of epoxy ring opening.

1.4.7 – Effect of current density

The effect of the current density is represented in Figure 1.18.

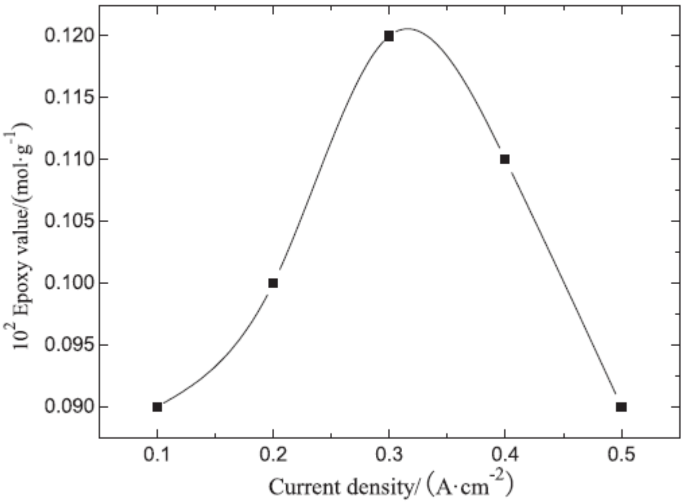


Figure 1.18. *Effect of current density on electrochemical epoxidation of castor oil (pH 6.5, 25 °C temperature, 3 h reaction time, 3 cm3 s−1 passing oxygen rate and 8 M ratio of castor oil double bonds to HCOOH).([15]).*

The optimum can be found at 0.3 Acm^{-2}. With lower current density a lower amount of hydrogen peroxide is produced and in consequence less peroxyformic acid is formed. This fact means a lower rate of epoxidation. At higher current density, side reactions as the production of molecular chlorine and oxygen at anode or molecular hydrogen formation at cathode (at the expense of H_2O_2) became important.

In conclusion, in order to summarize the main variable of the process, Table 1.6 is reported.

Table 1.6. *Recapitulatory table of the optimal values of the process variables. The process is carried out via electrosynthesis.*

Oil	Temperature	pH	Double bond / formic acid molar ratio	Bubbling rate (oxygen)	Current density	Time required to maximum yield
Castor oil	25°C	6.5	8:1	3 cm^3/s	0.3 A/cm^2	3 hours

1.5 Combined methods enhanced by ultrasound or dielectric heating

These methods are based on the previous ones, with the difference that they are enhanced by ultrasound or dielectric heating. The two methods are intended to improve the mass transfer between the inorganic and the organic phase.

As concerns the ultrasound route, few literature follows this way, essentially Chavan *et al.* ([12,21]), who have studied the matter previously in presence of phase transfer catalyst and successively with ion exchange resin. In this case the sonication causes cavitation that implies the formation of local intense peaks of pressure and temperature. This excitation could promote the mass transfer between phases.

As regards the epoxidation under radiowave irradiation, Leveneur ([20]) *et al.* and Aguilera *et al.* ([1]) have deeply studied the argument. In this case, the ε'' (responsible of the dielectric loss) is different for the two phases and so a non-homogeneous heating is obtained (much more intense in the aqueous phase). In consequence, a thermal gradient takes place between the two phases and the mass transfer is promoted.

1.5.1 – Ultrasonic epoxidation with phase transfer catalyst

As previously mentioned, this route was studied by Chavan *et al.* ([12]). The processed oil is soybean oil. The carrier of oxygen is acetic acid (acetic acid to unsaturation molar ratio 0.5:1), hydrogen peroxide at 30% wt. is used (hydrogen peroxide to unsaturation molar ratio 1.5:1), sulfuric acid is added as liquid catalyst (3%), tetra-n-butylammonium bromide is used as phase transfer catalyst *PTC* (*PTC* to unsaturation molar ratio 1:1). The process is carried out at 50°C. The sonication occurs thanks to the direct immersion of ultrasound horn in the reactor (500 ml), that sonicates the reaction mixture with waves at 25 kHz.

1.5.1.1 – Effect of pulse of ultrasound

The authors have studied the influence of the pulse of ultrasound, intended as 5 seconds ON and 5 seconds OFF, 10 seconds ON and 5 seconds OFF, 15 seconds ON and 5 OFF. It was found an improvement in the conversion, 81.5%, 83% and 84% respectively (after 4 hours), even if marginal. This aspect can be due to the more intense cavitational activity that is obtainable with longer pulse of ultrasound. Moreover, the influence of the pulse is much more noticeable in the early stages (1 hours) than after several hours. In addition, it was found that the relative percentage conversion of oxygen to oxirane decreases with an increase of the duration of the ultrasound pulse. In fact, this conversion passes from 83.5% for 5s ON and 5s OFF, to 76% for 10s ON and 5s OFF and 69.5% for 15s ON and 5s OFF after 4 hours. In consequence, the more intense cavitational activity do promote the side reactions with formation of α-glycol as it can be seen from Table 1.7.

Table 1.7. *Conversion of double bonds and relative conversion to oxirane oxygen for pulse of ultrasound at 25kHz.*

Duration	Conversion of double bonds (after 4 hours)	Relative conversion to oxirane oxygen (after 4 hours)
5s ON 5s OFF	81.5%	83.5%
10s ON 5s OFF	83%	76%
15s ON 5s OFF	84%	69.5%

1.5.1.2 – Effect of power of ultrasound

Three different power intensity was applied, 65.5, 91 and 110 watts. It was found that the more intense is the sonication, the higher is the conversion of the double bonds (Table 1.8). In addition, the relative conversion to oxirane oxygen increases with the power for 65.5 W and 91 W but decreases at 110 W (63.5%, 75% and 71.5% respectively, after 4 hours). A higher ultrasound power causes a cavitational activity so intense to promote the side reactions that bring the product to degradation (glycol).

Table 1.8. *Conversion of double bonds and relative conversion to oxirane oxygen for different levels of power of ultrasound.*

Power [W]	Conversion of double bonds (after 4 hours)	Relative conversion to oxirane oxygen (after 4 hours)
65.5	72.5%	63.5%
91	84.5%	75%
110	85.5%	71%

1.5.1.3 – Addition of a mechanical stirring system

The authors have tried a six-bladed turbine impeller to stir the reaction mixture. In this way, a study about the synergic effect of both stirring and ultrasound can carried out. The velocity of the impeller is equal to 300 rpm and both 25 kHz and 40 kHz ultrasound are tried. The results about the relative conversion to oxirane oxygen in presence of only ultrasound or in combination with stirring are reported in Table 1.9.

Table 1.9. *Relative conversion to oxirane oxygen after 8 hours in presence of absence of mechanical stirring.*

Time [h]	25kHz	40 kHz	25 kHz + 300 rpm	40kHz + 300 rpm
0	0	0	0	0
2	14.5	13	16	18.5
4	14.5	15.5	17	20
6	16	16.5	19	22
8	16.5	17.5	19.5	23

The addition of mechanical stirring increases the relative conversion of oxirane oxygen from 16.5 to 19.5 in the case of 20 kHz ultrasound and from 19.5 to 23 in the case of 40 kHz ultrasound. This fact is probably due to the improvement of the mass transfer.

In conclusion, in order to summarize the main variable of the process, Table 1.10 is reported.

Table 1.10. *Recapitulatory table of the optimal values of process variables. The process is carried out in the presence of a phase transfer catalyst and ultrasound irradiation.*

Temperature	H_2O_2 concentration	H_2O_2/double bond molar ratio	Acetic acid/double bond molar ratio	Sulfuric acid massive ratio
50°C	30% wt.	1.5:1	0.5:1	3%

Oil	PTC/double bond molar ratio	Ultrasound frequency	Ultrasound power	Ultrasound pulse	Time required
Soybean	1:1	25-40 kHz	200W/l (approx.)	5s ON, 5s OFF	4 hours

1.5.2 – Ultrasound epoxidation with Ion Exchange Resin

As the previous one, this route was studied by Chavan *et al.* (21). In this work the authors have studied the epoxidation of sunflower oil in the presence of an Ion Exchange Resin and this method represents an intensification of the route exposed in § 1.3 (tri-phase epoxidation). The carboxylic acid is acetic acid, hydrogen peroxide at 30% wt. is used and ion exchange resin Indion 225H is used as catalyst. The process is carried out at 60°C, the resin loading is 16% wt. of sunflower oil, the pulse of ultrasound is 5 seconds ON and 5 seconds OFF. Hydrogen peroxide to double bond molar ratio is 1.5:1 and acetic acid to double bond molar ratio is 0.5:1. The volume of the reactor is 300 ml.

1.5.2.1 – Effect of power of ultrasound

The authors have studied the effect of different ultrasonic power applied to the sample, 70, 80 and 90W. The results are indicated in Figure 1.19 and in Table 1.11. It is possible to see that after 7.5 hours, the conversion of the double bond is equal to 44.9, 44.3 and 61.7% for the three levels of power respectively. Relative percent conversion to oxirane oxygen is equal to 25.1%, 28.9% and 36.4% respectively. Also the side reactions are promoted by the excitation by ultrasound, in fact the relative conversion to α glycol is equal to 16.3%, 21.4% and 25.8% respectively. It can be said that, when the ultrasound power is increased, the probability that a cavitation event can occur increases. Due to this increase in the cavitational activity that enhances the mass transfer, all the reactions are promoted, both desired and undesired ones.

Table 1.11. *Conversion of double bond, relative conversion to oxirane oxygen and relative conversion to α-glycol after 7.5 hours for different power of ultrasound dissipation*

Power [W]	Conversion of double bonds (after 7.5 hours)	Relative conversion to oxirane oxygen (after 7.5 hours)	Relative conversion to α-glycol (after 7.5 hours)
70	44.9%	25.1%	16.3%
80	44.3%	28.9%	21.4%
90	61.7%	36.4%	25.8%

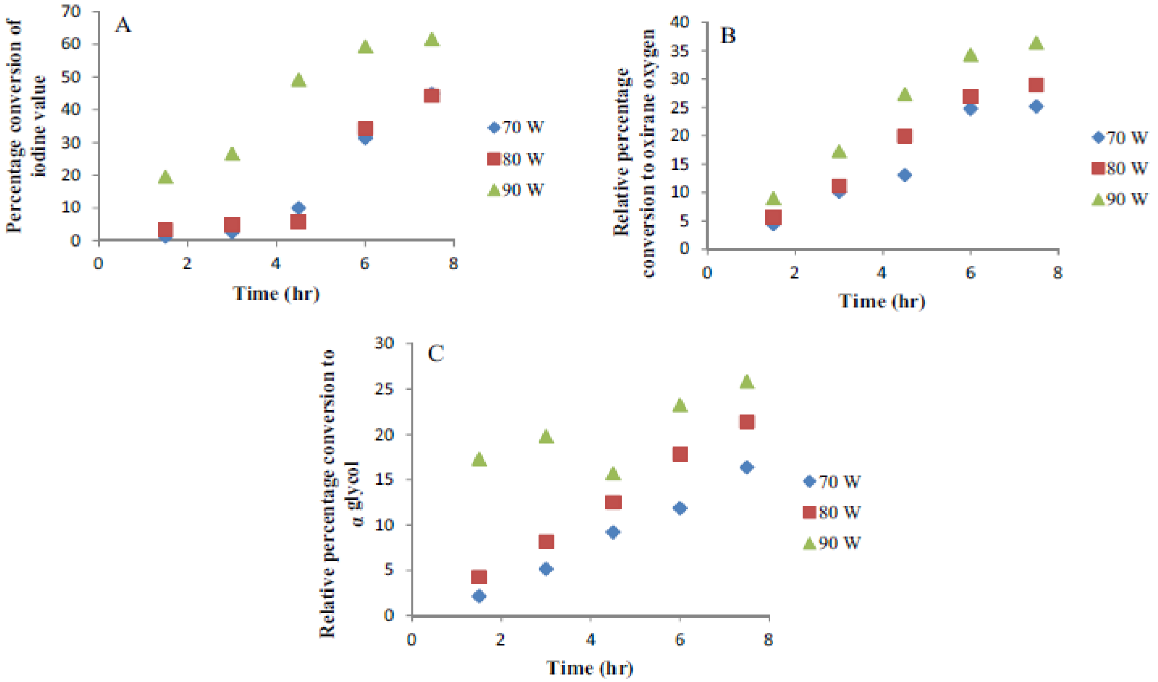


Figure 1.19. *Conversion of double bond (a), relative conversion to oxirane oxygen (b) and relative conversion to α-glycol versus time (c), parametric to the ultrasound power applied to the sample ([21])*

Thanks to this results, the optimal power can be found at 90W.

1.5.2.2 – Effect of temperature

The authors have studied the effect of the temperature, at 50°C, 60°C and 70°C. The conversion of the double bond and the relative conversion to oxirane oxygen increases when the temperature is increased from 50°C to 60°C whereas a marginal decrease occur further increasing to 70°C (Figure 1.20).

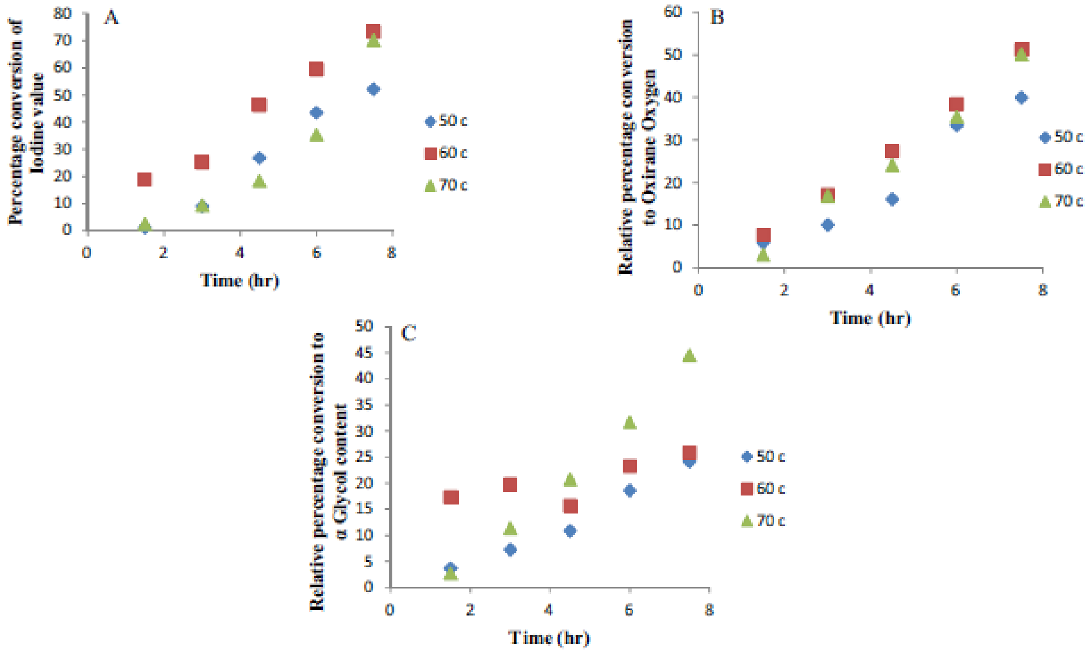


Figure 1.20. *Conversion of double bond (a), relative conversion to oxirane oxygen (b) and relative conversion to α-glycol versus time (c), parametric to the temperature* ([21])

This fact can be explained with the decrease in the cavitational activity at higher temperature due to the formation of vaporous cavities. Moreover, temperature boosts all the reactions and a larger quantity of α glycol can generate (Figure 1.20 C). For these reasons, the optimal temperature is at 60°C.

1.5.2.3 – Effect of catalyst loading

The effect of catalyst loading has been studied by the authors, imposing the ultrasound power at 90W and the temperature at 60°C. The other specifications are the same of that ones that were initially indicated. The catalyst loading was tested at 10, 15, 20, 25% wt. of the mass of sunflower oil. The results are reported in Figure 1.21.

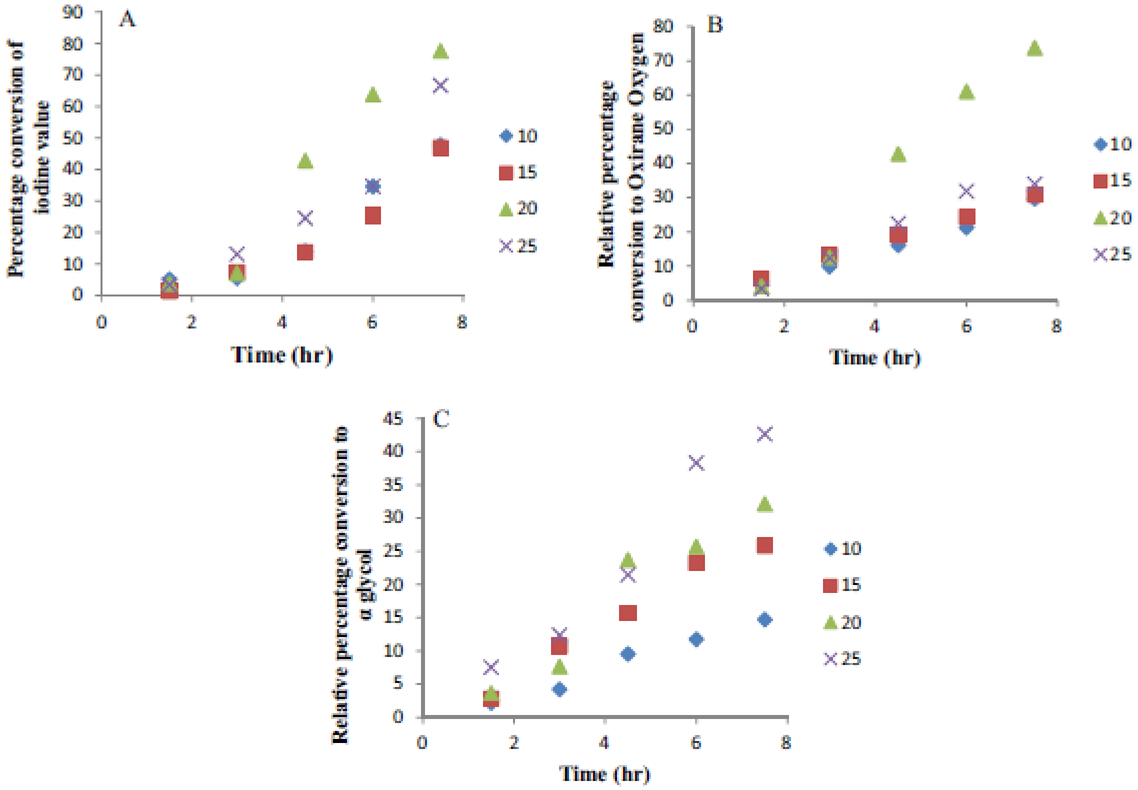


Figure 1.21. *Conversion of double bond (a), relative conversion to oxirane oxygen (b) and relative conversion to α-glycol versus time (c), parametric to the catalyst loading (*[21]*)*

It can be observed that, increasing the catalyst loading, an increase in double-bonds conversion and in the oxirane formation is noticeable up to 20%. At 25% the side reactions are so promoted that the epoxy ring opening can easily occur and the degradation of the product takes place. In consequence, the optimal loading is 20% of the oil.

1.5.2.4 – Effect of pulse of ultrasound

The effect of pulse of ultrasound has been studied by the authors. The specifications are the same of the previous points and the loading of the catalyst is chosen at its optimum (20%). The pulse that has been tested are 5 seconds ON, 5 seconds OFF and 10 seconds ON, 5 seconds OFF. It has been observed that the double bonds conversion is more or less the same in both cases whereas the relative conversion to oxirane oxygen is noticeably higher in the first case than the second one (73.8% and 32.2% respectively). Moreover, the relative conversion to α glycol is lower in the first case than in the second one (25.8% and 46%). It appears evident that larger duration of the pulse implies a higher possibility of the epoxy ring cleavage because of the longer duration of the cavitation activity. In conclusion, shorter pulses of ultrasound are beneficial, and 5s ON and 5s OFF is assumed as optimum.

1.5.2.5 – Combination of ultrasound bath with mechanical agitation

This possibility is considered because in absence of stirring the cavitational activity is concentrated in the proximity of the ultrasound horn. Stirring homogenizes the reaction mixture, reducing the proximity effect. In order to the test this possibility, the authors have employed an ultrasound bath at the available frequency of 40 kHz instead of 20 kHz, whereas the other conditions have been kept constant to that ones previously adopted. The results that has been obtained are reported in Figure 1.22.

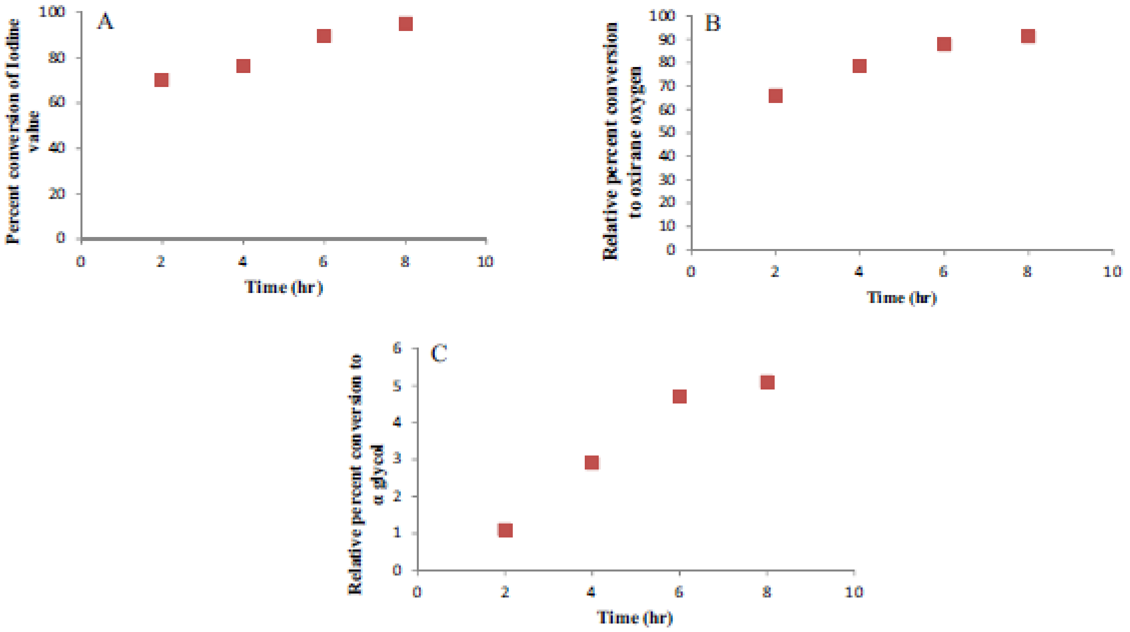


Figure 1.22. *Conversion of double bond (a), relative conversion to oxirane oxygen (b) and relative conversion to α-glycol versus time (c) in presence of both ultrasound sonication (40 kHz) and mechanical agitation (*[21]*).*

The conversion of the double bonds after 8 hours is equal to 95.3% whereas the relative conversion to oxirane oxygen is equal to 91.1%; both results are about 10% higher than ones obtainable without stirring. Relative percent conversion to α glycol is about 5% which is at least 5 times lower than in the case without mechanical agitation. In these way an optimal conversion of the double bonds can carried out, with minimal degradation of the product (high economical value). It appears evident that the combination of ultrasonic bath and mechanical agitation permits a controlled generation of the cavitation conditions at moderate intensity, which decreases the excess of cavitational activity in the proximity of the horn and in this way the epoxy ring opening is prevented. Moreover, the mechanical agitation permits an adequate mixing in the reactor, since the simple sonication cannot manage in this role. In conclusion, with this experimental set up, not the direct ultrasound irradiation (in the proximity of the transducer) but the indirect irradiation helps noticeably the conversion to oxirane oxygen highly preventing side reactions.

In order to summarize this method, the principal process variable are reported in Table 1.12.

Table 1.12. *Recapitulatory table of the optimal values of process variables. The process is carried out with ion exchange resin as catalyst under ultrasound irradiation.*

Temperature	Oil	H_2O_2 concentration	H_2O_2/double bond molar ratio	Acetic acid/double bond molar ratio	Ion exchange resin
60°C	Sunflower	30% wt.	1.5:1	0.5:1	Indion 225H

Ion exchange resin loading	Ultrasound frequency	Ultrasound pulse	Ultrasound power	Time required to maximum yield	Mechanical agitation
20%	25-40 kHz	5s ON, 5s OFF	300 W/l	8 hours	Highly required

1.5.3 – Epoxidation under microwave irradiation

This route has been studied by Leveneur *et al.* ([20]) and successively by Aguilera *et al.* ([1]). However, in this case only the first work is considered and the information that are reported in this paragraph are taken only from that work. The frequency of microwave (MW) irradiation that is used in this case is 2.45 GHz, that is the typical frequency for this operation. The generation of MW is carried out by a 2kW magnetron. The process is carried out at 60°C and acetic acid is chosen as oxygen carrier. A mechanical agitator is needed and its velocity is varied from 300 to 650 rpm. The fat acid taken into account is oleic acid. The initial amount of carboxylic acid varies from 0 to 30 % wt. whereas hydrogen peroxide from 3 to 10% wt. Since MW power absorption strictly depends on ε'' of the aqueous phase (the dielectric loss of the oil is negligible), the ratio between the two phases is critical. The authors have tried amount of oil with respect to the total mixture between 30 and 70% wt.

It is useful to remember that dielectric properties of both oil and water change a lot with temperature and with the extent of the reaction. According the authors, in the case of soybean oil $\varepsilon'=2.8$ and $\varepsilon''=0.15$. In the case of distilled water, according Lupi ([25]) ε' at 60°C is equal to 64 and ε''=4.9, however this values change if some salt is dissolved (ε'=67 and ε''=41.87) especially ε'' because of the increasing of the conduction contribute to dielectric loss. Since an aqueous solution is employed (not distilled water), ε'' of the aqueous phase is most likely two order of magnitude greater than the one of the oil. In conclusion, the dielectric heating occurs principally in the aqueous phase.

1.5.3.1 –Required input power

Since the temperature is imposed and equal to 60°C, the input power must be adjusted in order to maintain the temperature. After an initial equalization period, the power absorbed by the sample is in the order of magnitude of 10 W for both cases of 30 and 70 % wt. loading of oil. The volume that is considered is 50 ml.

1.5.3.2 – Effect of the rotating speed

The rotation speed is a parameter that governs the value of the mass transfer coefficient and it is critical for the process. The authors have found that the minimum speed to obtain a stable emulsion is 300 rpm. However, from Figure 1.23 it can be seen that under conventional heating (no microwave) the influence of the rotation speed is negligible in the range 400-650 rpm. In this case the medium droplet size is optimum and it does not affect the process.

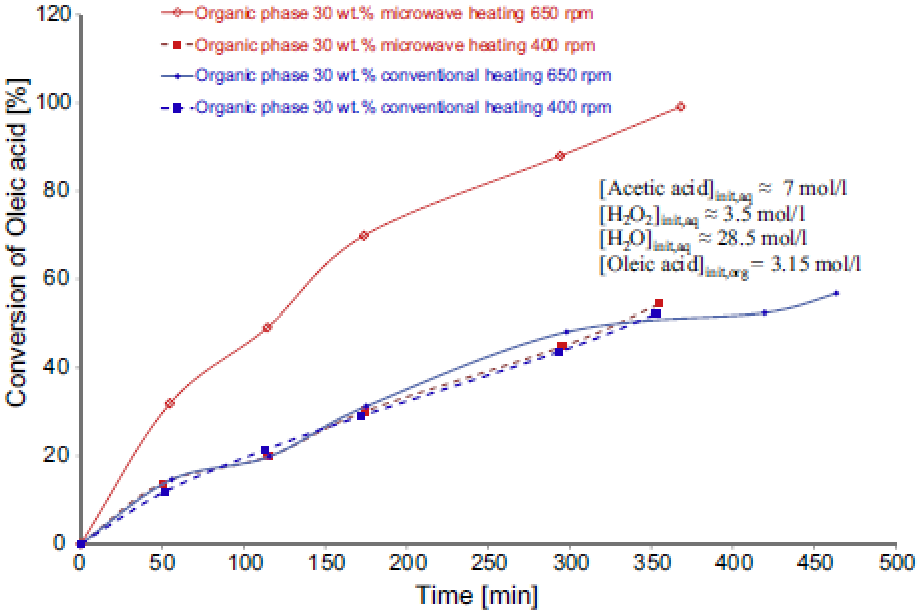


Figure 1.23. *Effect of the stirring speed on the oleic acid conversion at 60◦C in the presence of acetic acid. Both cases of conventional or MW heating are taken into account.*

On the other hand, a big difference in the conversion of oleic acid can be noticed when the rotation speed passes from 400 to 650 rpm in the case a microwave heating is applied. In fact, after 350 minutes (about 6 hours) the conversion is about 50 % at 400 rpm, whereas about 100% at 650 rpm. All these data are referred to 30% wt. loading of oil. It is evident that, at a fixed temperature, microwave irradiation makes the difference in the process, accelerating the conversion. According the authors, the energy delivered to reaction mixture could be more efficiently dissipated if microwave radiation is applied and this fact could improve the mass transfer and in particular the aqueous mass transfer coefficient.

1.5.3.3 – Effect of organic phase massive fraction

The authors have tried to change the organic-to-aqueous phase ratio since the dielectric properties are expected to change. As it can be noticed in Figure 1.24, in the case of experiment carried out with massive fraction of organic phase equal to 70% the effect of microwave irradiation is less evident than the case of massive fraction of organic phase equal to 30%. In fact, after 6 hours, in the case of 70% wt. of organic phase, the conversion is about 10% with conventional heating and about 12-13% with MW heating. Whereas, in the case of 30% of organic phase the conversion passes from about 50% (conventional heating) to 100% (MW heating).

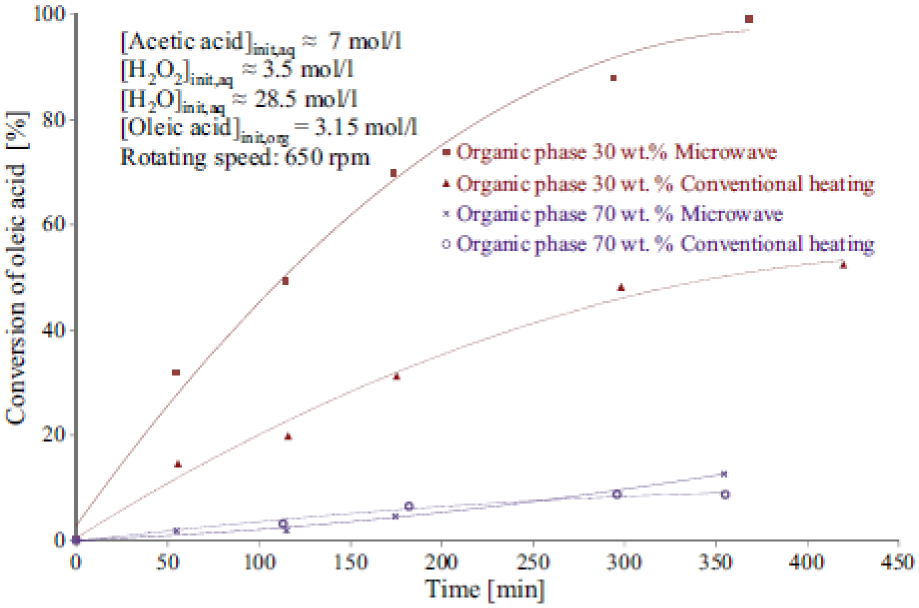


Figure 1.24. *Influence of the heating source and massive fraction of organic phase on the oleic acid conversion in the presence of acetic acid at 650 rpm and 60°C.*

The authors do not explain the reason of this fact. However, at 70% wt. of organic phase, the small difference in conversion between different heating sources could be due to the smaller amount of aqueous phase, that is responsible of the dielectric heating. Moreover, at 70% wt. of organic phase, in both cases of heating, the conversion is much smaller than the one of the case at 30% wt. since less acetic acid and hydrogen peroxide are available.

From Figure 1.25 it is possible to have an idea of the evolution of mole fraction of epoxide with the time elapsed from the beginning of the reaction.

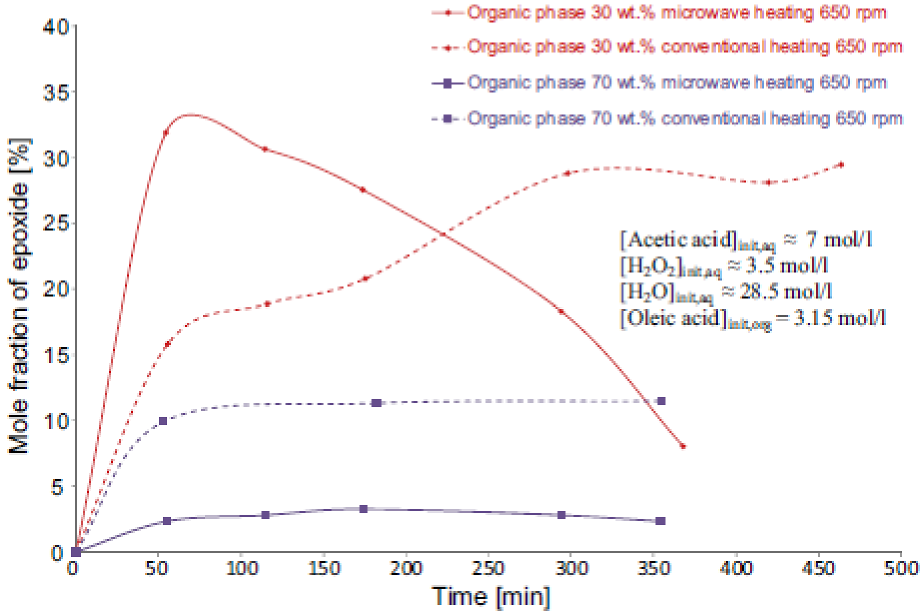


Figure 1.25. *Influence of the heating source and massive fraction of organic phase on the mole fraction of epoxide in the presence of acetic acid at 650 rpm and 60°C.*

In the case of 30% of organic phase, the formation of epoxide is greatly accelerated with respect to conventional heating. However, the epoxy ring opening begins relevant after only 1 hour so all the reactions the whole process is greatly accelerated. According the authors, this fact demonstrates that mass transfer is improved under microwave irradiation. In fact, since energy dissipation is more efficient, the aqueous mass transfer coefficient is higher that lead to a better diffusion of hydroxonium ions to the interface. This fact accelerates both the desired and the side reactions.

In order to summarize this method, the principal process variable are reported in Table 1.13.

Table 1.13. *Recapitulatory table of the optimal values of process variables. The process is carried out with no kind of catalyst and under microwave irradiation.*

Temperature	Initial amount of oil	Oil	Acetic acid/double bond molar ratio	H_2O_2/double bond molar ratio
60°C	30% wt.	Oleic acid	2.2:1	1.1:1

Impeller velocity	MW frequency	MW power	Time required to maximum yield
650 rpm	2.45 GHz	200 W/l	1 hour (6 hours to 100% conversion)

1.6 Other methods

In addition to all these methods, there are a few routes of epoxidation that are not classifiable and have a minor importance, at least nowadays. For this reason, these methods are only sketched and not explained.

A first method consists in epoxidation in presence of silver as catalyst. This route is old and cheap and it permits very low yield (11,12).

An alternative route is epoxidation with halohydrines in presence of hypohalous acid (11,12) but this solution appears to be not environment-friendly.

Another method is explained by Di Serio *et al.* (26) that uses Nb_2O_5-SiO_2 catalysts in soybean oil epoxidation in presence of hydrogen peroxide. The catalyst is prepared by sol-gel technique. The catalyst has showed a good activity in epoxidation but low selectivity.

An alternative route for the epoxidation of soybean oil is reported by Jiang et al. (27). The catalyst is based on methyltrioxorhenium that is immobilized with brushes of poly(4-vinylpyridine) grafted onto holloysite nanotubes by surface-initiated atom transfer radical polymerization.

In conclusion, epoxidation of vegetable oils has been attempted with a cumene-O_2 system by Scotti *et al* (28). With this route the epoxidation of esters of vegetable oil is carried out using cumene as oxygen carrier. Cumene firstly reacts with O_2 generating cumene hydroperoxide, that reacts with the esters forming the epoxide. A catalyst is needed and copper supported on alumina is used.

1.7 Conclusions

In conclusion, it can be seen that a lot of literature and several different methods can be used in order to epoxidize vegetable oils. Biphasic epoxidation is the typical method used in industrial processes and it is well known. The triphasic epoxidation using alumina or ion exchange resin appears a new method, in which catalyst can be simply separated by filtration and reused. The electrochemical epoxidation represents a more complex method that solves the hazard of storage and handling hydrogen peroxide because this reactant is produced in situ in the reactor. The improvement in terms of time of the process is noticeable (3h instead of 6-8 hours of the previous methods). Methods that use ultrasound and especially microwave heating can boost the reaction. In this way, in the case of microwave heating, the maximum yield can be reached after only 1 hour, even if the complete conversion can be reached after 6 hours.

In conclusion, each method has its own peculiarities and advantages and all the methods are extremely interesting since they can represent a future solution and improvement to the traditional process, in terms of profitability and productivity. The increasing demand of epoxidated vegetable oil can promote further improvement in this branch of the research.

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Chapter 2

Calorimetric methods and instrumentation

In this chapter a short description of the methods and the instrumentation used for the calorimetric studies is presented. In particular, a preliminary part about the safety parameters, techniques, principles of measurement and operation modes is provided. This is a general description useful to frame the calorimetric analysis. Secondly, the description of the instrumentation used for the specific calorimetric analysis of this work is presented. The two piece of instrumentation used for this thesis are the Thermal Screening Unit (TSU) and the calorimetric reactor.

TSU is a small reactor (few milliliters) employed to obtain preliminary information. In fact, with TSU, it is possible to determine the temperature at which the runaway reactions take place, both of the hydrogen peroxide-carboxylic acid system and the oil-hydrogen peroxide-carboxylic acid system. Also the information of the pressures is recorded. This information is extremely useful to evaluate the safety condition for the epoxidation process end the thermal stability of the reaction mixture. In this way, information about the maximum temperature at which the process can carried out is obtained. Data of pressure can be used to properly design the reactor.

The second apparatus consists in a stirred tank reactor (250 ml) in which epoxidation is carried out. It permits to record temperatures, pressure and heat flow during the experiment in order to carry out calorimetric analysis on the system (i.e. heat of reaction).

2.1 - Safety parameters, techniques, principles of measurement and operation modes of thermal measurements

In this chapter, the definition of the general safety relevant parameters, techniques, principles of measurement and operation modes of thermal measurement are reported. These concepts are taken from *Safety Engineering in Practice vol. 6, HarsBook by Dechema* ([1]).

2.1.1 - Definitions of safety relevant parameters

It must be reminded that the following parameters could be influenced by the experimental conditions and procedures. Moreover, the parameters are classified in four categories:

temperature, pressure, heat or power and time. Usually temperature and heat are taken into account to evaluate the possibility of a runaway event. However, pressure is the variable that can bring about injure the operators or damage the equipment also provoking the release to the environment of chemical dangerous material. The higher the temperature, pressure and released heat are, the more severe are the consequences in case of accidental event.

2.1.1.1 - Temperature

The following temperatures are indicated as safety relevant parameter:

- $\boldsymbol{T_p}$: process temperature;
- $\boldsymbol{MSTR}$: Maximum Temperature attainable by the Synthesis Reaction. This parameter is the maximum temperature that can be reached during a synthesis reaction when adiabatic conditions are maintained. For a batch process, MSTR can be determined exploiting the adiabatic calorimetry or it can be estimated knowing the enthalpy of reaction ΔH_r using equation (1):

  $$MTSR = T_p - \Delta H_r / C_p. \tag{2.1}$$

  It is to remind that for the calculation of this parameter the responsible of the increase of temperature is uniquely the desired reaction. In this case, ΔH_r is the enthalpy of reaction of the desired one.
- $\boldsymbol{T_{cf}}$: Temperature after cooling failure. This parameter indicates the expected final temperature of a reaction mixture after the failure of the cooling system. In some cases, this temperature is equivalent to MSTR.
- $\boldsymbol{\Delta_{AD}T_d}$: adiabatic temperature increase. This parameter is the increase of temperature in adiabatic condition due to both desired and undesired reactions.
- $\boldsymbol{T_d}$ or $\boldsymbol{T_{onset}}$. These parameters represent the lowest temperature at which exothermic reaction is revealed. This temperature is not the real temperature at which the reaction occurs but it depends on the sensitivity of the instrumentation. The higher the sensitivity is, the lower is this temperature.
- $\boldsymbol{SADT}$: Self accelerating decomposition temperature. This parameter indicates the temperature that the cooling medium of a reactor has to attain in such a way that the temperature of the reactor reaches the No Return point. In this case the thermal power generated by the process equals the maximum cooling capacity of the cooling system.
- $\boldsymbol{T_{dg}}$: Onset Temperature for the Production of Decomposition Gases.

- **AZT_t**: Maximum temperature at which no decomposition occurs after a time t.
- ***Minimum Safe Temperature***. This parameter represents the minimum temperature that can be reached by the cooling medium otherwise the thermal control of the system is lost.
- ***Maximum Self Heating rate.*** This parameter indicates the maximum rate of increase of temperature under adiabatic conditions.

2.1.1.2 - Heat or power

The following heats/powers are indicated as safety relevant parameter:

- $\dot{Q}_r$: Power released. This parameter indicates the thermal power released by the process at a certain time.
- $\dot{Q}_r^{MAX}$: Maximum power released. This parameter represents the maximum value that $\dot{Q}_r$ can reach.
- Q_r: Evolved Heat. This parameter indicates the total heat released by the process in the whole time of reaction. It takes into account the different reaction that can take place and it is determinable integrating $\dot{Q}_r$ in the considered time domain.
- $Accum$: Accumulation of Unreacted Materials or Thermal potential. This parameter indicated the amount of heat that can be released by the system after the stopping of the feeds.

2.1.1.3 - Time

The following times are indicated as safety relevant parameter:

- **TMR_{ad}**: Time to Maximum Rate under adiabatic conditions. This parameter indicates the time required to reach the maximum self-heating rate, due to side reactions or decomposition, when adiabatic conditions are maintained.
- ***Induction Time***: Induction Time, Isothermal Induction Time, Autocatalytic Induction Time or Induction Period. This parameter represents the time after which exothermic activity occurs when isothermal conditions are maintained. The induction time depends on temperature, concentrations of inhibitors, catalyst or impurities.

2.1.2 – Techniques and instruments

In this paragraph the principal techniques of calorimetry are just sketched up:

- ***DTA***: Differential Thermal Analysis. This technique consists of measurements of the difference in temperature that exists between the sample and the reference, both collocated in a proper oven and both subjected to the same temperature regime. The mass of the sample is in the order of magnitude of mg.
- ***DSC***: Differential Scanning Calorimetry. This technique consists of measurement of the difference of the heat released or absorbed between the sample and the reference. Both the sample and the reference are collocated in a proper oven and both subjected to the same temperature regime. Also in this case, the mass of the sample is in the order of magnitude of milligrams.

Both DTA and DSC are the most used techniques in the characterization of many materials, such as polymers, metals and cermics.

- ***µ-C***: Micro-Calorimetry. This technique is essentially a *DSC* carried out in a larger scale and for this reason much more sensitive. Moreover, it is possible to reproduce many experimental conditions such as stirring and dosing that are impossible on a smaller scale. The mass of the sample is in the order of magnitude of grams.
- ***RC***: Reaction Calorimetry. This technique is used to simulate the process in the large industrial conditions. In fact, it is possible to measure the heat flow rate (absorbed or released) due to reactions or physical changes of the sample. Non differential instrumentation is used, even if in some cases, in order to improve the measurements, differential measurements are introduced. Several principles of measurement are employed, such as Heat Flow, Heat Balance, Power Compensation, Isoperibolic Balance and Calvet. The mass of the sample is in the order of magnitude of grams or kilograms.
- ***AdC***: Adiabatic Calorimetry. In this technique, temperature and pressure are measured when adiabatic conditions are maintained. In order to that, the heat transfer between the sample and the surroundings is minimised as possible by one of many techniques. The mass of the sample is in the order of magnitude of grams.
- ***Pseudo adiabatic***. In this technique, the measurement of the changes of the difference in temperature between the sample and its surroundings is carried out when a specific temperature regime is set. Since there is not a reference, this technique is not a differential one. The mass of the sample is in the order of magnitude of grams.

2.1.3 – Principles of measurement

In this paragraph, the main principles of measurement used in calorimetry are just sketched up. The objective of these measurement is the determination of $\dot{Q}_{FLOW}$, i.e. the thermal power evolved by the sample.

- ***Heat Flow***: $\dot{Q}_{FLOW}$ is calculated according equation (2.2):

  $$\dot{Q}_{FLOW} = (U \cdot A) \cdot \Delta T. \tag{2.2}$$

  ΔT is the measured variable and $U \cdot A$, i.e. the product between the heat transfer coefficient *U* and the transfer area *A* is determined through calibration.
- ***Heat Balance***: $\dot{Q}_{FLOW}$ is calculated through an energy balance on the jacket, as shown in equation (2.3)

  $$\dot{Q}_{FLOW} = \dot{m}_J \cdot cp_j \cdot \left(T_{jin} - T_{jout}\right) \tag{2.3}$$

  The measured variable are T_{jin} and T_{jout}, i.e. the temperatures of the cooling fluid at the inlet and the outlet of the jacket. The remaining terms $\dot{m}_J \cdot cp_j$ are calculated through calibration, also considering the heat losses from the jacket. This principle is used mainly in reaction calorimetry.
- ***Calvet***: $\dot{Q}_{FLOW}$is determined through the heat balance at a secondary wall that surround the sample container. The measured variable is the difference in temperature between the internal and the external surfaces of the secondary wall, determined with extreme accuracy thanks to a set of thermocouples. The geometry thickness and conductivity of this wall are known. The instrument based on this principle are the most sensitive but the permit only low heating rates and temperatures. This principle is used in microcalorimetry, *DSC* and *RC*.
- ***Power compensation (heat flux)****:* this principle is applied with slightly differences according to the used technique, *DSC* or *RC*. In the first case, the difference in temperature that could exist between the external walls of the sample crucible and the ones of the reference crucible is measured and maintained as low as possible by controlling the power delivered to the sample crucible. In the second case, the heat transfer between the sample and the surroundings is maintained as constant as possible and the temperature of the sample is kept close to the set point. In both cases $\dot{Q}_{FLOW}$ is calculated by subtracting a baseline value to the supplied electrical power.

- ***Isoperibolic Balance:*** with this principle, $\dot{Q}_{FLOW}$ is calculated using a heat balance around the ballast, that is a vessel collocated between the system and an isothermal jacket, in order to maintain the system quasi-isothermal. The heat transfer coefficient is determined by calibration using an electrical calibrated heater.
- ***Adiabatic Balance:*** with this principle, $\dot{Q}_{FLOW}$ is not calculable because it is equal (or near) to zero. The measured variable is the increase of the adiabatic temperature. This principle is mainly applied to adiabatic calorimetry and the several instrumentation differ for the φ-factor that is defined as the ratio between the true adiabatic temperature increase of the sample and the measured one, that is relative to both sample and cell. The lower is the φ-factor the better are the obtained results. This principle is mainly applied to adiabatic calorimetry.

2.1.4 – Operation modes

- ***Temperature scanning***: a temperature ramp with constant rate is applied to the sample. With this operation mode it is possible to obtain information about heat capacity, power released, the temperature at which exothermic reactions start, changes in pressure due to gas evolved during the test
- ***Isothermal***: the sample is constrained at a constant temperature. The obtained data are the power released, induction time and time to peak of heat generation. This operation mode is complementary to the previous one and it is mainly applied to reaction calorimetry.
- ***Isoperibolic***: the temperature of the surroundings of the sample (generally the jacket) is maintained constant. The produced data are difficult to analyse.
- ***Adiabatic***: no heat is applied and adiabatic conditions are maintained. The data that can be obtained are temperature and pressure increases, T_d or T_{onset}, $MSTR$, $\Delta_{AD}T_d$, TMR_{ad}.
- ***Pseudo-adiabatic***: an initial temperature ramp is applied to the sample and, when the heat evolved from it exceeds the net heat loss, the sample is maintained in adiabatic condition, in order to self-heat. This mode cannot be used to obtain data for kinetic modelling.

- ***Temperature modulated***: a sinusoidal change in the temperature of the sample is applied in both scanning and isothermal experiment. It is possible to know $U \cdot A$ and C_p.

2.2 – Thermal Screening Unit (TSU)

In order to determine the temperature at which runaway reactions start and to have a precise idea of the pressure involved in this case, a study of the system has been carried out using *TSU*. Using TSU it is possible to obtain temperature and pressure profiles along the elapsed time. On the base of these data it is possible to have an idea of the conversion of the studied reactions. *TSU* is graphically represented in Figure 2.1.

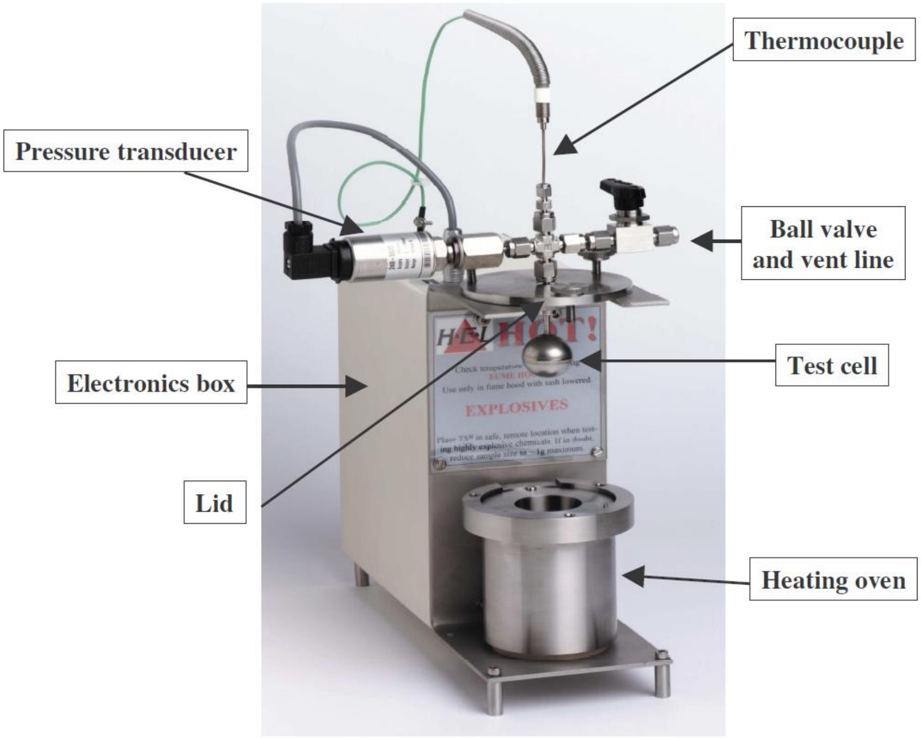

Figure 2.1. *Thermal screening unit by HEL.*

TSU is mainly made of a sample cell, an oven and an electronic device. The sample is fastened to the bottom side of a lid whereas a pressure transducer, a thermocouple and a vent line are connected to the top side of it. When the *TSU* tests are not running, the lid is held by a stand. During the operation, the lid is screwed to the top of the oven, in order to hold the cell inside it. The cell has a spherical shape and the tip of the thermocouple is held in such a way that it can measure the temperature inside the cell. The cell has a volume of about 9 ml but no more than

2 ml of mixture can be loaded in it, to avoid overloading. The internal electronic of the *TSU* device can communicate with a computer via RS232 port (serial port) in such a way to obtain the right control using the software *WinIso* supplied by the producer. The software permits also the collecting of data. *TSU* permits to perform tests by different operation modes, such as isothermal or ramped modes or combination of both. In the first case it is possible to set the setpoint temperature and the duration of the test. In the second case it is possible to set the maximum temperature and the rate of increase of temperature. In both cases a maximum pressure can be set for a safety reason. The temperature control is guaranteed by the internal *PID* control (Proportional-Integrative-Derivative). It is reminded that the way the controller acts towards the temperature directly affects the results in the case runaway reactions occurs.

2.3 – Calorimetric Reactor

The calorimetric reactor is a batch, stirred and jacketed tank by *BüchiGlasUster* (Figure 2.2). This reactor is used to carry out the epoxidation of soybean oil. It permits to record temperatures and pressure in order 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*. This apparatus permits to set a temperature program with an excellent accuracy.

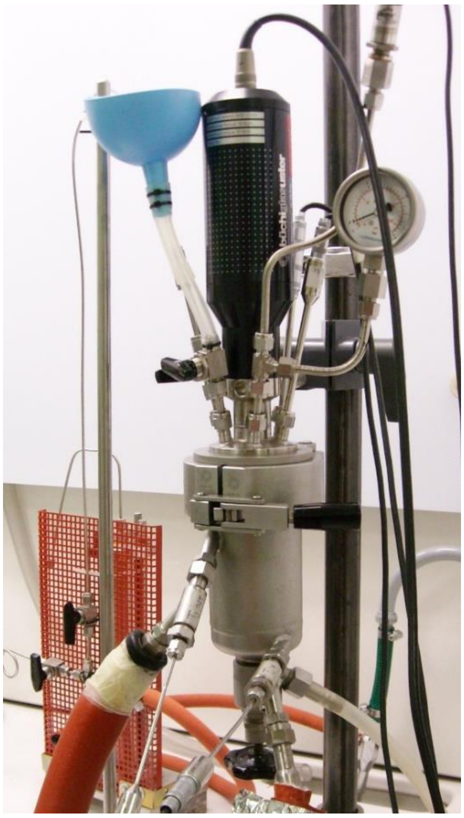

Figure 2.2. *Calorimetric reactor by BüchiGlasUster.*

Figure 2.2. *Thermocryostat by Huber used for the temperature control of the calorimetric reactor.*

Three thermocouples Pt100 are installed in the reactor and at the inlet and at the outlet of the jacket. A pressure transducer is installed in the reactor, whereas a rupture disc guarantees the safety of the equipment. An analogic manometer permits to monitor the pressure in the case the pressure transducer is not working. A stack of electronic analog to digital converters (by *National Instrument*) permits to collect data of the tree temperatures and of the pressure and to send them to a PC via USB port. An *ad hoc* software realized using *LabView* (*National Instrument*) is used to record data and to visualize them on a monitor in real time. 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. The motor is controlled by an electronic interface that permits a precise regulation by the software or a rough regulation by a knob on the frontal panel of the interface.

2.3.1 – Equipment for the determination of the heat exchange coefficient

In order to determine the heat exchange coefficient a proper method has been applied. A well determined thermal power is generated inside the reactor and its temperature is recorded. Both from the thermal transient and from the steady state, different information can be obtained.

As regards the cooling transient, approximating the system to a first order, it is possible to estimate the time constant τ. This time constant is equal to $\frac{m \cdot cp}{U \cdot A}$ as can be seen from the equation 2.4:

$$\frac{T(t)-T_{jacket}}{T(t_0)-T_{jacket}} = e^{-\frac{U \cdot A}{m \cdot cp} \cdot (t-t_0)} = e^{-\frac{t-t_0}{\tau}} \tag{2.4}$$

where $U \cdot A$ is the global heat exchange coefficient [W/K], $m \cdot cp$ is the thermal capacity of the mixture inside the reactor [J/K] and t_0 is the initial instant at which cooling starts.
As regards the steady state, it is possible to estimate $U \cdot A$, as can be seen from equation 2.2:

$$Q = U \cdot A \cdot (T - T_{jacket}) \tag{2.5}$$

In this way it is possible to have information about $U \cdot A$ and $m \cdot cp$.

In order to do this, an electrical heater is used and a 3D printer ceramic heater was chosen for this application. This kind of heater is shown in the Figure 2.3 and it has small dimensions (20 mm of length and 6 mm diameter), very low cost, low voltage (24V DC) and good power (40 W nominal).

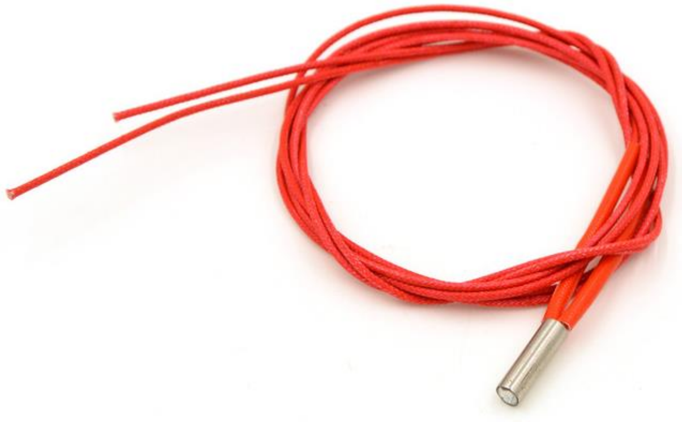

Figure 2.3. *Ceramic heater used for the determination of the heat exchange coefficient. This heater is commercially available for 3D printer.*

However, during the operation of this ceramic resistor, the internal resistance and consequently the absorbed electrical power can change. In this way, a constant well determined thermal generation (that is indispensable to solve eq. 2.2) can result quite difficult. Moreover, the possibility of changing the generated power has been taken into account, in order to evaluate its influence in the heat exchange coefficient. For both reason, a simple DC regulated power supply is not enough. In fact, in addition to it, a precise automatic power controller was designed and built.

2.3.1.1 – Automatic power controller

For the reasons earlier explained, an automatic power controller is needed. This system has been design and built *ad hoc*. The control is achieved using a feedback controller. In fact, the measured instant power that is applied to the resistor is compared with the desired power (setpoint) and, on the base of this difference, the microcontroller adjusts the voltage applied to the resistor. This system is made of many units:

- a data collector unit that measures both the voltage applied at the resistor and the current flowing through it. The data are digitalized by an ADC (analog to digital converter);
- a controller unit that compute the power applied to the resistor in each instant. After a comparison with the setpoint power, the microcontroller takes a decision and send a PWM (pulse width modulation) output signal to the converter unit;
- a converter unit that takes the signal from the microcontroller and converts it into an analog signal:
- an actuator that brings the voltage applied to the resistor to the value set by the microcontroller.

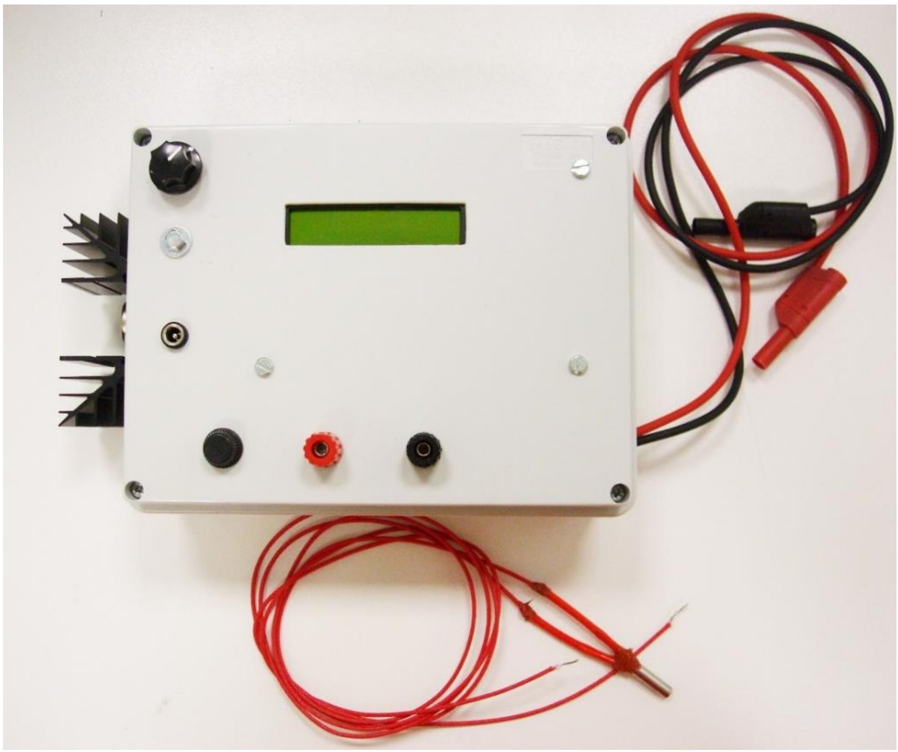

Figure 2.4. *Automatic power controller and ceramic heater.*

The system is based on a platform called *Genuino* (*Arduino*) that mounts an ATmega 328 microcontroller. *Genuino* has 14 digital input/output pins, 6 of which can work also as PWM output (*Pulse Width Modulation*). *Genuino* has also 6 analog inputs. It is reminded that PWM is a particular digital technology that consists in modulating the duty cycle of a fixed frequency square wave signal. The duty cycle is the percentage of a period at which the signal is in an active state (high level).

Signals applied to the analog inputs are sampled and digitalized by the ADC integrated in the microcontroller and a number from 0 (0 Volts input) to 1023 (maximum Volts input) is assigned. The maximum voltage corresponding to the number 1023 can be set from 0 to 5V, so the resolution can vary. In this specific case *external reference* option is applied and the maximum voltage is set equal to 3.3V. All the outputs can work as strictly digital, *i.e.* high and low levels (5 and 0V respectively). In the case of that outputs that can also work with PWM, the output signal is a square wave of 5V peak, at a frequency of 490 Hz. The duty cycle of these waves is settable by the user by a number that goes from 0 (0% duty cycle) to 255 (100% duty cycle).
In a more practical way, the system can be described analyzing the schematic circuit.

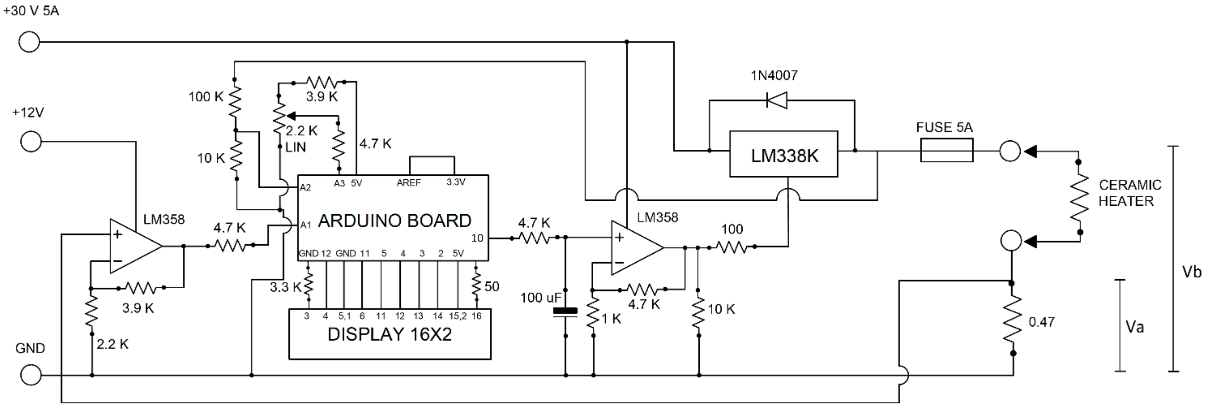

Figure 2.4. *Schematic diagram of the automatic power controller.*

As can be seen from the schematic, both the current flowing through the ceramic heater and the voltage across it are indirectly measured. In order to obtain these two data, two voltages are measured and a small 0.47ohm resistor is connected in series to the ceramic heater. In this way one voltage data is obtained across the 0.47 resistor (Va in Figure 2.4). The other voltage is obtained across the series of the ceramic heater and the resistor (Vb in Figure 2.4). Both voltages are referred to the ground pole.

Va is amplified by an operational amplifier LM358 with a gain of about 2.8 and sent to the microcontroller (input A1). This operation is indispensable in order to optimize the 1023 levels available at the ADC and to maximize the resolution.

Vb is divided by a voltage divider (1:11 ratio) to low the voltage and it is sent to the microcontroller (input A2). It is reminded that the input signal sent to the microcontroller has to be a maximum voltage of 5V (3.3V in this case of *external reference mode*).

After a calibration and a fitting of the data performed using *Matlab* (bt *Mathworks*), it is possible to obtain the two calibration curves related to the current (function of Va) and the voltage across the ceramic heater (function of (Vb and Va).

Thanks to an algorithm stored into the flash memory of the microcontroller, the two information on current and voltage are computed by mean of the two calibration curves. After that, the electrical power absorbed by the heater is calculated using the equation 2.6:

$$P = V \cdot I. \qquad (2.7)$$

Once the power is calculated, the microcontroller reads the value of the power setpoint. The power setpoint is set by the user acting on the potentiometer (see schematic in Figure 2.4). The power is settable between 5 and 35W. This potentiometer is a voltage divider that send a variable voltage signal to the analog input A3. By mean of a linear law, the microcontroller computes the correct value of the power setpoint.

Once the power setpoint and the real power have been computed, the two data are compared in order to generate the error as shown in equation 2.8:

$$e = P_{setpoint} - P_{real}. \qquad (2.8)$$

At this point, the microcontroller takes a decision setting the PWM output 10. In fact, if the error is positive, the algorithm rises by a unit the number by mean of which the microcontroller set the duty cycle (0-255, 0-100%). Vice versa, if the error is negative, the numbers is lowed by a unit. After this operation, a time delay is set. If the modulus of the error is greater than 2W, the delay is equal to 10ms. If the modulus of the error is lower than 2W the time delay is equal to 300ms. In this way, when the error is large, the control is very fast. At the contrary, when the error is not large, a slow control is obtained in order to obtain a fine and precise control.

This loop is repeated iteratively. The values of power setpoint, read power, current and voltage are indicated on the 16X2 lcd display.

As regards the PWM-analog converter and the actuator, the system is made of a filter, an operational amplifier and a voltage regulator. In fact, the output signal coming from output 10 passes into a low pass filter in order to convert 5V PWM signal into analog 0-5V signal. The filter is made of a 4.7kΩ resistor and a 100µF condenser. The condenser is much larger than the one that is theoretically needed (4.7-10 µF) to make more stable the regulation. The analog signal so formed is amplified by a LM358 operation amplifier (gain about 6). In this way the analog signal passes from 0-5V to about 0-30V. This signal drives the linear voltage regulator LM338K that power supplies the ceramic heater.

In conclusion the power is well controlled and the precision is around 1-3%.

Bibliographic references

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Chapter 3
Experimental procedure

In this chapter, the materials and the methods, used to carry out the experiments, are explained. First of all, a list of the materials that are used is presented. Then the methodologies used to carry out the experiments are exposed

It is reminded that, in this work, hydrogen peroxide 34wt.% is used instead the one at 60wt.% commonly used. Even if the reaction conditions are weaker, in this way the risk of detonation or runaway is reduced. Moreover, acetic acid is used instead of formic acid. In this way the risk of corrosion of the instrumentations is reduced, even if acetic acid is less reactive.

3.1 - Materials

The acetic acid 98%, the hydrogen peroxide 34%, the ion exchange resin *Amberlite IR120* (by *Dow chemical*) and the sulfuric acid are purchased from *Sigma-Aldrich*. Soybean oil in a food grade is purchased in a supermarket (*Despar*).

3.2 – Experimental methodologies

In this paragraph the methodologies used for the preliminary tests with the Thermal Screening unit (TSU), the calibration of the calorimetric reactor and the epoxidation process in the calorimetric reactor are explained.

3.2.1 Preliminary tests with the TSU reactor

The mixtures under test in TSU reactor are two:

- Mixture 1: 15.85wt.% of acetic acid, 84.15wt.% of hydrogen peroxide.
- Mixture 2: 7.7wt.% of acetic acid, 40.9wt.% of hydrogen peroxide and 51.4wt.% of soybean oil (i.e. 48.6wt.% of Mixture 1 and 51.4wt.% of soybean oil).

These proportions are calculated in order to obtain an acetic acid:hydrogen peroxide:double bonds molar ratio equal to 0.5:1.5:1. This is the typical ratio that can be found in the literature (Chapter 1)

In both cases, the mixture is loaded in the spherical cell of the TSU reactor in a quantity between 1.6 and 2.0g (to avoid overload). The cell is strictly screwed on the lid in such a way the thermocouple can enter the sample and the seal is ensured. The seal is tested by introducing nitrogen in the cell: once the valve is closed, the pressure must remain constant. The gas is so discharged, the purge valve is closed and the test can be performed. Isothermal tests at 70°C, 90°C and 100°C are performed with

Mixture 1, to study the uncontrolled decomposition of hydrogen peroxide. Duration is 150 minutes. In the case of Mixture 2, the isothermal tests are performed at 50°C, 60°C and 70°C to carry out a safety study in the typical temperature range in which epoxidation is carried out. Duration is 150 minutes to compare the result with the previous ones. Isothermal tests are carried out also for 500 minutes, that is the time scale of the epoxidation process.

3.2.2 Calibration of the Calorimetric Reactor: heat exchange coefficient

The heat exchange coefficient of the calorimetric reactor is determined generating some well determined thermal power in the reactor. The calorimetric reactor is filled with 205.6g of Mixture 2 (i.e. 100g of Mixture 1 and 105.6g of Mixture 2). It is important to use the same reaction mixture of the process in such a way the calculation of the heat exchange coefficient is as accurate as possible. No sulfuric acid nor ion exchange resin are introduced in such a way the reaction of epoxidation does not occur. In this way no enthalpy of reaction is released and the calculation is correct. The fact that, without acid catalyst, the epoxidation does not take place is demonstrated in the chapter dedicated to the results (Chapter 5).

The ceramic heater, after proper insulation of the electric terminals with some sealant, is introduced in the reactor. The impeller speed is set on 500rpm. The Huber thermocryostat is set to 60°C (typical temperature used in the epoxidation processes) and a time equal to about 40 minutes must elapse to obtain the thermal steady state. Once the heater is connected to the automatic power controller, the power is set. Different powers are used: 20W, 25W and 35W. The duration of the test is about 15 minutes in such a way the transient is extinguished and the data are complete. The data of temperature are collected by three thermocouples, one in the reactor and two at the inlet and at the outlet of the jacket, as previously explained (§2.3). The collected data are elaborated using an *adhoc* algorithm in *Matlab*.

3.2.3 Epoxidation in the calorimetric reactor

The epoxidation is carried out with 205.6g of Mixture 2 (i.e. 100g of Mixture 1 and 105.6g of Mixture 2), in such a way the acetic acid:hydrogen peroxide:double molar ratio bonds equal to 0.5:1.5:1 (base case). 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 liquid can enter the reactor, the vacuum is created in it using a Venturi water pump. In the case 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.

Moreover, in the case the ion exchange resin *Amberlite IR120* is added, the resin is loaded in the reactor since the beginning, with the oil. This is necessary since it is quite difficult to introduce the resin by the top valve of the reactor. Moreover, the oil can entrain the small particles of the resin very good when the oil and the resin are poured in the reactor.

In this part, the effect of several process variable is studied: the presence of sulfuric acid or ion exchange resin, the mixing program, the sulfuric acid concentration, the loading of the resin and the concentration of acetic acid. The sensitivity analysis of the concentration of sulfuric acid is carried out at 2wt.%, 3wt.% and 4wt.% with respect to the oil. In this way the amount of sulfuric acid has to be added is equal to 2.11g, 3.17g, 4.22g. The sensitivity analysis of the loading of the resin is performed at 10wt.% 25wt.% and 40wt.% with respect to the oil. The amount of resin that has to be loaded is equal to 10.56g, 26.4g, 42.24g. The sensitivity analysis of the concentration acetic acid is performed 0.5: and 1:1 acetic acid:double bonds molar ratios. The first case corresponds to the base case (Mixture 2). The second case requires the loading of 31.70g of acetic acid instead of 15.85g. The effect of the temperature is not studied since in the literature it is an evidence that an excessive temperature (70°C) promotes the formation of by-products (glycols) and degrades the oil. A low temperature does not permit a good rate of reaction (50°C). Consequently, the temperature of 60°C is uniformly considered the best compromise. Moreover, also the sensitivity analysis on the concentration of hydrogen peroxide is neglected since in literature it appears evident that it has a weak effect in a wide range of concentration. Only if a high excess of hydrogen peroxide is added, the selectivity decreases since the formation of glycols is promoted.

The sample are analyzed by FTIR spectroscopy.

The epoxidated oil has a white colour and is very viscous with respect to the virgin oil, especially when stored at low temperature (4°C) in fridge.

Chapter 4

Preliminary tests and calibration

In this chapter the results of the different preliminary tests are exposed. First of all, the tests about the measure of the density of acetic acid-hydrogen peroxide mixture are reported. Second, the tests carried out with TSU reactor are exposed. These tests are useful to obtain information about the temperature at which runaway reactions start and the pressure involved in this case. At last, the results of the calibration of the calorimetric reactor are presented. In this case, the heat exchange coefficient and the effective heat capacity were determined experimentally.

The acetic acid-hydrogen peroxide mixture is the mixture used in the epoxidation of soybean oil. These tests are necessary because hydrogen peroxide can decompose to water and oxygen according the equation 4.1.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \qquad \Delta H^0 = -98.2 kJ/mol \tag{4.1}$$

The reaction is greatly exothermic and hydrogen peroxide is really instable. This is the reason for which particular attention must be given to this runaway reaction. The exothermic character of this reaction could lead to sudden increase of temperature and pressure and in consequence to mechanical failure of the reactor, damages to the plant and hazard for the operators.

4.1 – Measure of density of acetic acid – hydrogen peroxide mixture

Since the data of density of the mixture made of acetic acid and hydrogen peroxide is necessary in the next paragraph, several tests has been carried out to obtain a good result.
The mixture under tests is made of acetic acid and hydrogen peroxide. This mixture is composed as follows: 84.15 wt.% of hydrogen peroxide 32% and 15.85 wt.% at 98%. In the case hypothetical case in which oil is added with weight ratio oil:mixture 1.06:1, the previous percentages correspond to hydrogen peroxide:double bond and acetic acid: double bond equal to 1.5:1 and 0.5:1 respectively. These ratios are the classical reported by the literature in the process of epoxidation (see Chapter 1).

The tests have been performed using a graduated cylinder and a balance. After introducing a well determined volume of mixture, the samples have been weighted and the density was calculated. The results are reported in Table 4.1.

Table 4.1. *Density of the mixture made of 15.85% acetic acid at 98% and 84.15% hydrogen peroxide 32%.*

Test N°	Density [g/ml]
1	1.10177
2	1.10533
3	1.10108
4	1.10555
5	1.10543
6	1.10515
7	1.10427
Mean	**1.10410**

The mean value of these seven tests is 1.10410 g/ml.

4.2 – Preliminary tests in TSU apparatus

These tests have been performed in order to understand the temperature at which runaway phenomena start and the pressure involved in this case. TSU is presented in Chapter 2.
The mixtures posed under test are:

1. 84.15 wt.% hydrogen peroxide (32 wt.%), 15.85 wt.% acetic acid
2. Acetic acid – hydrogen peroxide (as the precedent point) and soybean oil in ratio 1:1.06

The tests performed are ramped tests or isothermal tests. In the first case, the rate of increase of temperature is equal to 2°C/min up to 200°C. In the case of isothermal tests, the temperature chosen are 70, 90 and 100°C for Mixture 1, 50, 60 and 70°C for Mixture 2. The duration of the tests goes from 150 minutes (Mixture 1, 2) to 500 minutes (Mixture 2).

4.2.1 Preliminary tests with Mixture 1: hydrogen peroxide and acetic acid

The results of ramped and isothermal tests are presented in Figure 4.1, 4.2, 4.3, 4.4.

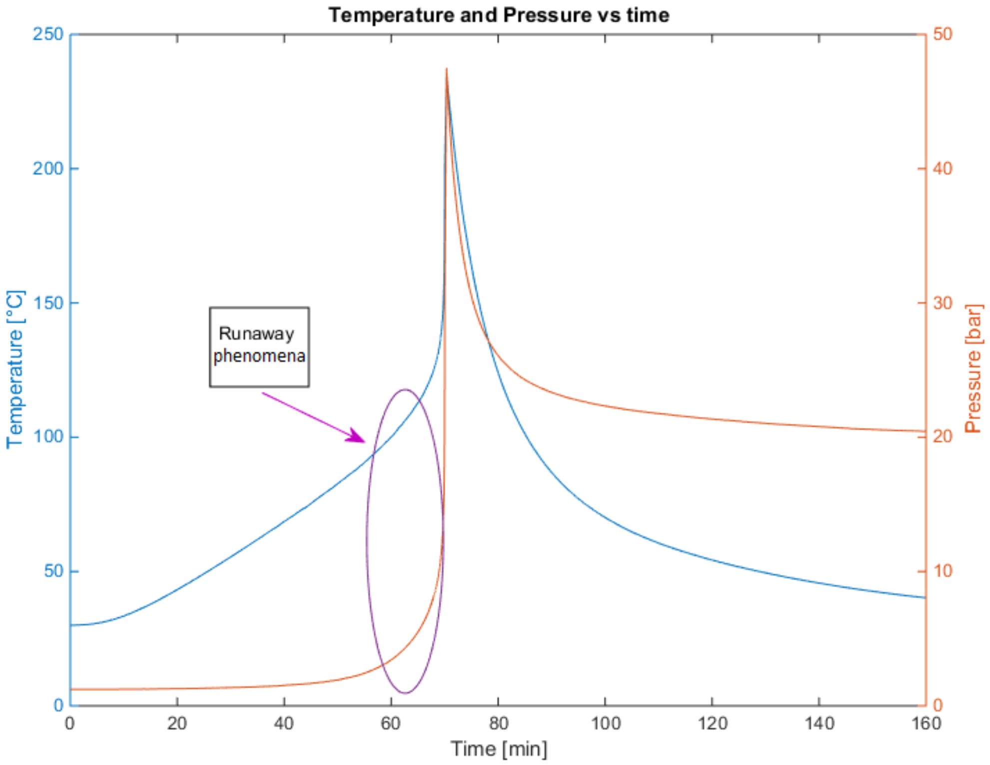

Figure 4.1. *Ramped test (2°C/min) of hydrogen peroxide- acetic acid 15.85% and 84.15% (32 wt.%). Ellipse highlights the interval in which runaway phenomena starts.*

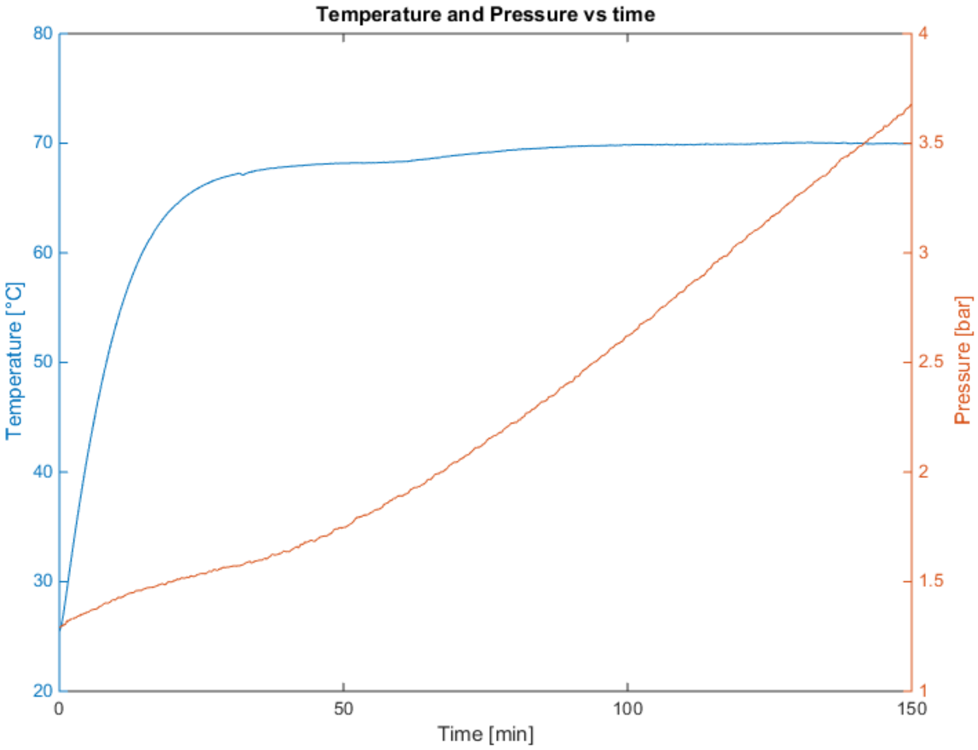

Figure 4.2. *Isothermal test at 70°C of hydrogen peroxide- acetic acid 15.85% and 84.15% (32 wt.%)*

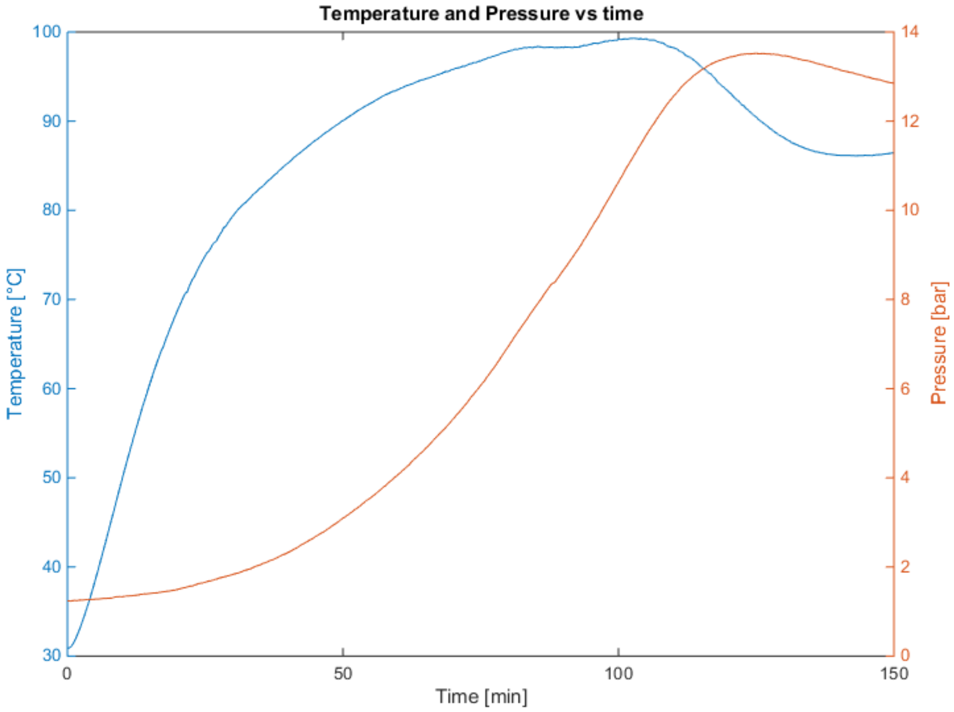

Figure 4.3. *Isothermal test at 90°C of hydrogen peroxide- acetic acid 15.85% and 84.15% (32 wt.%)*

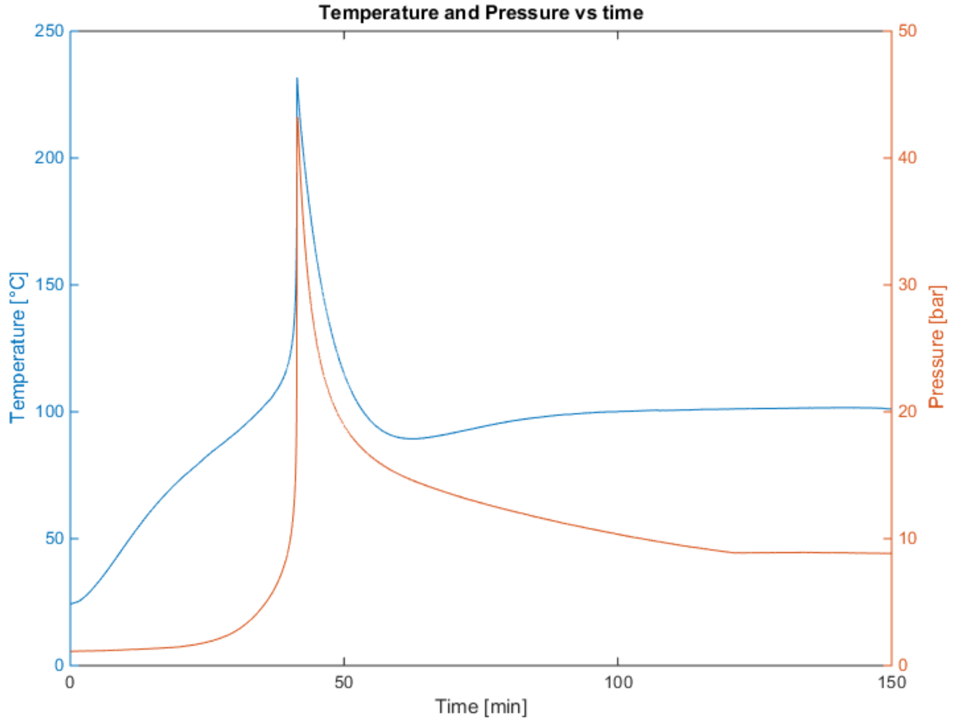

Figure 4.4. *Isothermal test at 100°C of hydrogen peroxide- acetic acid 15.85% and 84.15% (32 wt.%)*

As concerns the ramped test, as can be seen from Figure 4.1, runaway phenomena start around 100°C. This behaviour can be seen from a sudden increase of pressure that presents a maximum equal to 47.51 bar after 70 minutes. At this point the temperature is equal to 236°C. It is evident that such conditions are quite drastic and this verifies that the decomposition of hydrogen peroxide represents a serious risk for the equipment and the safety for the operators.

As concerns the isothermal test at 70°C, the pressure increases up to 3.68 bar after 150 minutes. Temperature overshoot are not evident so only a controlled decomposition occurs. It can be concluded that no runaway risk exists. It can be noticed that pressure increase is quite linear from about 70 minutes.

As concerns the isothermal test at 90°C, the pressure increases up to 13.52 bar. As regards the temperature, it is evident a thermal overshoot equal to 9.31°C (peak of 99.31°C). In this case the maximum of pressure is slightly shifted (in late) with respect to the temperature.

Since an overshoot is present, the TSU internal controller cannot control the temperature and face the great heat generation of the reaction. Consequently, the decomposition of the hydrogen peroxide is not controlled. It can be concluded that at 90°C the runaway risk is present, even if the peaks of pressure and temperature are not so evident as in the case of the ramped test. It is reminded that in this case in which runaway reaction occurs not in a very pronounced way, the way the TSU controller acts strongly affects the test. Also in this case the increase of pressure is quite linear from 60 to 110 minutes.

As concerns the isothermal test at 100°C, the pressure increases up to 43.24 bar after 41 minutes. At this time, it is present a peak of temperature equal to 213.7°C. It is obvious that an overshoot of 113.7°C represents a serious risk of totally uncontrolled decomposition of hydrogen peroxide. The conditions are very strong, both as regards the pressure and the temperature.

In conclusion, from these tests it can be concluded that the temperature of 90°C can be considered as a threshold value beyond which runaway phenomena occurs.

In order to have an estimation of the rate of decomposition in the linear interval concerning the isothermal tests at 70 and 90°C, a deeper study can be carried out. In fact, the amount of molecular oxygen that is produced can be calculated from the pressure. It is necessary to know the mass of the mixture in the cell, the density (determined at §4.1) and the volume of the cell including the dead volume of piping and valves (9.5 ml). In this way the amount of molecular oxygen can be plotted vs time and a linear fitting can be performed, as can be seen from Figures 4.5 and 4.6.

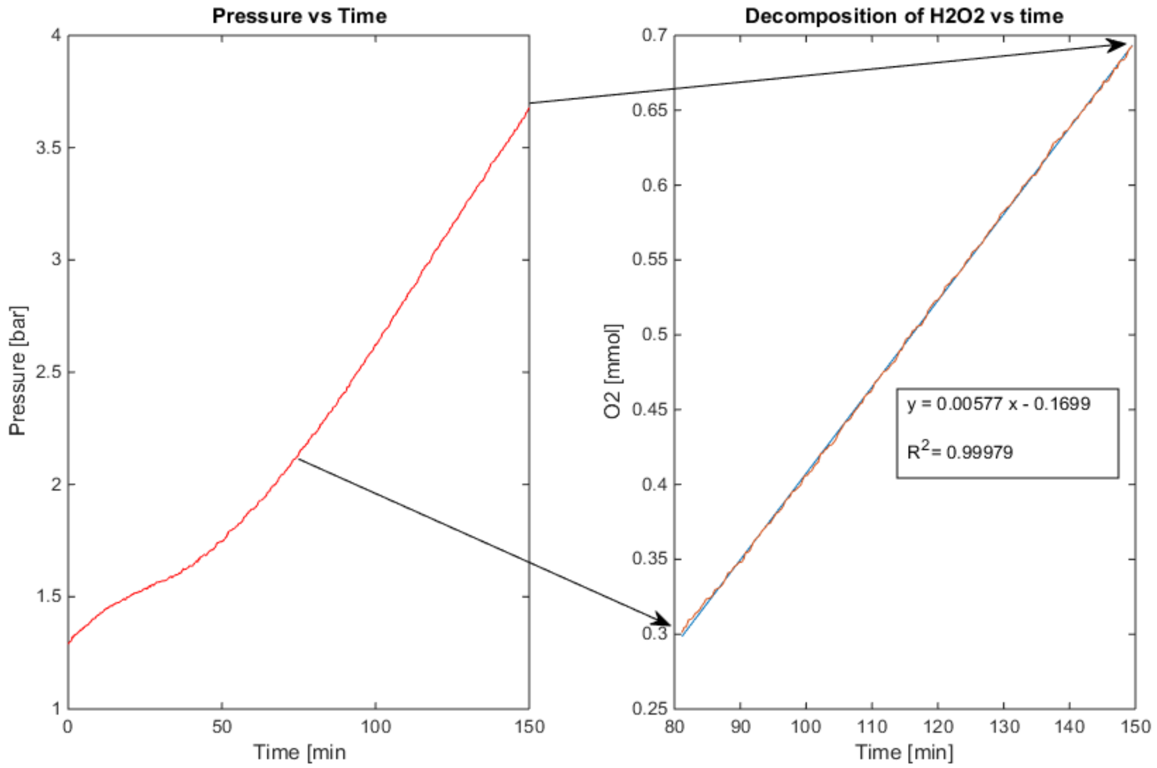

Figure 4.5. *Left: pressure vs time in isothermal test at 70°C (as Figure 4.2). Right amount of molecular oxygen produced in isothermal test at 70°C by decomposition of H_2O_2. (red) and its fitting (blue). Sample mixture is Mixture 1. The rate of decomposition is equal to 0.00577 mmol/min. R^2 is equal to 0.99979*

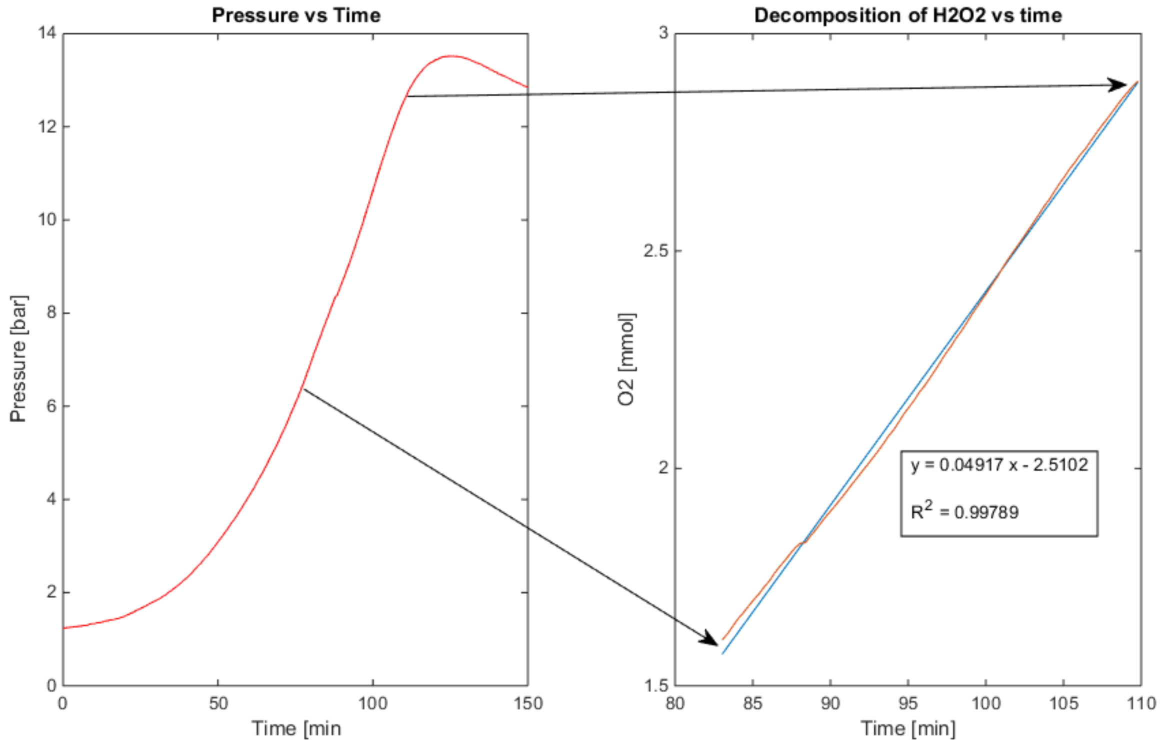

Figure 4.6. *Left: pressure vs time in isothermal test at 90°C (as Figure 4.3). Right amount of molecular oxygen produced in isothermal test at 90°C by decomposition of H_2O_2. (red) and its fitting (blue). Sample mixture is mixture 1. The rate of decomposition is equal to 0.04917 mmol/min. R^2 is equal to 0.99789*

As can be seen from Figure 4.5 and 4.6, it can be noticed that the decomposition of H_2O_2 has a much greater rate at 90°C than at 70°C. In fact, at 70°C the rate of production of O_2 is equal to 0.00577 mmol/min whereas at 90°C it is equal to 0.04917 mmol/min. The fitting is very good in both cases since the coefficient of determination R^2 is equal to 0.99979 and 0.99789 respectively. It can be concluded that from 70°C to 90°C, an increase equal to one order of magnitude of the rate of the decomposition of H_2O_2 can be observed.

As concerns the conversion of the decomposition of H_2O_2, the conversion can be plotted vs time from the temperature and pressure profiles as can be seen in Figure 4.7 and 4.8.

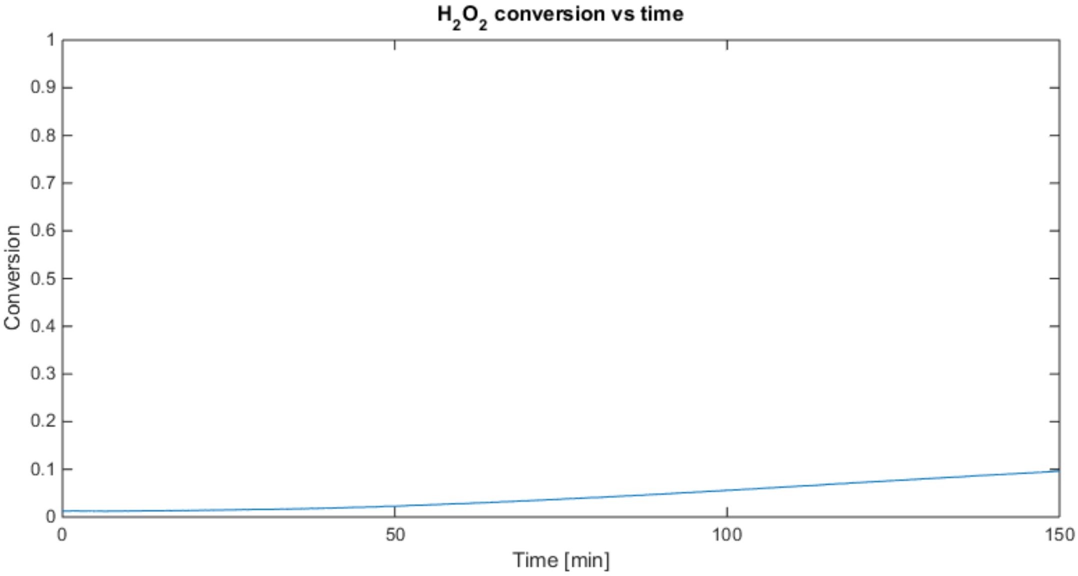

Figure 4.7. *Temperature, pressure and conversion vs. time from an isothermal test at 70°C. Sample mixture is mixture 1.*

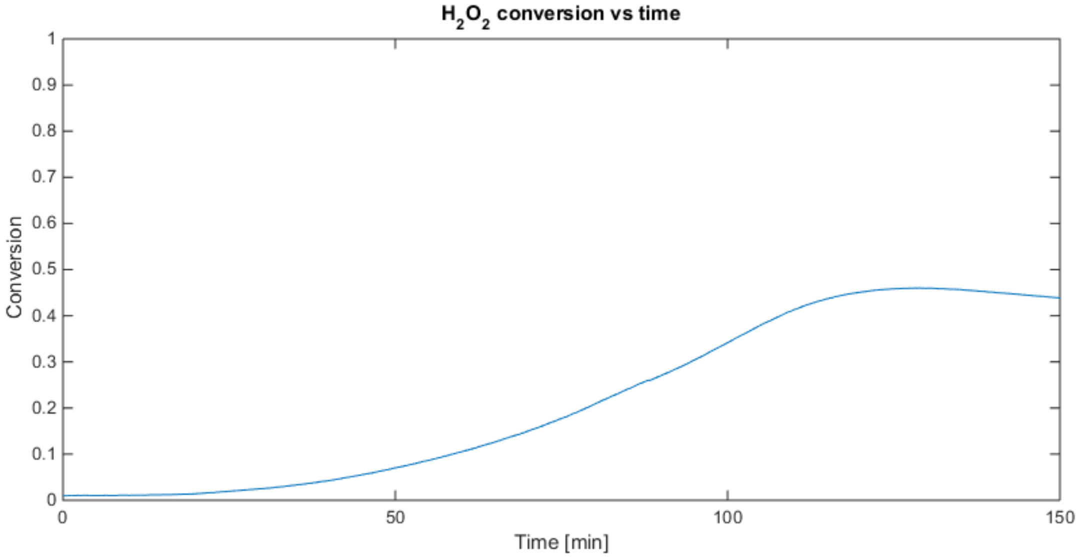

Figure 4.8. *Temperature, pressure and conversion vs. time from an isothermal test at 90°C. Sample mixture is mixture 1.*

As can be seen from Figure 4.7, in the case of isothermal test at 70°C the conversion is equal to 9.643% after 150 minutes. In the case of isothermal test at 90°C (Figure 4.8) the conversion is equal to 43.95% after 150 minutes. In this way the conversion increase of 4-5 times. These results are obtained under the hypothesis that the gas phase in the cell is simply made of air and the O_2 produced from the decomposition of H_2O_2. Consequently, the steam produced from the water inside the cell is neglected. The calculations are carried out assuming that the ideal gas law describes the system in a sufficiently accurate way. These assumptions are good for the isothermal test at 70°C and 90°C. However, at 90°C the conversion profile indicates a slight decrease when the temperature decrease. This fact is simply due to the error introduced by the limits of the assumptions. In fact, in this case a small amount of water passes to the vapour phase and successively condenses when temperature decreases.

As concerns the isothermal test at 100°C, the conversion is not calculated since a peak of temperature equal to 236°C and pressure of 47.51 bar implies the necessity of a proper thermodynamic modelling. Since this effort falls outside the focus of the thesis, a thermodynamic modelling is not carried out. However, at such a temperature it can be estimated that the conversion is nearly total.

It is reminded that these tests are carried out to have a simple estimation of the temperature and the pressure in case of runaway phenomena and how the temperature affects the conversion and the rate of reaction. For these reason, the assumptions maintained up to now are considered good enough.

4.2.2 Preliminary tests with Mixture 2: hydrogen peroxide, acetic acid and soybean oil

The results of ramped and isothermal tests with Mixture 2 are presented in the following Figures 4.9, 4.10, 4.11, 4.12, 4.13, 4.14.

It is reminded that Mixture 2 is made of acetic acid and hydrogen peroxide 32% (15.85wt.% and 84.15 wt.% respectively) and soybean oil in ratio 1:1.06.

The tests are carried out at 50, 60 and 70°C. The setpoint temperature of the isothermal tests is set not beyond 70°C, because degradation reactions could seriously degrade the oil. Isothermal tests have a duration of 150 mins and, for the last two temperatures, tests with a duration of 500 mins are carried out. A ramped test is also performed. The duration of 500 mins have the meaning to simulate the process of epoxidation in which about 8 hours are required (see Chapter 1).

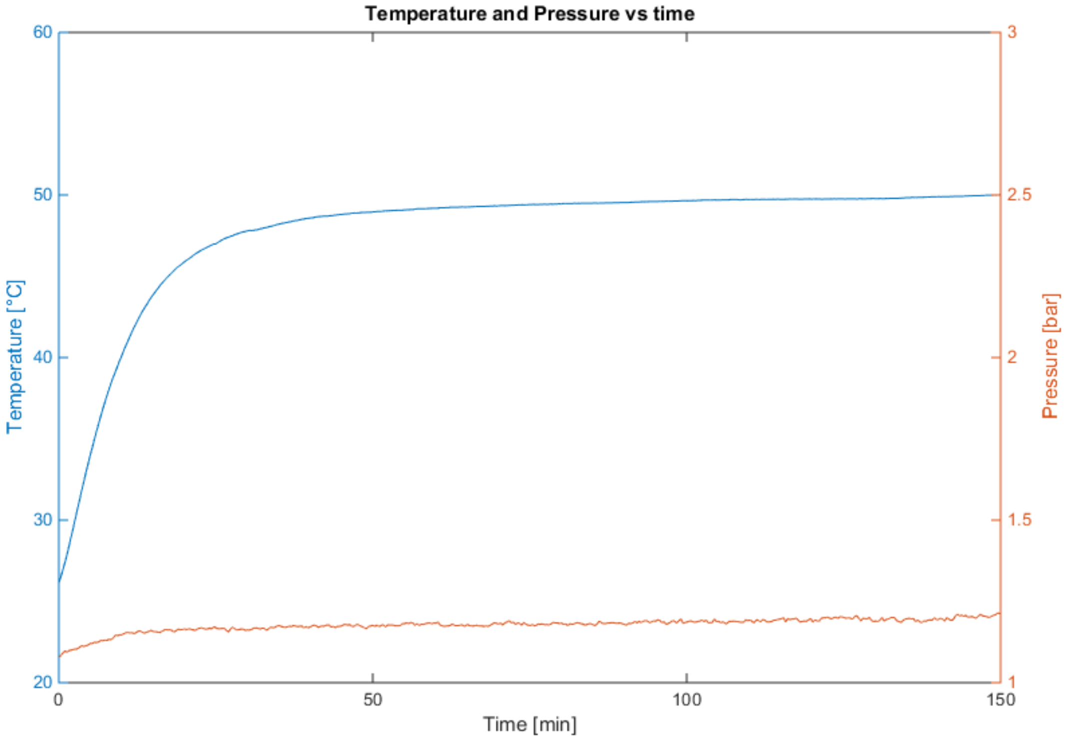

Figure 4.9. *Isothermal test at 50°C of Mixture 2. Duration 150 mins.*

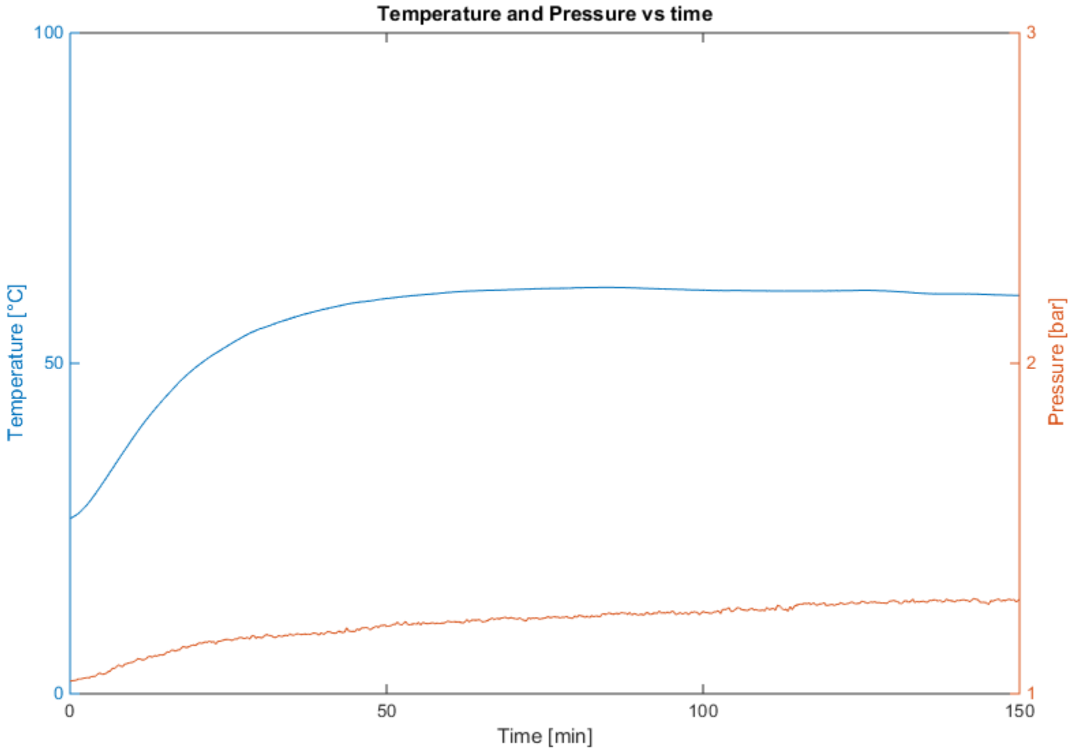

Figure 4.10. *Isothermal test at 60°C of Mixture 2. Duration 150 mins.*

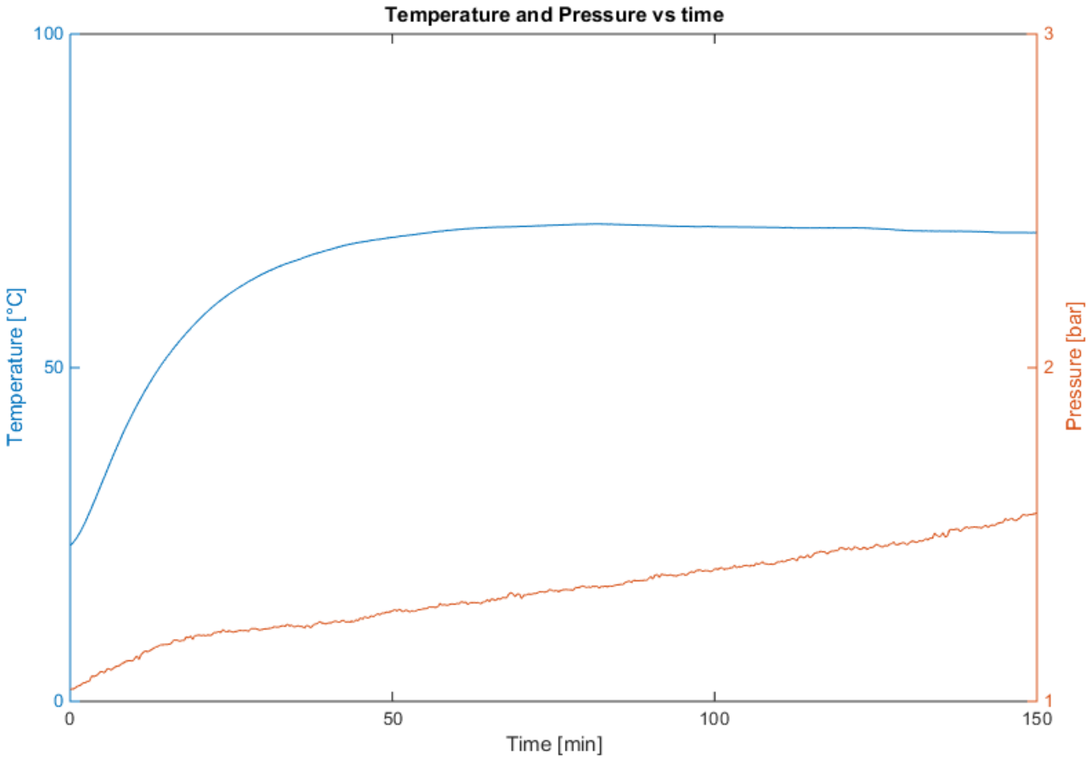

Figure 4.11. *Isothermal test at 70°C of Mixture 2. Duration 150 mins.*

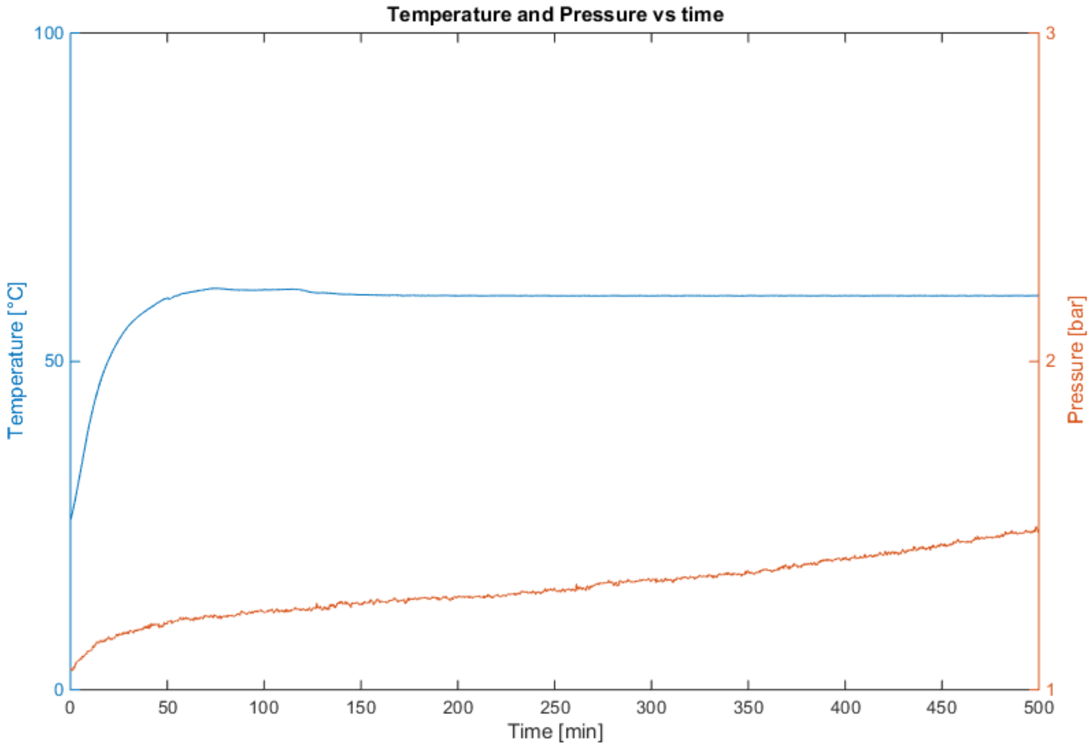

Figure 4.12. *Isothermal test at 60°C of Mixture 2. Duration 500 mins.*

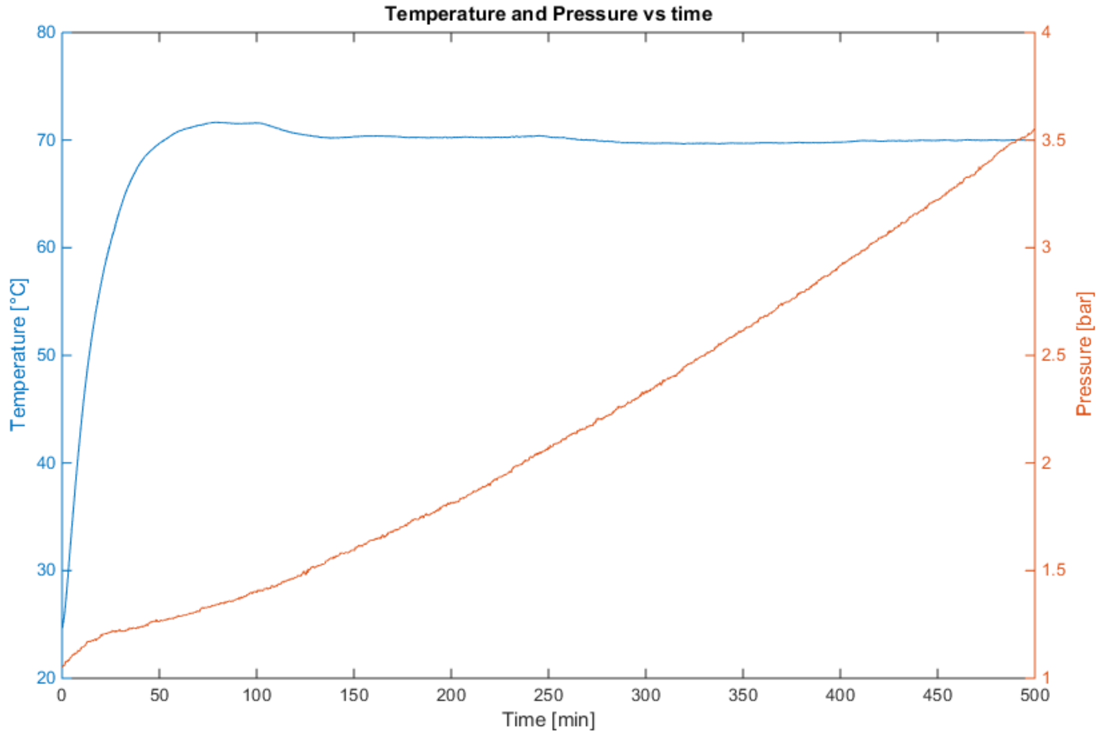

Figure 4.13. *Isothermal test at 70°C of Mixture 2. Duration 500 mins.*

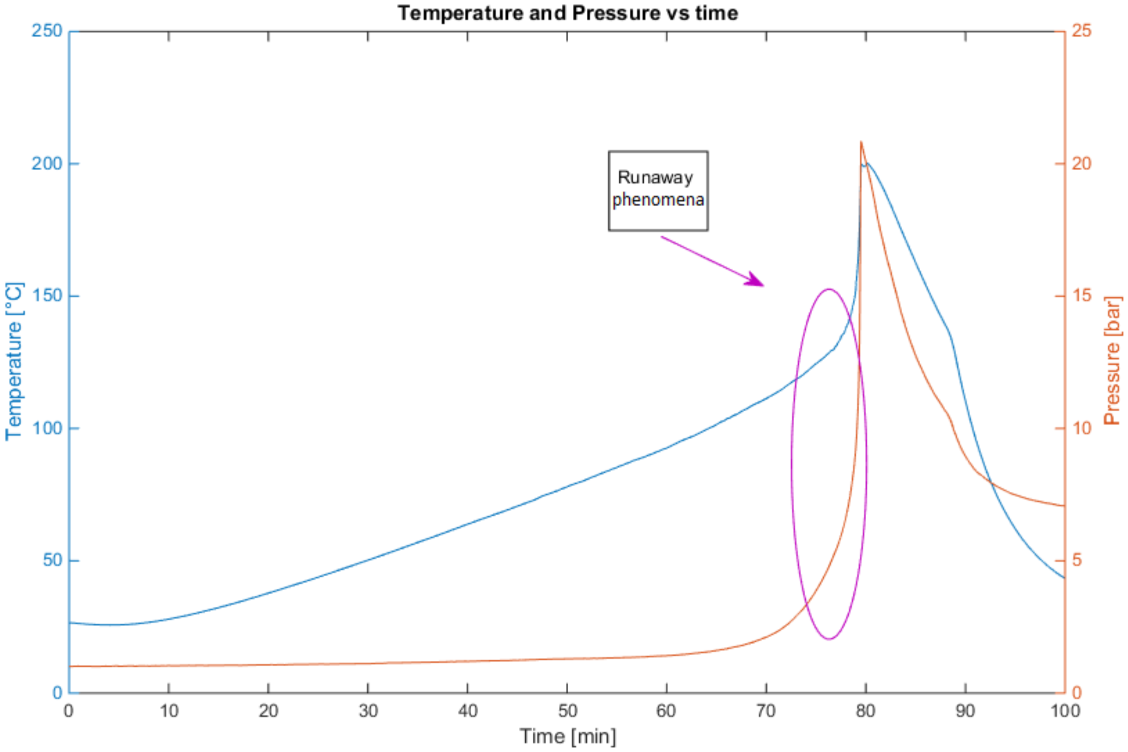

Figure 4.14. *Ramped test of Mixture 2. Rate 2°C/min.*
Ellipse highlights the interval in which runaway phenomena starts.

As can be seen in the previous Figures 4.9, 4.10, 4.11, in the case of the isothermal test with a duration of 150 minutes, the pressure reaches the values of 1.185, 1.2020, 1.4135 bar for 50, 60, 70°C temperature setpoint respectively. With respect to the previous tests without oil (Mixture 1), the pressure that is reached is noticeably lower. In the case of 70°C, the pressure reached with Mixture 1 is 3.68 bar whereas with Mixture 2 is 1.4135 bar. It can be concluded that the presence of the oil decreases the risk of uncontrolled decomposition of hydrogen peroxide. This is confirmed from the ramped tests (Figure 4.14) in which the runaway phenomena occur at 125-130°C, 20-30°C higher than the case of Mixture 1 (Figure 4.1)

In the case of tests of 500 minutes, the pressure reaches the values of 1.4058 and 3.3253 bar for the case of 60 and 70°C respectively. In addition, moderate thermal overshoots are present but they can be due to inevitable small overshoots of temperature controller of TSU.

In conclusion it can be said that the process can be carried out in safety conditions since the pressure is in the order of 1-3.5 bar.

In this case no calculation on the conversion of the decomposition of hydrogen peroxide are carried out because of the presence of other reactions as peroxidation of acetic acid or epoxidation of oil.

4.3 – Determination of the heat transfer coefficient of the calorimetric reactor

In order to determine the heat exchange coefficient in a calorimetric reactor a proper method has been applied. This method is anticipated in Chapter 2, in which the automatic power controller is described. A well determined thermal power is generated inside the reactor and its temperature is recorded. Both from the thermal transient and from the steady state, different information can be obtained.

In fact, as regards the cooling transient, approximating the system to a first order, it is possible to estimate the time constant τ. This time constant is equal to $\frac{m\cdot cp}{U\cdot A}$ as can be seen from the equation 4.2:

$$\frac{T(t)-T_{jacket}}{T(t_0)-T_{jacket}} = e^{-\frac{U\cdot A}{m\cdot cp}\cdot(t-t_0)} = e^{-\frac{t-t_0}{\tau}} \qquad \text{(4.2 or 2.4))}$$

where $U \cdot A$ is the global heat exchange coefficient [W/K], $m \cdot cp$ is the thermal capacity of the mixture inside the reactor [J/K] and t_0 is the initial instant at which cooling starts.

This model can be rigorously derived from the heat balance of the reactor during the cooling:

$$m \cdot cp \cdot \frac{dT}{dt} = -\, U \cdot A \cdot (T - T_{jacket}). \tag{4.3}$$

Arranging the equation 4.3, the equation 4.4 can be obtained:

$$\frac{dT}{T - T_{jacket}} = -\, \frac{U \cdot A}{m \cdot cp} \cdot dt \tag{4.4}$$

which, properly integrated, lead to the equation 4.2.

As regards the steady state, it is possible to estimate $U \cdot A$, as can be seen from equation 4.5:

$$Q = U \cdot A \cdot (T - T_{jacket}) \qquad \text{(4.5 or 2.5)}$$

In this way it is possible to have information about $U \cdot A$ and $m \cdot cp$.

4.3.1 Heat transfer coefficient: study on the cooling transient

As regards the cooling transient, the determination of τ is carried out by passing to logarithms the equation 4.2. In this way it is possible to obtain equation 4.6:

$$\ln\big(T(t) - T_{jacket}\big) \;=\; -\frac{U \cdot A}{m \cdot cp} \cdot (t - t_0) + ln\big(T(t_0) - T_{jacket}\big) \;=$$

$$= \; -\frac{t - t_0}{\tau} + ln\big(T(t_0) - T_{jacket}\big). \tag{4.6}$$

In this way equation 4.6 is a straight line with a general form as follows:

$$y = -\frac{1}{\tau} x + q. \tag{4.7}$$

Generating some thermal power inside the reactor, as described earlier, the collected data of temperature are elaborated in order to compute the difference $T(t) - T_{jacket}$, i.e. $\Delta T(t)$, in which *t* is a generic instant. Successively $\ln\big(T(t) - T_{jacket}\big)$ is calculated and a linear fitting is performed. This procedure is repeated for different values of thermal power, 20, 25 and 35W. Each test and its fitting is represented in Figures 4.15, 4.16, 4.17.

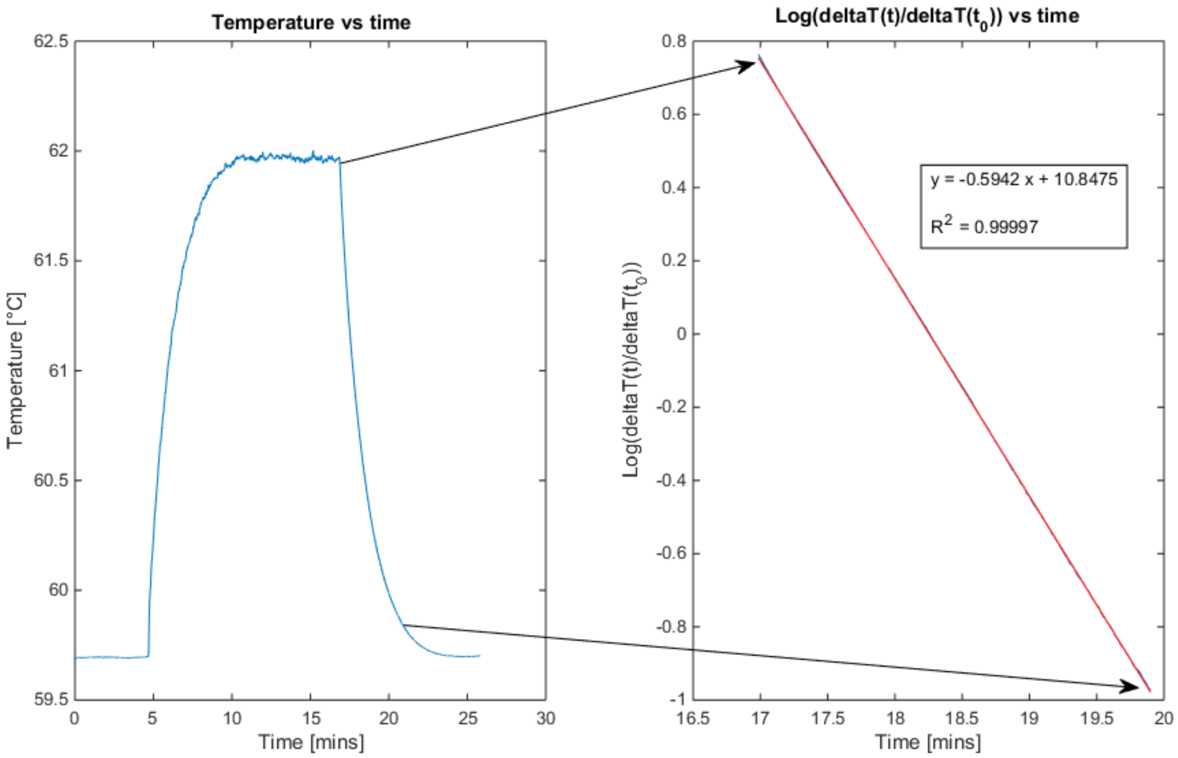

Figure 4.15. *Left: thermal transient obtained generating a thermal power of 20W inside the reactor. Right: logarithm of $\Delta T(t)$ (blue) and its fitting (red). The fitting indicates a τ^{-1} equal to 0.5942 min^{-1}. R^2 is equal to 0.99997.*

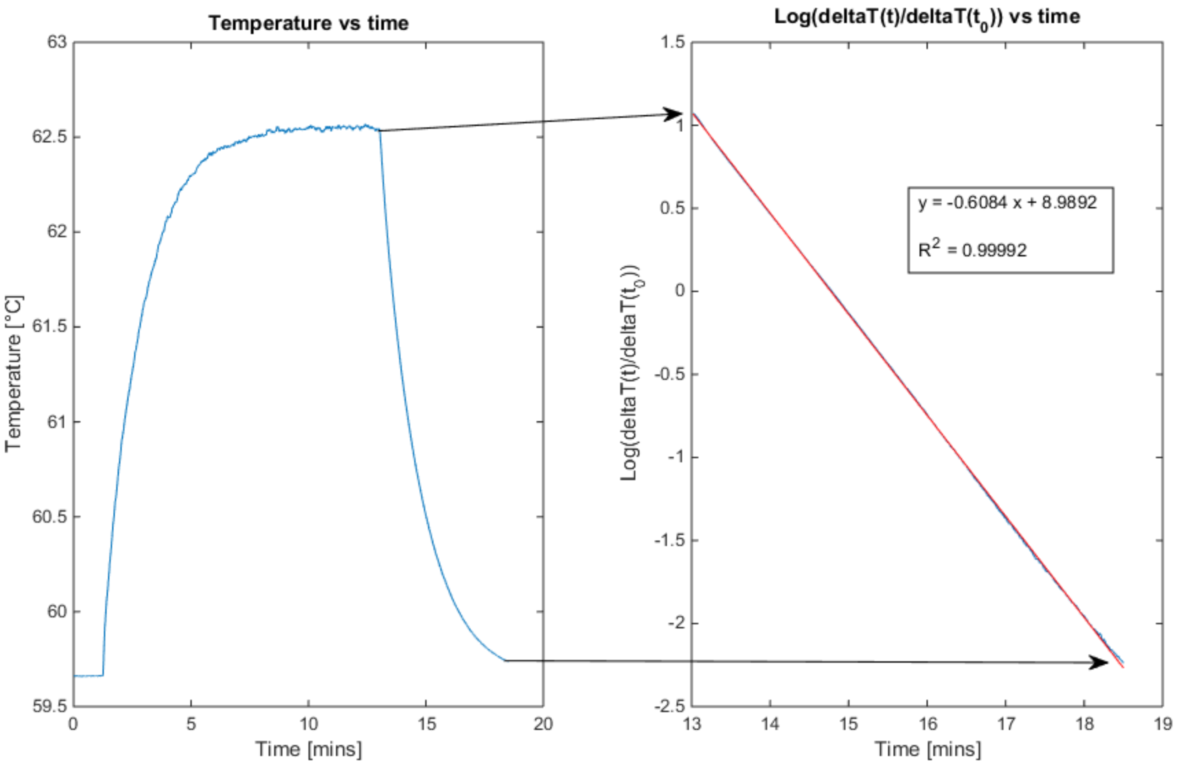

Figure 4.16. *Left: thermal transient obtained generating a thermal power of 25W inside the reactor. Right: logarithm of $\Delta T(t)$ (blue) and its fitting (red). The fitting indicates a τ^{-1} equal to 0.6084 min^{-1}. R^2 is equal to 0.99992.*

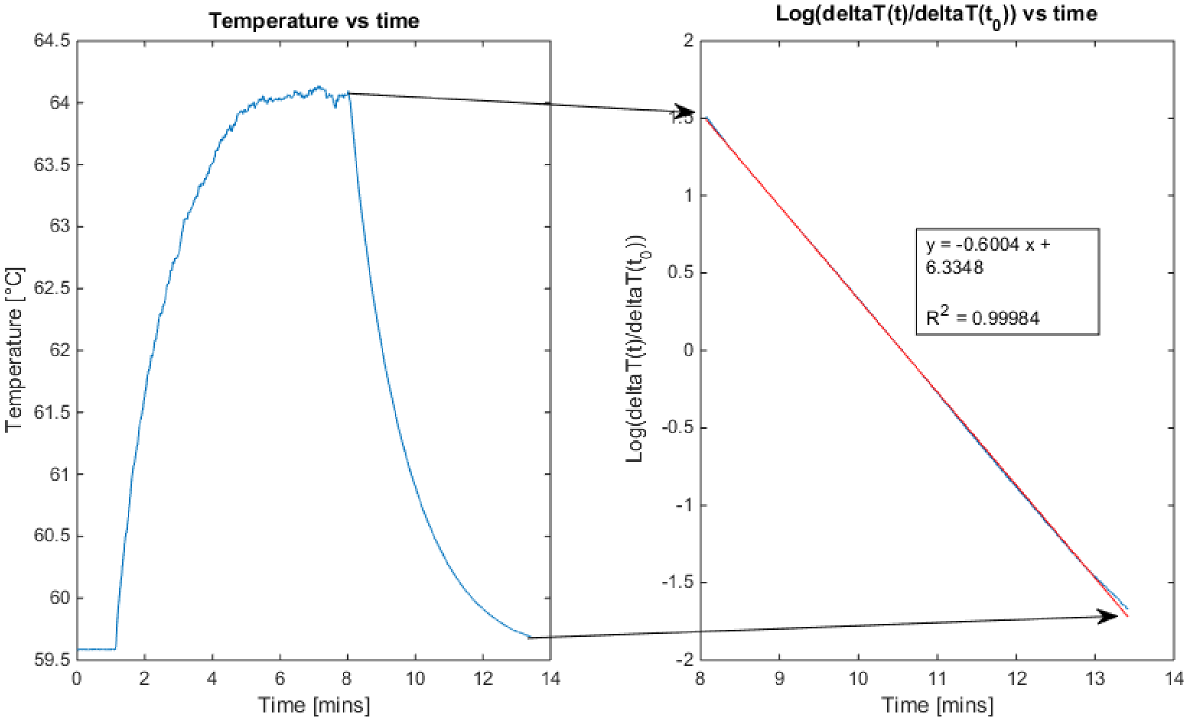

Figure 4.16. *Left: thermal transient obtained generating a thermal power of 35W inside the reactor. Right: logarithm of $\Delta T(t)$ (blue) and its fitting (red). The fitting indicates a τ^{-1} equal to 0.6004 min^{-1}. R^2 is equal to 0.99984.*

In these tests, the reactor is loaded with 206 grams of Mixture 2, i.e. 100 g of acetic acid-hydrogen peroxide mixture and 106 g of oil. In this way the reactor is loaded with the same amount and the typical mixture used for the epoxidation. The impeller velocity is fixed and equal to 500 rpm.

As concerns the fitting, in the case of 20, 25 and 35W the values of τ are 0.5942, 0.6084 and 0.6004 min^{-1}. These values are very similar, even though they are obtained with different power. This fact confirms the quality of these data. Moreover, the fitting is excellent, since R^2 is greater than 0.999. In the first two cases, R^2 is even greater than 0.9999. The results are summarized in Table 4.2.

Table 4.2. *Values of τ and $\frac{U \cdot A}{m \cdot cp}$ obtained by fitting of data using power 20, 25, 35 W.*

Power [W]	τ^{-1} [min^{-1}]	τ [min]	$\tau^{-1}[s^{-1}] = \frac{U \cdot A}{m \cdot cp}$	$\tau\ [s] = \frac{m \cdot cp}{U \cdot A}$
20	0.5942	1.6829	0.009903	100.974
25	0.6084	1.6437	0.010140	98.622
35	0.6004	1.6656	0.010007	99.936
Mean value	**0.6010**	**1.6639**	**0.010017**	**99.834**

In conclusion, the mean value 99.834 seconds is considered. This values indicates that the transient extinguish after 400-500 seconds (4-5τ). The table indicates τ and τ^{-1} with the units of measurement of minutes or seconds. The value is transformed from minutes to second in order to report it in International System of Units. In this way, calculation of $U \cdot A$ and $m \cdot cp$ are direct and simpler.

4.3.2 Heat transfer coefficient: study on the steady state

As concerns the thermal steady state, data obtained with 20 and 25 W are considered. In these case, the values of temperature at the steady state are 61.9669 and 62.5478 °C. Using equation 4.5 it is possible to obtain $U \cdot A$. Table 4.3 indicates the results.

Table 4.3. *Values of temperature in the reactor and in the jacket and U · A. Tests at 20 and 25 W.*

Power [W]	T [°C]	T_{jacket} [°C]	ΔT [°C]	$U \cdot A$ [W/K]
20	61.9669	59.65	2.317	8.632
25	62.5478	59.65	2.898	8.627
		Mean value		**8.630**

From the previous table it can be noticed that the value of $U \cdot A$ determined for the two value of power are very similar. This fact confirm that data are good. The mean value of 8.630W/K is considered.

For the sake of correctness, it is to remind that $U \cdot A$ could be determined from the value of $\frac{U \cdot A}{m \cdot cp}$ previously determined by simple substitution of the value of $m \cdot cp$ of the mixture. This approach is not completely correct because the impeller inside the reactor has its own heat capacity. Moreover, this approach does not consider the value of the heat losses of that part of the reactor that are not covered by the jacket. At the contrary, with the approach employed in this work, $U \cdot A$ is computed in the steady state and on the base of this value and the one of τ determined in the cooling transient, the effective $m \cdot cp$ can be computed. This value is not the theoretical one but the effective one, since it includes the capacity of the impeller and the losses. On the base of τ and $U \cdot A$, the value of $m \cdot cp$ results equal to 861.6 J/K. Knowing that the heat specific capacity is 3.014 J/gK (1), 1.875 J/gK (2) and 2.32 J/gK (3) for hydrogen peroxide 32%, soybean oil and acetic acid respectively the theoretical heat capacity is 488.4 J/K (ideal mixture). This value is much lower than one previously determined (861.6 J/K) for the reason previously exposed. This result demonstrates that this approach, that uses both steady and transient data, is much more accurate than the one based solely on the transient.

In conclusion, Table 4.4 summarizes the results obtained in this paragraph.

Table 4.4. *Values of* τ, τ^{-1}, *effective and theoretical heat capacity.*

τ [s] $= \frac{m \cdot cp}{U \cdot A}$	τ^{-1}[s^{-1}] $= \frac{U \cdot A}{m \cdot cp}$	$U \cdot A$ [W/K]	Effective heat capacity [J/K]	Theoretical Heat capacity [J/K]
99.834	0.010017	8.630	861.6	488.4

Bibliographic references

1. http://www.h2o2.com/technical-library/physical-chemical-properties/thermodynamic-properties/default.aspx?pid=36&name=Heat-Capacity accessed 6/8/2016
2. http://webbook.nist.gov/cgi/cbook.cgi?ID=C64197&Mask=2 accessed 6/8/2016
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Chapter 5

Results and discussion

In this chapter the results of the study on the epoxidation are exposed. The analytical results of the experimental runs are compared in order to define the correct strategy. The analysis of the samples are carried out by Fourier Transformed InfraRed spectroscopy (FTIR). First the spectrum of the virgin oil is presented as a reference, then the results obtained in several different conditions are showed. Then the principal process variables on which it is possible to act on the system are studied and optimized.

In this chapter the effect of the presence of sulfuric acid is studied, the influence of the stirring regime, the impeller and the mixing program are examined. In addition, the concentrations of sulfuric and acetic acid are optimized. After this first part of the study,study, the possibility of carrying out the reaction in presence of ion exchange resin instead of sulfuric acid is exposed. Similarly to the process carried out with sulfuric acid, the loading of resin is optimized. Finally, the a study of the heat of reaction is reported.

The results of the study exposed in this chapter are mainly qualitative, but for every sample the estimation of conversion and selectivity is reported. In order to do that, the amount of residual double bonds, the one of the glycol and the epoxides formed have been determined. A precise method to evaluate the epoxy content is the one that uses hydrobromic acid and some pH indicator ([1]). This method is quite expensive, difficult to implement and its calibration requires a lot of time, even if it is very accurate. The presented results, instead, are obtained by FTIR analysis because it is a user friendly, simple and immediate method. This method permits to understand if epoxides are present but not to perform accurate calculation on its quantity (for this scope, the previous method is the best one). However, by FTIR analysis, the peaks associated to double bonds (reactant) and glycols (by-product) are well evident and good calculations can be carried out. These two values are enough to estimate conversion and selectivity. Anyway, it is reminded the focus of this work is to understand if the process can be carried out by non-conventional methods and to perform sensitivity analysis of the main process variables in the both cases of conventional and non-conventional methods. For these reasons, FTIR spectroscopy is enough. 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} ([2]).

Obviously, a deeper study using hydrobromic acid titration can be carried out in a future work.

5.1 – Virgin soybean oil

The FTIR spectrum of soybean oil is presented in Figure 5.1.

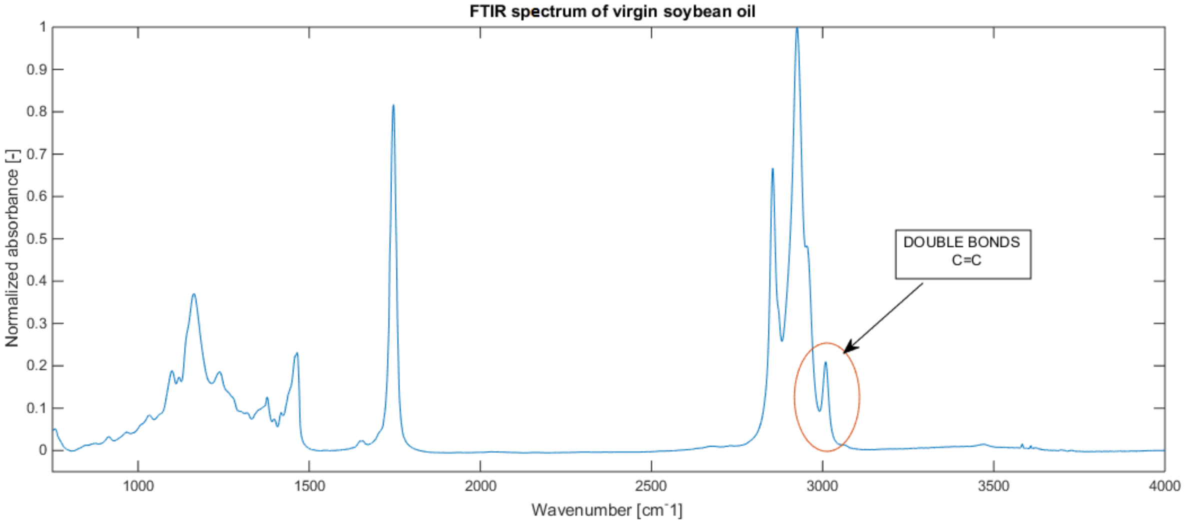

Figure 5.1. *FTIR spectrum of virgin soybean oil.*

As can be seen in Figure 5.1, the peak that appears at about 3010 cm^{-1} indicates the presence of double bonds C=C (unsaturations). If the intensity of this peak lows during the epoxidation process, it means that the conversion increases and the amount of double bonds decreases. If some glycols appear, a very intense peak from 3000 to 4000 cm^{-1} can be seen (centred on 3500 cm^{-1}). Evaluating these two peaks, information on conversion and selectivity can be obtained. The previous spectrum can be considered as a reference in order to evaluate the results.

5.2 – 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. Acetic acid: double bonds molar ratio is equal to 0.5:1 and hydrogen peroxide: double bonds is equal to 1.5:1. These ratios are the classical one that can be found in literature (Chapter 1). Time duration of the process is 4 hours whereas impeller speed is equal to 500 rpm. Setpoint temperature is 60°C.

As indicated in Chapter 3, in order to obtain these proportion, 105.6 g of oil, 84.15g of hydrogen peroxide 32wt.% and 15.85g of acetic acid are loaded. It is reminded that the instant in which the injection of hydrogen peroxide-acetic acid mixture occurs is considered as starting time. All these instructions are exposed in Chapter 3 and they are here recalled for practicality.

5.2.1 Process carried out in absence of sulfuric acid

As regards the process carried out without sulfuric acid, the result is indicated in Figure 5.2 (FTIR spectrum). This sample is the number 7.

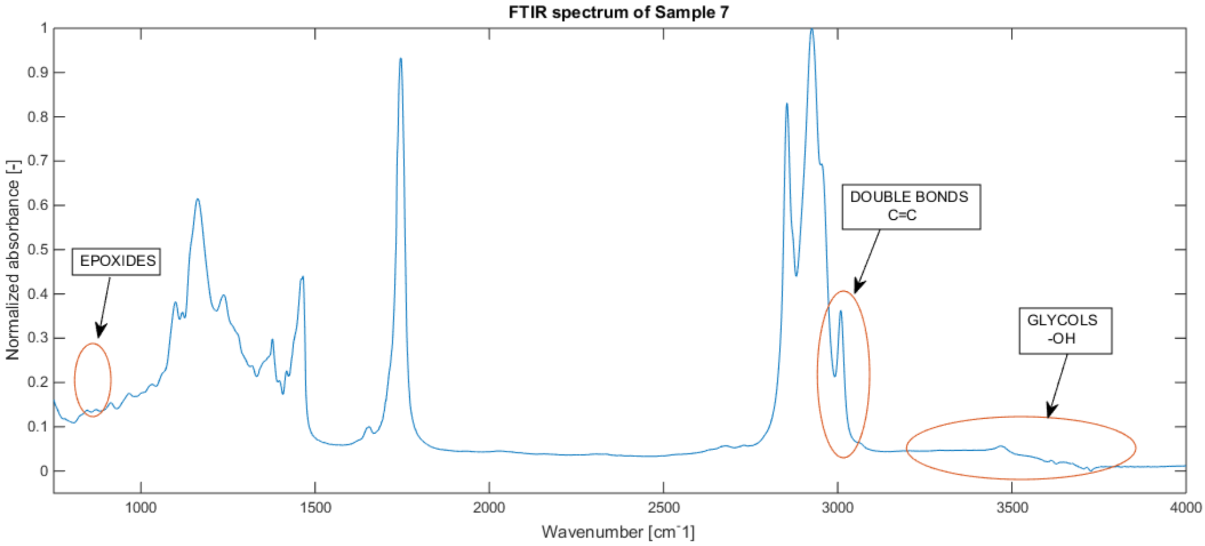

Figure 5.2. *FTIR spectrum of Sample 7. Process carried out without sulfuric acid for 4 hours. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Impeller speed 500 rpm.*

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%. A further confirm of this fact is that there are no peaks associated to epoxides (820-830 cm^{-1}). Some glycols are produced, but in very small amount. The reaction of epoxidation is so slow that is negligible and that small amount of epoxide produced reacts to glycols. In conclusion, the process cannot be carried out without sulfuric acid, if acetic acid and diluted hydrogen peroxide (32wt.%) are used. In order to corroborate this experimental evidence, the thermal profile along time can be observed (Figure 5.3).

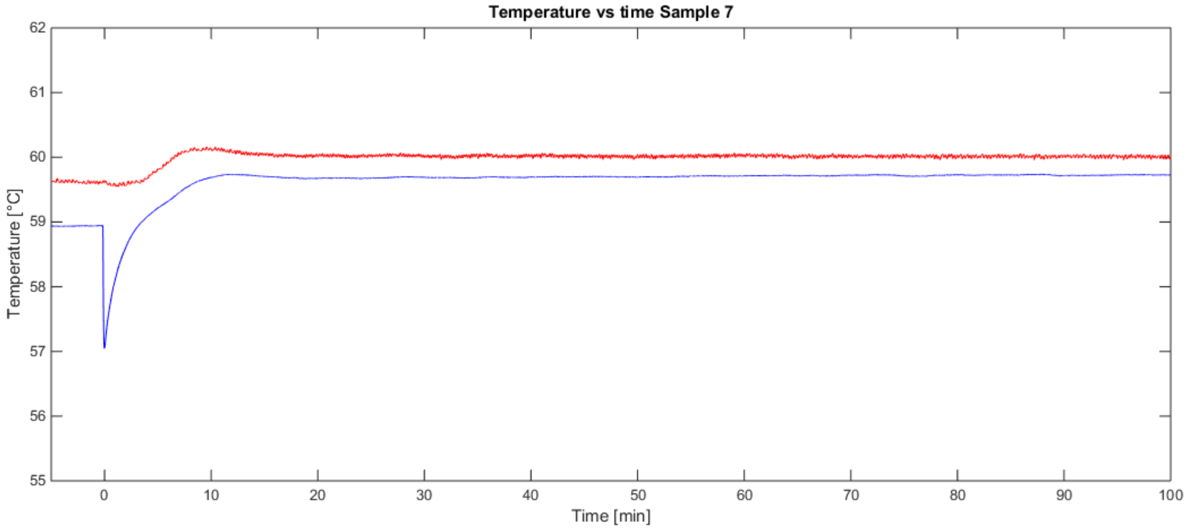

Figure 5.3. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 7*

visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Impeller speed 500 rpm.

The thermal profile (blue curve) indicates the total absence of thermal overshoots that can be due to exhotermic reactions (epoxidation). This fact confirms that epoxidation is so slow that can be considered negligible. For the sake of correctness, a slight overshoot can be noticed at time equal to 0 minutes (injection instant). In fact, the adding of the acetic acid – hydrogen peroxide mixture causes a sudden decrease of the temperature inside the reactor, because the mixture is a little cooler than 60°C. After that, the controller drastically reacts to face this temperature variation, causing an excessive increase of the temperature in the jacket (controller overshoot). This fact reflects an overshoot in the temperature inside the reactor.

5.2.2 Process carried out in presence of sulfuric acid

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 FTIR analysis of the product after 4 hours can be seen in Figure 5.4. The sample is number 8.

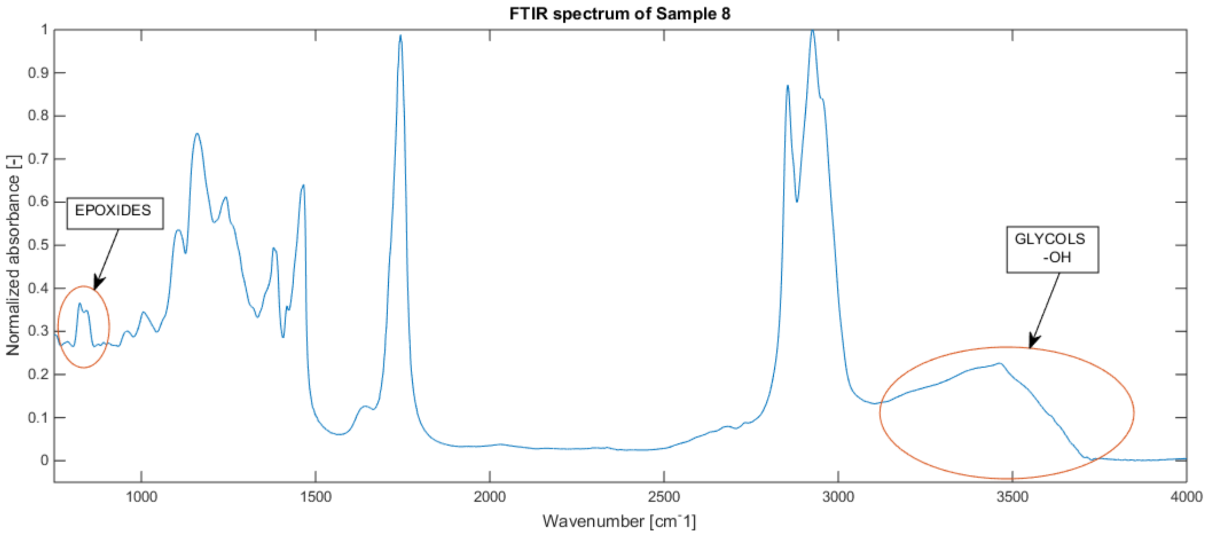

Figure 5.4. *FTIR spectrum of Sample 8. Process carried for 4 hours. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil. Impeller speed 500 rpm.*

As can be seen from the FTIR analysis, the result of sample 8 is totally different from sample 7. First of all, a noticeable peak associable to epoxides is present. Consequently, epoxidation takes place. Moreover, a noticeable peak due to the presence of glycols appears so they are surely present as by-products. Moreover, the peak of double bonds cannot be seen in this spectrum. The presence of the large -OH band makes difficult to understand if the C=C peak is small or totally absent. For these reason, it is impossible to attribute a value to the height of the peak of double bonds but it is surely smaller than 0.13. This is a good evidence because in the previous case (sample 7) the height of this peak was 0.3883. This means that a big amount of C=C reacts. However, because of the -OH band, it is impossible to know if the conversion is partial or total.

In conclusion, on the base of this analysis, it can be said that both main and secondary reactions take place, that epoxides and glycols are surely present and that double bonds surely react.

The fact that the reaction of epoxidation takes places is confirmed by the temperature profiles. The great exhotermic character of epoxidation reflects in great thermal overshoot in the reactor (Figure 5.5).

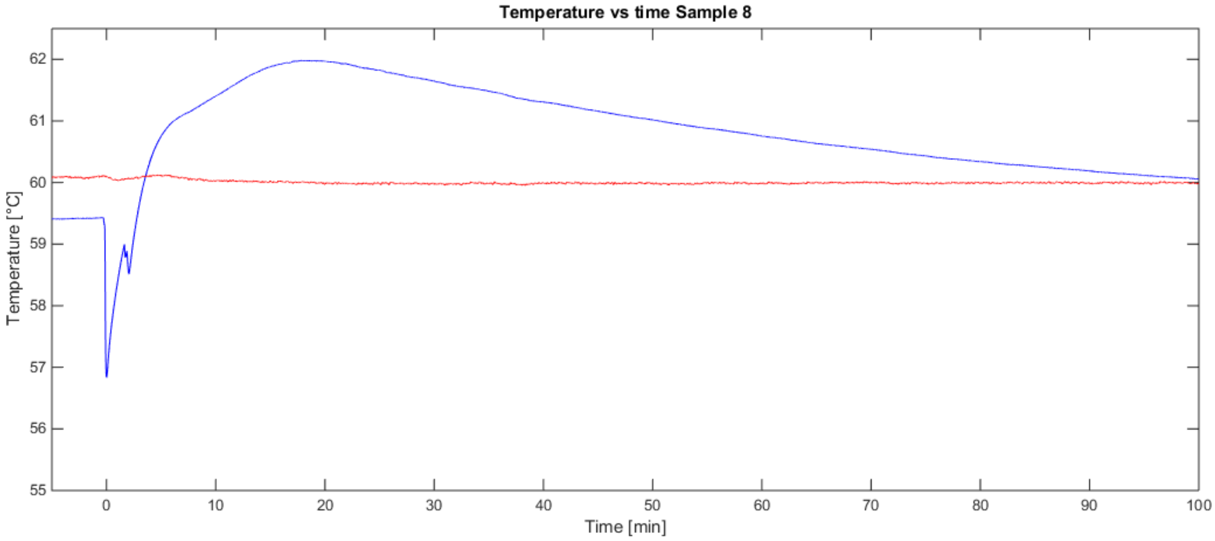

Figure 5.5. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 8 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil. Impeller speed 500 rpm.*

As can be seen in Figure 5.5, a great thermal overshoot is noticeable (62.17°C). With such a temperature peak, it is an experimental evidence that epoxidation reaction takes place. This fact is accordance with the results obtained from the FTIR analysis. In consequence to this, it is also evident that sulfuric acid has a strong catalytic activity towards the epoxidation.

Other interesting information are given by this thermal profile. In fact, after two hours, a strong mixing at 1500 rpm is carried out for 1 minute. After that, 500 rpm is set again. After this, another thermal peak occur, as can be seen in Figure 5.6. 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.

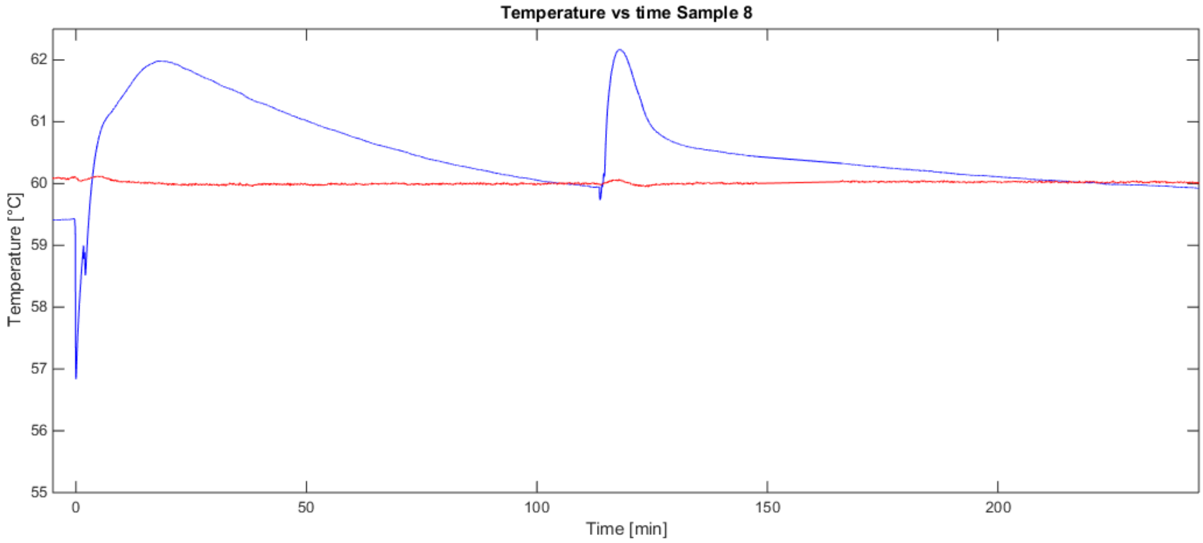

Figure 5.6. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 8 visualized up to 240 mins (total time). Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30 seconds after 2 hours.*

Once that conversion has been proven to be nearly total, selectivity can be calculated. In fact, the -OH band can be compared with a reference one, obtained by FTIR spectrum of glycols of soybean oil. These glycols are obtained by complete conversion of soybean oil to glycols. In order to perform the comparison, the peak between 3000 and 4000 cm^{-1} can be normalized once the background has been removed. The selectivity can be calculated using equation 5.1:

$$Selectivity = 1 - \frac{height\ OH\ peak\ sample}{height\ OH\ peak\ reference} \qquad if\ conversion\ \rightarrow 100\% \tag{5.1}$$

The selectivity so calculated is significant only if the conversion is nearly total, otherwise it is overestimated. Since there is a good proof that conversion is nearly total, the selectivity so calculated can be considered correct. The comparison between the sample and the reference spectra is presented in Figure 5.7. Spectra are visualized only from 2400 to 4000 cm^{-1} in order to better highlight the -OH band.

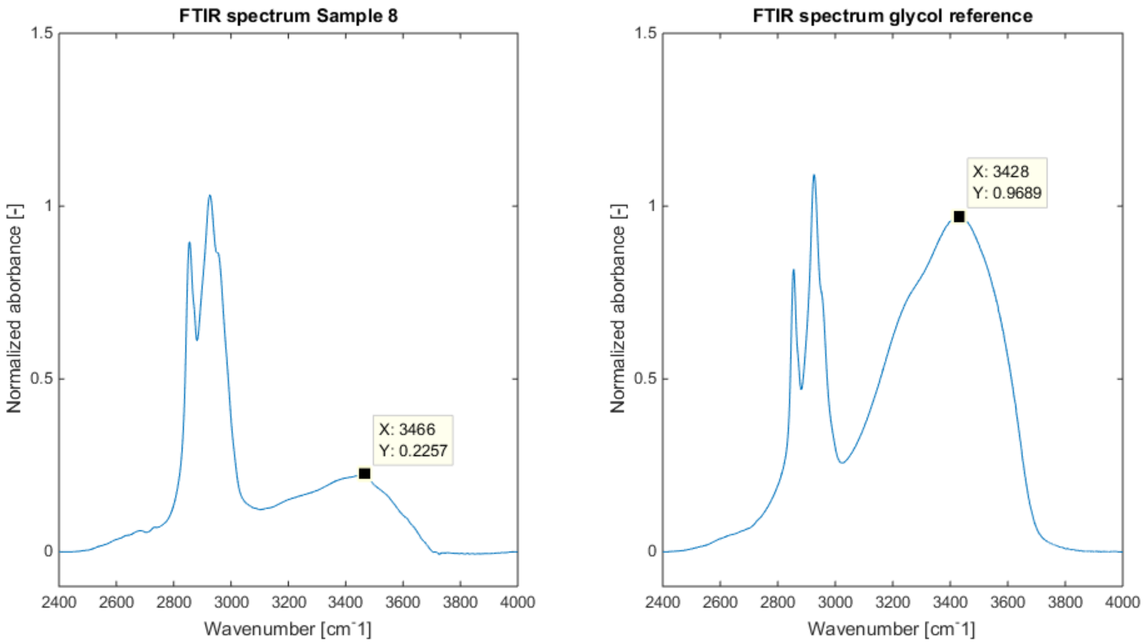

Figure 5.7. *Comparison between -OH peak of Sample 8 and the reference of glycols. Both the spectra are normalized once the background is subtracted.*
The height of the peaks represented in the figure permit the estimation of the selectivity.

The height of the OH band is 0.2257 and 0.9689 for sample 8 and reference respectively. The selectivity can be estimated equal to 77%. The amount of glycols is quite relevant.

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. In this way epoxides can be easily formed even if also some by-product can be produced.

5.3 – Effect of mixing regime and mixing program

From the previous paragraph, the necessity of a good study of the mixing regime appears. In fact, dealing with a by-phasic system, mixing and mass transfer between phases is crucial. In fact, if the impeller speed is too low, a good mass transfer is not achieved. If the impeller speed is too high, the rate determining step is not the mass transfer but the rate of reaction, so the process is in kinetic control. Moreover, if the impeller speed is too high, epoxides are more exposed to acid and water and glycols can be formed, so a good compromise must be found. This fact was studied by Aguilera *et al*. ([3]). 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.

In the case of sample 8, it can be seen that mixing problems occurs. In fact, after a strong mixing at 1500 rpm for 1 min, the temperature increases once again. This means that the impeller does not work with the whole mass of mixture but the upper part of the oil segregates and remains unreacted. When an energetic mixing is applied, the reacted oil (epoxidized) is taken away from the impeller and the unreacted oil can be mixed with the aqueous phase. This fact implies a new thermal peak.

This fact can be resolved in many ways. The first is to increase the impeller speed up to 1500 rpm, in order to avoid segregation. This is not a feasible solution because of the degradation of the oil. Another solution is to use other impellers, as the pitched blade one. This impeller is an axial one and can involve the entire volume of liquid. However, it is not good to create good emulsions. A good impeller could be the BTD one, that reduces the dead zones with respect to the Rushton turbine, that is used in this work. Another solution could be install two Rushton turbine on the same shaft to create better dispersion. The last two cases could be interesting to study in a future work. However, these impellers are not available and the single Rushton turbine will be used. It is to remind that Rushton turbine could give segregation problems but surely creates a good emulsion. Moreover, this fact could not be a problem. In fact, changing the impeller could not give better results in terms of rate of reactions or selectivity.

Another variable that can be manipulated is the mixing program. In fact, maintaining the same impeller speed is not effective in this case. With fixed speed, segregation or degradation surely occurs with a low or high speed. The solution is 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 impeller 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 5.8 The sample is the number 9. 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 8.

With this value, it is possible to evaluate the thermal power delivered by the process, that is equal to about 20.9 W, that is quite noticeable. This estimation is based on the value of the heat exchange coefficient determined in Chapter 4. The fact that the rate of reaction is meanly higher than the case of sample 8 is demonstrated by the fact that after about 3.5 hours no thermal overshoots are appreciable. This is a very important result, since sample 8 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.

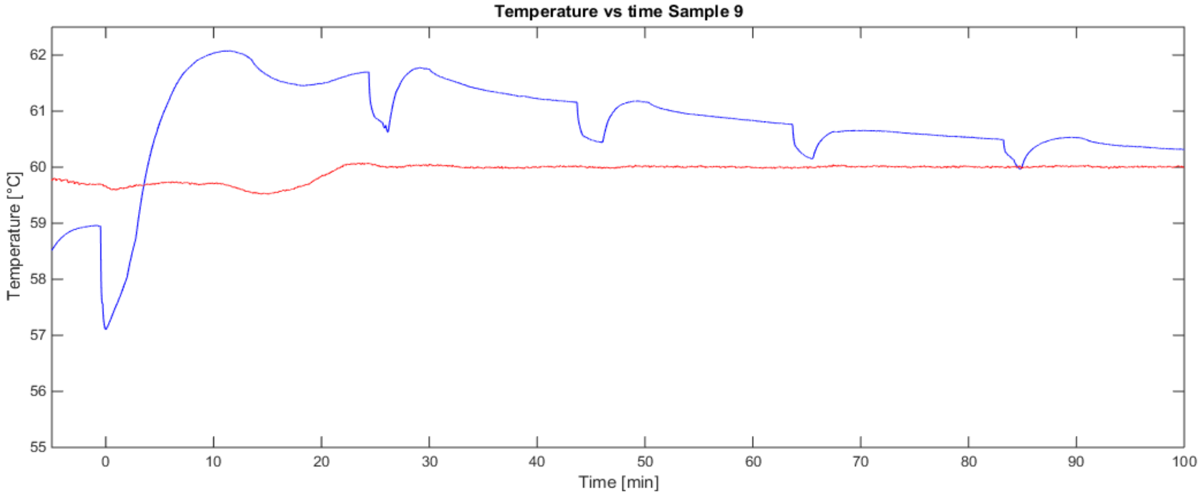

Figure 5.8. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 9 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

As concerns the selectivity, the FTIR analysis of sample 9 is exposed in Figure 5.9. The duration of the process is 4 hours.

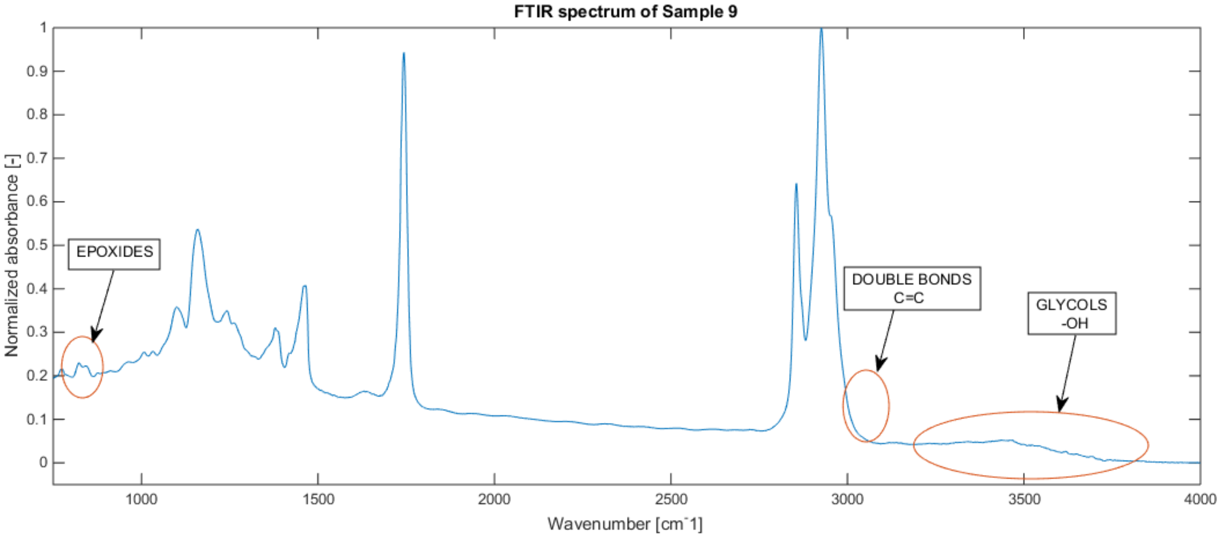

Figure 5.9. *FTIR spectrum of Sample 9. Process carried out for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 minutes. Impeller speed 500 rpm. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil.*

The result is evident. The peak at 820 cm^{-1} indicates the presence of epoxides. Moreover, glycols are present in traces, and its peak is barely noticeable. The double bonds peak is totally absent. These three data confirm that conversion is nearly total (~100%) and the products are nearly totally epoxides. Since conversion is total, selectivity can be calculated similarly to sample 8. Figure 5.10 represents the spectrum of sample 9 and the reference, only from 2400 to 4000 cm^{-1} to better highlight the OH peak. Background is subtracted and spectra are normalized.

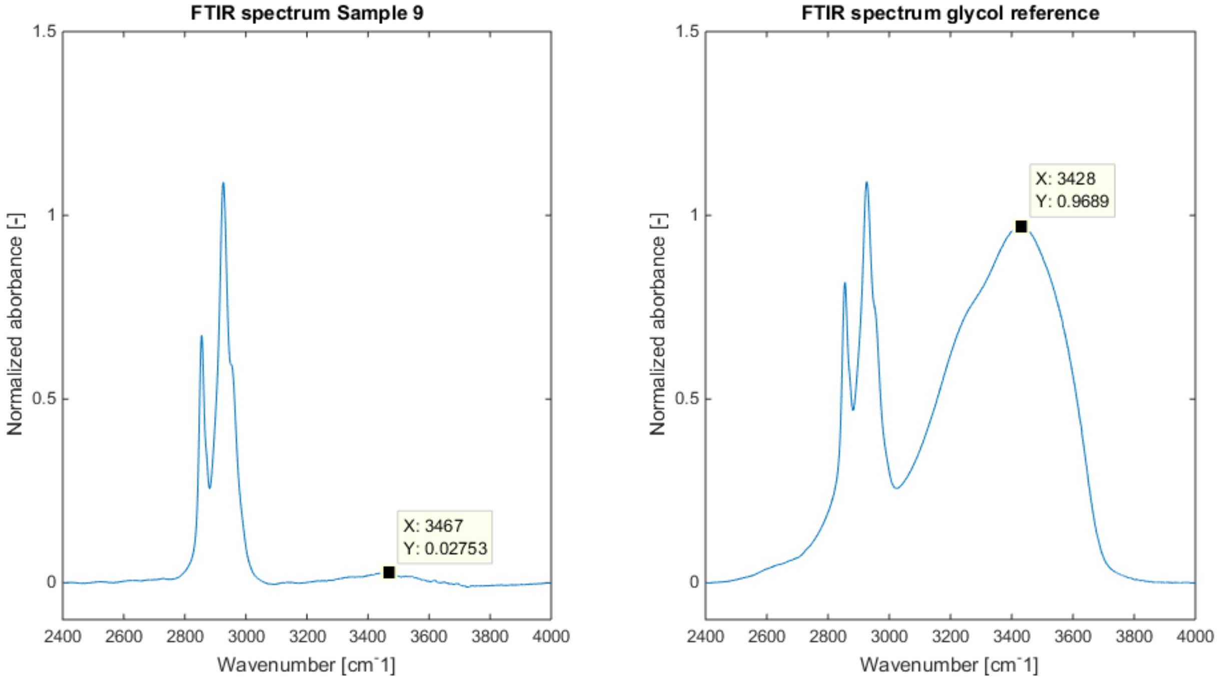

Figure 5.10. *Comparison between -OH peak of Sample 9 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the peaks permits the estimation of the selectivity.*

In the case of sample 9, the height of the peak is equal to 0.027. The selectivity is estimated equal to better than 97%. Selectivity is very good and the improvement with respect to sample 8 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. The improvement is very noticeable, if one takes into account that samples 8 and 9 are obtained with the same reactants but with a different mixing program. This evidence is very important because a proper mixing program is fundamental in order to obtain a good product. This a good innovation because mixing program is as important as the mixing regime, which is well taken into account in the literature. All these results are summed up in Table 5.1.

Table 5.1. *Main results of sample carried out with or without remixing. Red colour highlights the most effective condition.*

Remixing	Yes	Not
Sample	9	8
Conversion after 4h (estimated)	~100%	~100%
Selectivity after 4h (estimated)	97%	77%
Time required to complete conversion (estimated)	3.5	4

5.4 – Effect of the concentration of sulfuric acid

In order to study to optimize the concentration of sulfuric acid, a sensitivity study is performed. The sulfuric acid is loaded at 2, 3 and 4 wt.% with respect to the oil. The conditions are identical to the ones of sample 9, i.e. acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Remixing is carried out for 30 seconds at interval of 20 minutes. Time duration of the process is equal to 4 hours.

Since the result with 3wt.% of acid has been previously exposed (sample 9), only the ones at 2 and 4wt.% are here presented. They are sample 11 and 12 respectively. As concern the FTIR spectra, they are represented in Figures 5.11 and 5.12 (samples 11 and 12 respectively).

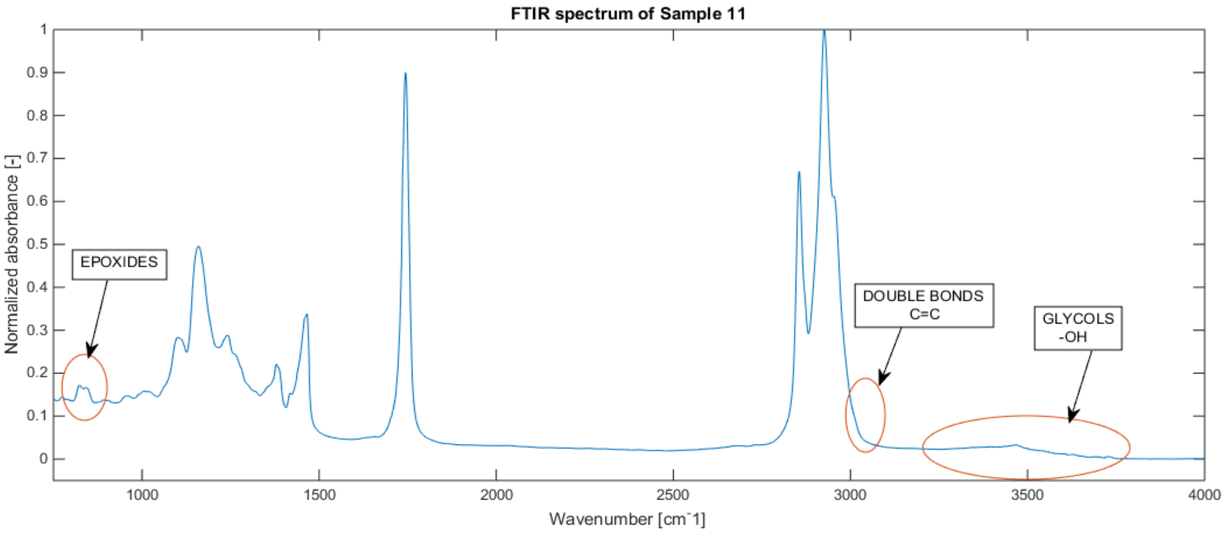

Figure 5.11. *FTIR spectrum of Sample 11. Process carried out for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 mins. Impeller speed 500 rpm.Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 2wt.% with respect to oil.*

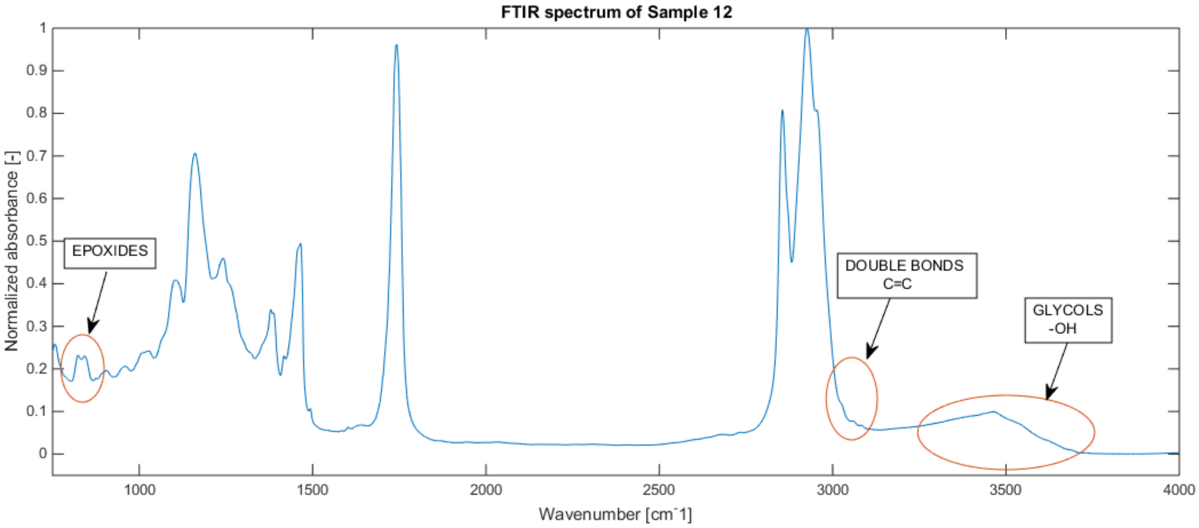

Figure 5.12. *FTIR spectrum of Sample 12. Process carried for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 mins. Impeller speed 500 rpm. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 4wt.% with respect to oil.*

As can be noticed from the previous spectra, the peak of double bonds cannot be appreciated in both cases. In consequence, the conversion can be considered nearly total (~100%). Moreover, epoxides are produced in both cases since its peak is well evident. Since conversion is total, selectivity can be calculated as previously done. Figures 5.13 and 5.14 represent the spectra of sample 11 and 12 compared to the reference, only from 2400 to 4000 cm^{-1} to better highlight the OH peak. Background is subtracted and spectra are normalized.

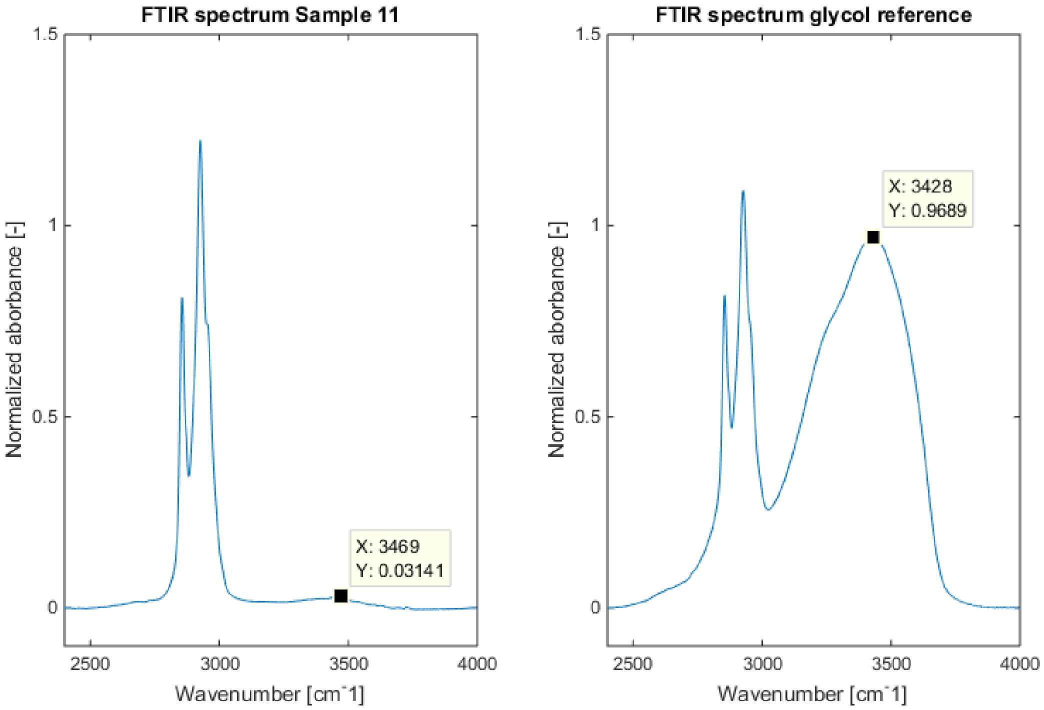

Figure 5.13. *Comparison between -OH peak of Sample 11 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the peaks permits the estimation of the selectivity.*

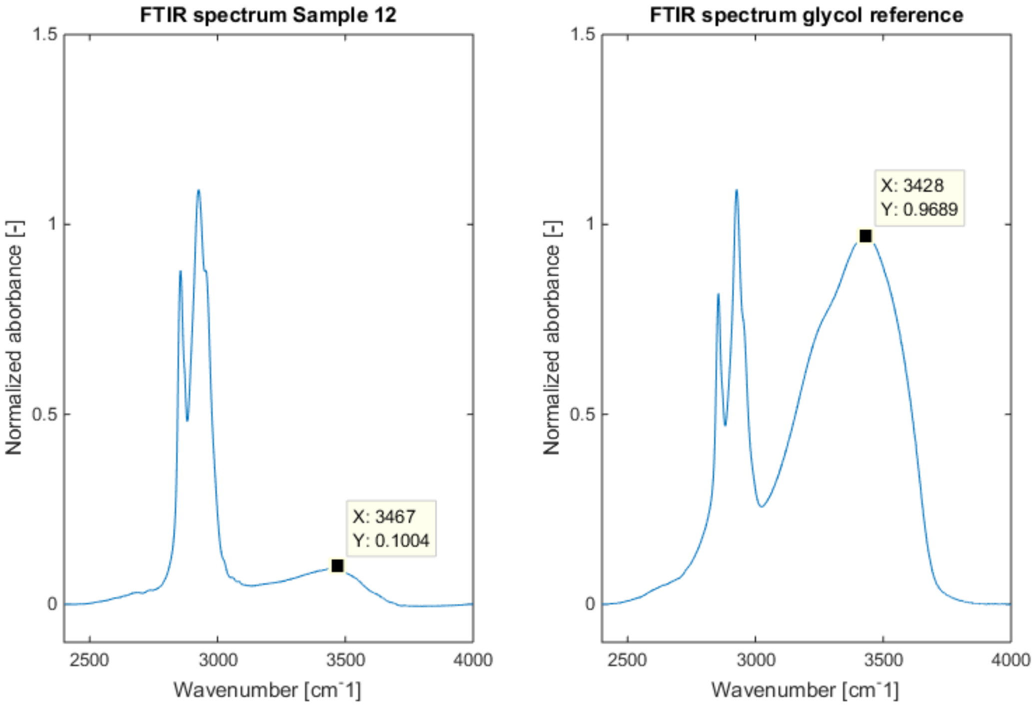

Figure 5.14. *Comparison between -OH peak of Sample 12 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the peaks permits the estimation of the selectivity.*

The height of the OH peak is 0.03 and 0.10 for sample 11 and 12 respectively. Including sample 9, which calculation has been carried out at §5.3, the selectivity is equal to 97% for 2wt.% and 3wt% of sulfuric acid whereas it decreases to 90% for 4wt.% (with respect to the mass of oil). This fact means that an excessive amount of sulfuric acid is detrimental for the selectivity, since strong acids catalyses the epoxy ring opening and the formation of glycols. This evidence is summed up in Figure 5.15. It is reminded that concentration of sulfuric acid equal to 2wt.%, 3wt.% and 4wt.% corresponds to samples 11, 9 and 12 respectively.

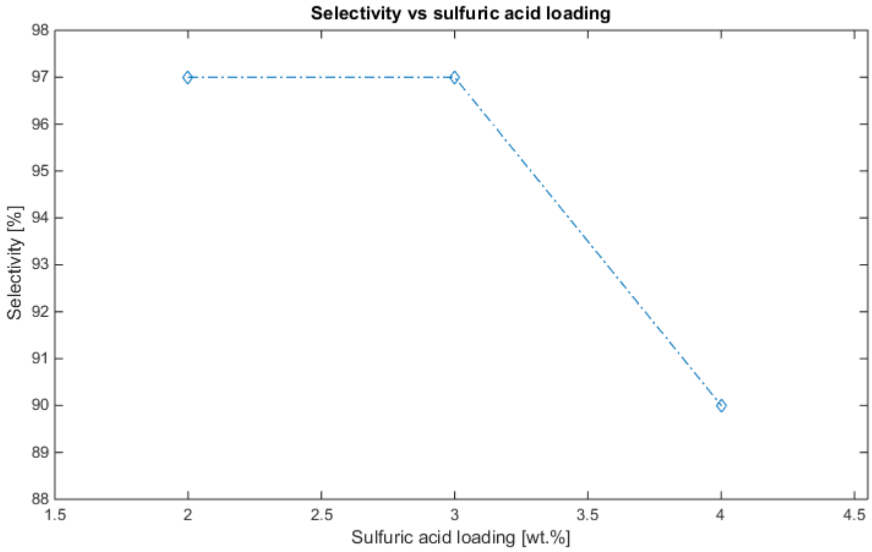

Figure 5.15. *Selectivity vs loading of sulfuric acid. Concentration of 2wt.%, 3wt.% and 4wt.% corresponds to sample 11, 9 and 12 respectively.*

As regard the thermal study, the temperature profiles are represented Figure 5.16 and 5.17.

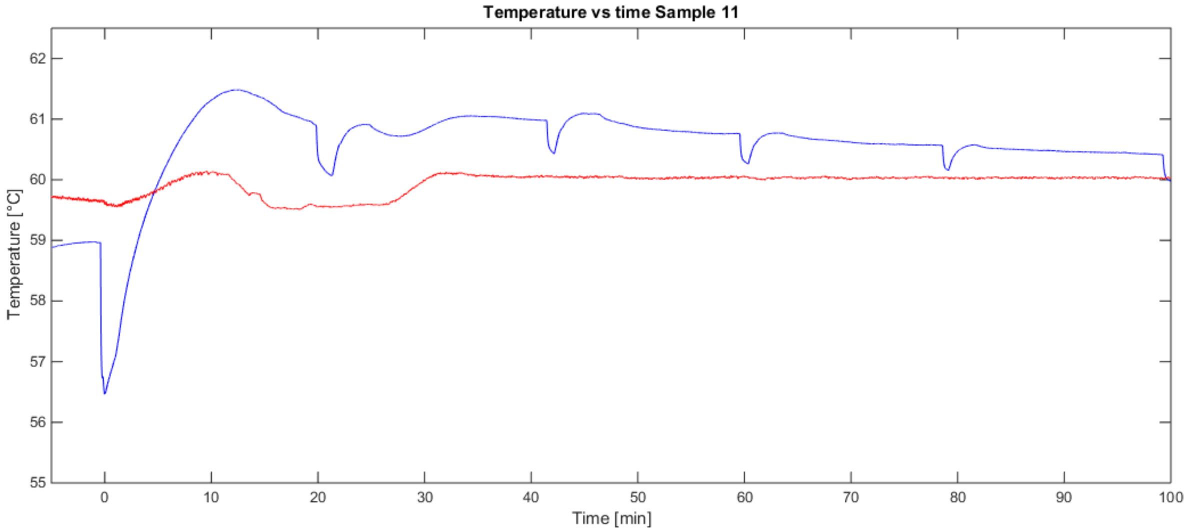

Figure 5.16. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 11 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 2wt.% with respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

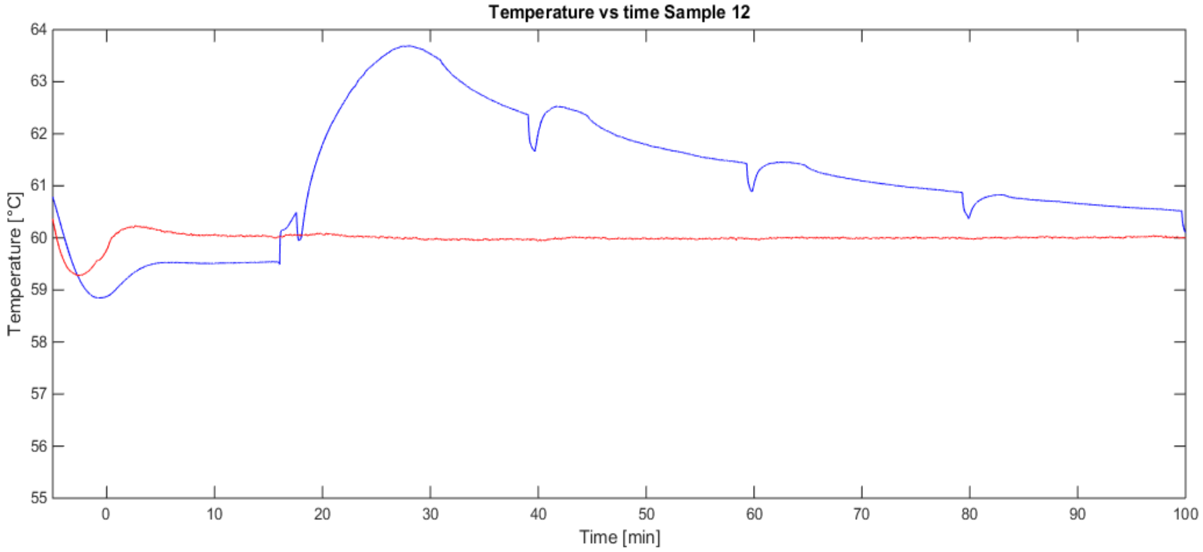

Figure 5.16. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 12 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 4wt.% with respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

As can be seen in Figure 5.8, 5.15 and 5.16, the temperature overshoot increases if the concentration of sulfuric acid increases. The peak of temperature is equal to 61.49°C, 62.07°C and 63.68°C for 2wt.%, 3wt.% and 4wt.% of sulfuric acid. This permits to calculate the thermal power generated at the beginning and it is equal to 15.9W, 20.9W and 34.8W. It is clear that the higher is the concentration of sulfuric acid, the higher is the rate of reaction and, consequently, the thermal power generated. This effect is well represented in Figure 5.17.

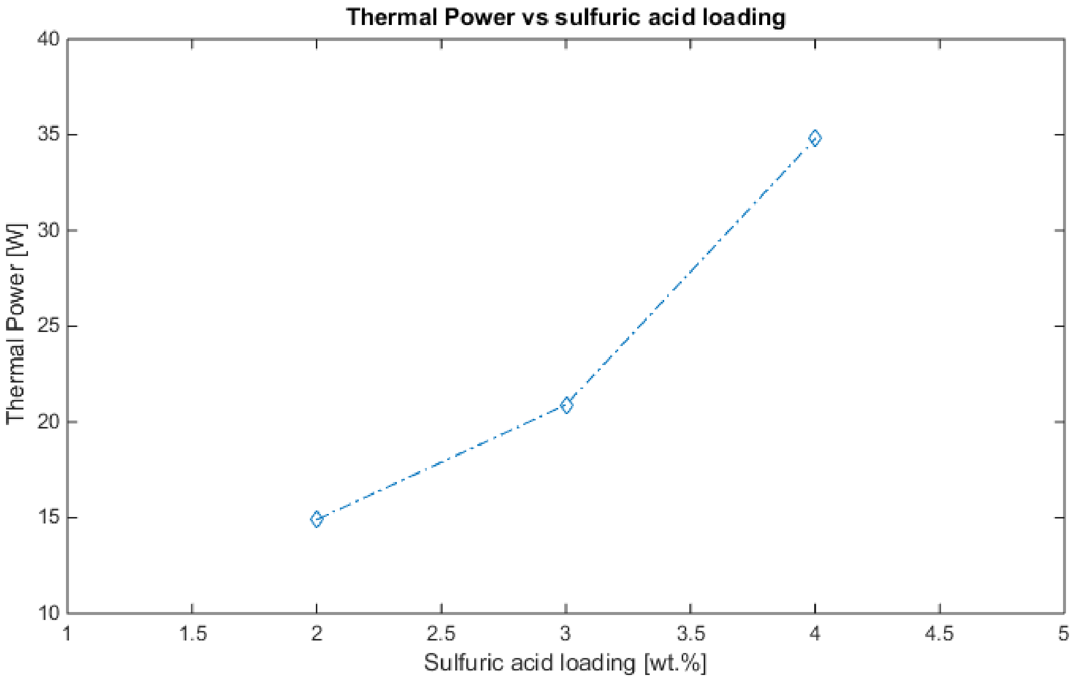

Figure 5.17. *Thermal power generated in the early stages of the reaction vs concentration of sulfuric acid. Concentration of 2wt.%, 3wt.% and 4wt.% correspond to samples 11, 9 and 12.*

The relation between power and concentration of sulfuric acid appears to be more than linear. Anyway, it must be taken into account that, in sample 12, the temperature at the instant of injection, decreases only to 58.8°C, whereas in all the other cases temperature decreases to 56.5-57°C. This fact is purely due to the procedure and to the handling of the hot hydrogen peroxide-acetic acid mixture. In fact, while transferring the solution from the thermostatic bath to the reactor, according to the speed of the operation, the mixture can cool down more or less. This aspect could partially affect the datum of peak temperature of Sample 12. Reasonably, the trend can be considered linear or slightly more than linear since the trend in Figure 5.17 could be slightly overestimated.

However, beyond this fine clarification, the important result of this sensitivity study is that there is a direct and well evident relation between rate of reaction (and consequently thermal power) and concentration of sulfuric acid. In consequence, it is evident that sulfuric acid has a strong catalytic activity towards the epoxidation. This fact confirms what exposed at §5.2.

As regards the time required to extinguish temperature overshoots, 4h, 3.5 and 3h are required for 2wt.%, 3wt.% and 4wt.% respectively (samples 11, 9, 12). When the temperature overshoots extinguish, the conversion is considered total. However, deeper analysis could be carried out to make more accurate this evaluation.

In conclusion, sulfuric acid hugely boosts the epoxidation with its strong catalytic activity, reducing the required time to complete conversion. However, the good compromise is at 3wt.%, where selectivity excellent selectivity is maintained but lower time to the process are needed. Table 5.2 sums up what exposed in this paragraph.

Table 5.2. *Main results obtained for different concentration of sulfuric acid. The red colour highlights the more effective concentration of sulfuric acid.*

Concentration of H_2SO_4	2wt.%	3wt.%	4wt.%
Sample N°	11	9	12
Thermal power generated at the beginning	14.9W	20.9W	34.8W
Time required to complete conversion	4h	3.5h	3h
Selectivity after 4h	97%	97%	90%

5.5 – Effect of concentration of acetic acid

In this paragraph the effect of different concentrations of acetic acid are studied. The acetic ratio acetic acid:double bonds equal to 0.5:1 has been studied with sample 9 at §5.3. In this paragraph that ratio is increased to 1:1 in order to understand the effect on conversion and selectivity. All the other conditions are maintained fixed. Sulfuric acid is at 3wt.% with respect to the oil. Time duration equal to 4 hours. This effect is studied with sample 13. Its FTIR analysis is reported in Figure 5.18.

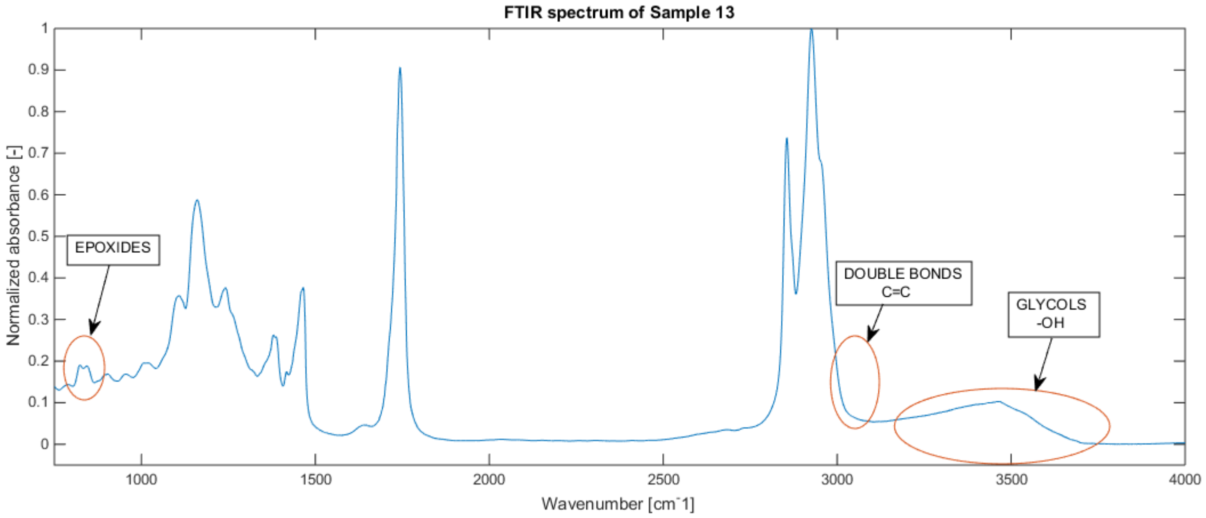

Figure 5.18. *FTIR spectrum of Sample 13. Process carried for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 mins. Impeller speed 500 rpm. Acetic acid:double bonds equal to 1:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil.*

It can be seen that no peaks related to double bonds are present so the conversion is considered nearly total. Epoxides are produced since its peak is well evident. A noticeable band due to -OH (glycols) is evident. Comparing to sample 9, the amount of glycols is higher. In order to quantify this fact, the selectivity is calculated using equation 5.1 and the method previously used. Figure 5.19 represents the spectrum of sample 13 compared to the reference, only from 2400 to 4000 cm^{-1} to better highlight the OH peak. Background is subtracted and spectra are normalized on the higher peak.

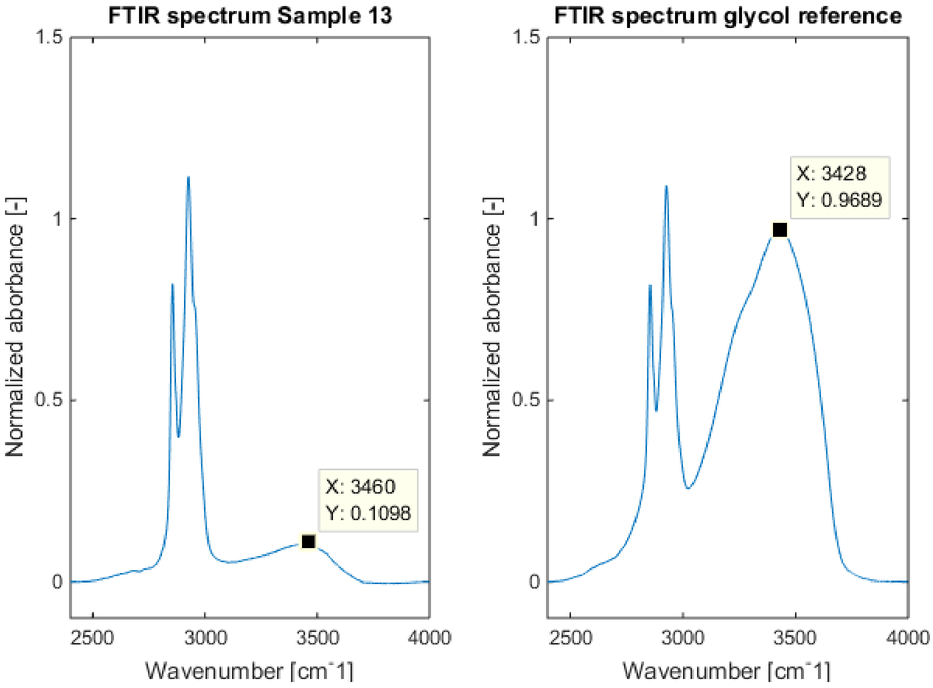

Figure 5.19. *Comparison between -OH peak of Sample 13 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the peaks permits the estimation of the selectivity.*

The height of the OH band is equal to 0.1098. Consequently, the selectivity is equal to 89%. It is evident that increasing the acetic acid : double bond ratio from 0.5 :1 to 1:1 decreases the selectivity from 97% (sample 9) to 89% (sample 13).

As regard the temperature profile, it is represented in Figure 5.20.

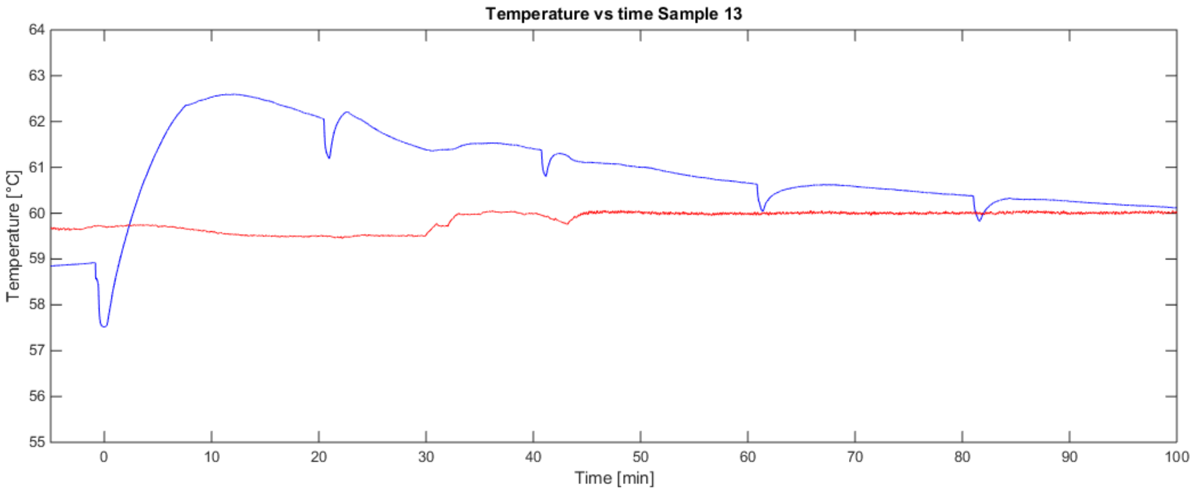

Figure 5.20. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 13 visualized up to 100 mins. Acetic acid:double bonds equal to 1:1 and hydrogen peroxide:double bonds equal to 1.5:1. Sulfuric acid 3wt.% with respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

As can be seen in Figure 5.20, the peak of temperature at the beginning is equal to 62.59°C. This means that thermal power is equal to 25.4W, whereas with molar ratio acetic acid : double bonds equal to 0.5:1 it is equal to 20.9 W (sample 9). It can be concluded that doubling the amount of acetic acid the thermal power generated at the beginning is 22% more than the base case (sample 9). Consequently, the rate of reaction is higher. This is confirmed by the time required to extinguish thermal overshoot that is about 3 h, that is considered the time required to complete conversion. This value is lower than the one obtained with sample 9 (3.5h). Hence, the higher rate of reaction is confirmed also by this fact.

In conclusion, increasing the amount of acetic acid increases the amount of peroxyacetic acid that is formed. This implies that the rate of reaction is higher but the greater amount of acid promotes the epoxy ring opening and the formation of glycols. This confirm what found in literature (Chapter 1). The most effective acetic acid : double bonds molar ratio is 0,5:1. Table 5.3 summarize these data.

Table 5.2. *Main results obtained for differentacetic acid : double bonds molar ratio. The red colour highlights the more effective choice*

Acetic acid : double bonds ratio	0.5:1	1:1
Conversion after 4h	~100%	~100%
Selectivity after 4h	97%	89%
Thermal Power at the beginning	20.9W	25.4W
Timer required to complete conversion (estimated)	3.5h	3h

5.6 – Effect of loading of ion exchange resin

In this paragraph the presence of ion exchange resin instead of the sulfuric acid is studied. The resin is *Amberlite IR120* by Dow chemical and it is strongly acidic. Thanks to its acidic behaviour, this resin is very interesting to be studied for its catalytic potential. Three loading are tested, 10wt.%, 25wt.% and 40wt.% with respect to oil. The samples are samples are 14, 15 and 16. Time duration of the process is equal to 4 hours. The FTIR analysis of the results are shown in Figures 5.21, 5.22 and 5.23. The process is carried out for 4 hours.

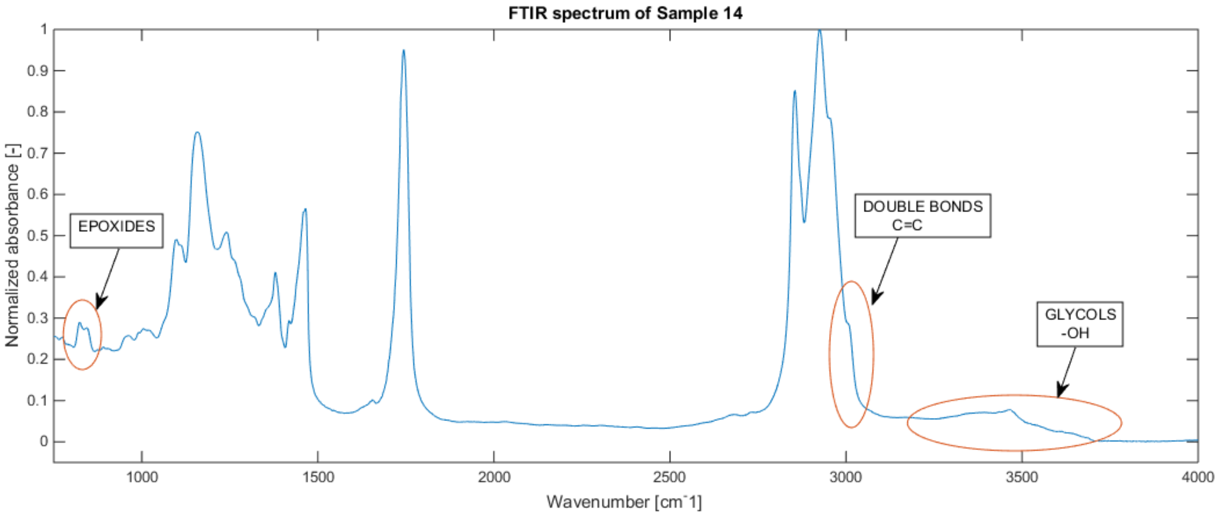

Figure 5.21. *FTIR spectrum of Sample 14. Process carried for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 mins. Impeller speed 500 rpm. Acetic acid:double bonds equal to 1:1 and hydrogen peroxide:double bonds equal to 1.5:1. Ion exchange resin Amberlite IR120 10wt.% with respect to oil.*

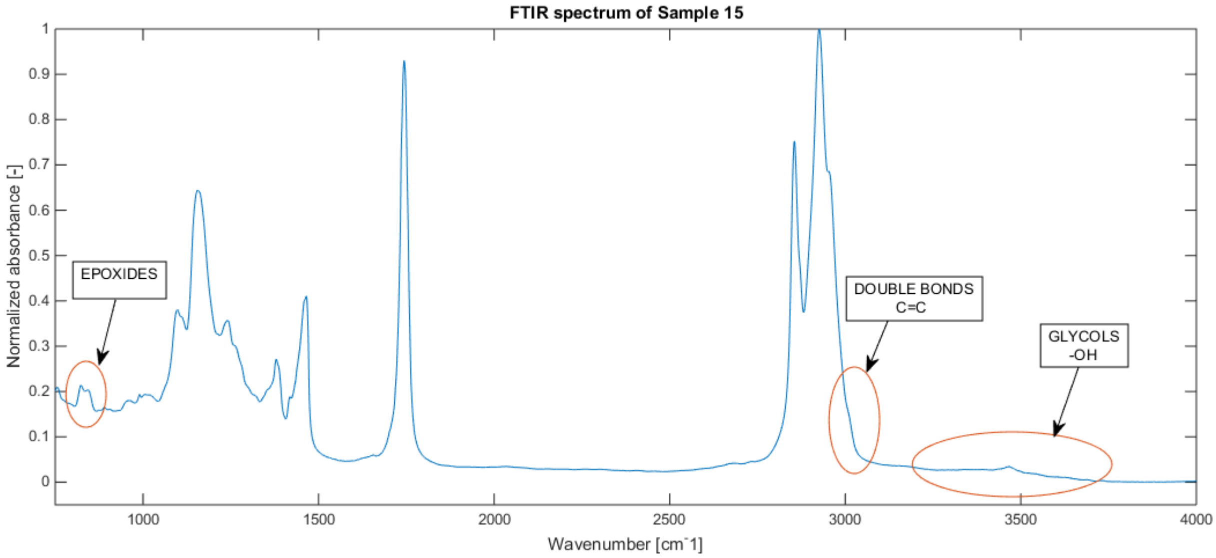

Figure 5.22. *FTIR spectrum of Sample 15. Process carried for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 mins. Impeller speed 500 rpm. Acetic acid:double bonds equal to 1:1 and hydrogen peroxide:double bonds equal to 1.5:1. Ion exchange resin Amberlite IR120 25wt.% with respect to oil.*

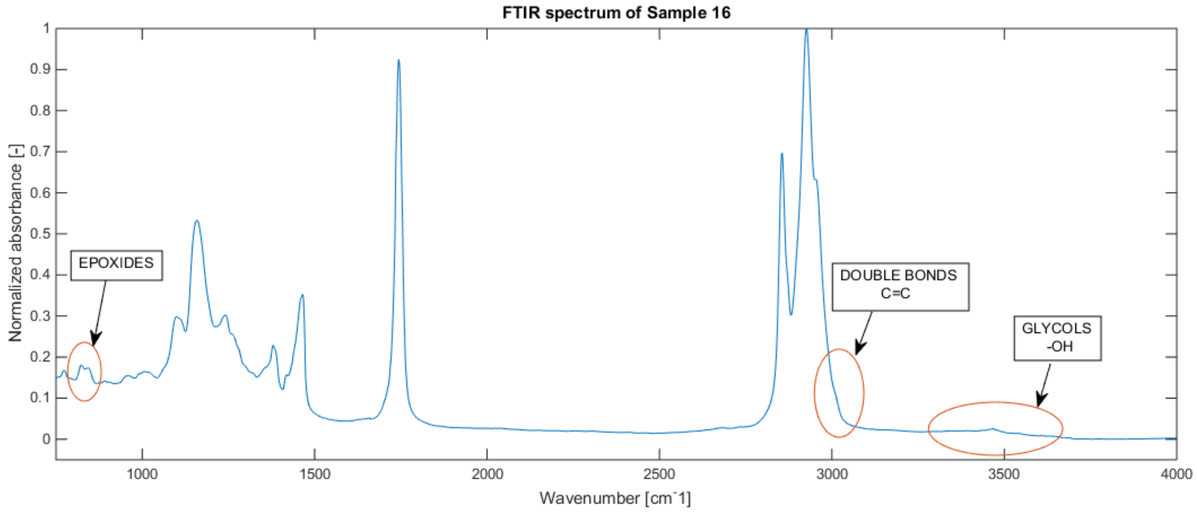

Figure 5.23. *FTIR spectrum of Sample 16. Process carried for 4 hours with remixing at 1500 rpm for 30s at intervals of 20 mins. Impeller speed 500 rpm. Acetic acid:double bonds equal to 1:1 and hydrogen peroxide:double bonds equal to 1.5:1. Ion exchange resin Amberlite IR120 40wt.% with respect to oil.*

Observing the previous FTIR analysis, in every case epoxides are produced since epoxy peak is well evident. Moreover, there are some problems to correctly appreciate the double bonds peak. In the case of 10% of resin loading (sample 14-Figure 5.21), the double bonds peak seems to be shifted towards lower values of wavenumber. In this way the peak at 2900 cm-1 and the one of the double bonds are partially superposed. This peak is lower than the case in which neither sulfuric acid nor resin are loaded, i.e. sample 7. In the case of sample 14, the height of the peak is 0.2891 (Figure 5.24) whereas in the case of sample 7 the height is 0.3883. Both spectra are normalized and the background is subtracted. This is a very qualitative evaluation. If a rough estimation is performed, the conversion can be calculated by equation 5.2

$$Conversion = 1 - \frac{height\ C{=}C\ peak\ sample}{height\ C{=}C\ peak\ reference} \tag{5.2}$$

According this formula, the conversion is about 25%. This value has to be considered an approximatively estimation, since the peak of C=C is superposed with the one at 2900 cm^{-1} and its height can be strongly affected.

However, the fact that part of the oil is converted represents a good result, because the acidic resin shows a certain catalytic activity towards the epoxidation, even if weaker than sulfuric acid. Moreover, some glycols are produced. In order to deliver an approximatively estimation of the amount of glycols that have been formed, the selectivity can be calculated with equation 5.3.

$$Selectivity = 1 - \frac{height\ OH\ peak\ sample}{height\ OH\ peak\ reference} \cdot \frac{1}{Conversion} \tag{5.3}$$

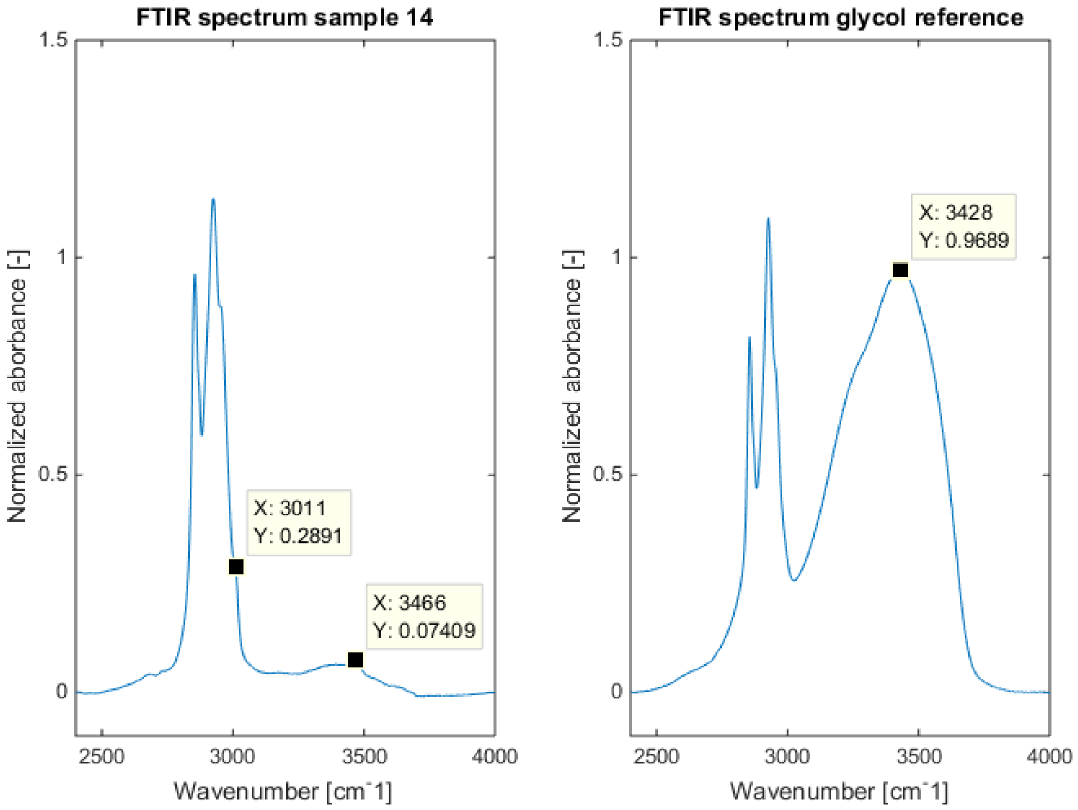

Figure 5.24. *Comparison between spectra of Sample 14 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the -OH peaks permits the estimation of the selectivity. The height of C=C peak permits the calculation of conversion.*

The selectivity calculated using eq. 5.3 and the spectra in Figure 5.24 is equal to 71%. Figure 5.24 represents the spectrum of sample 14 compared to the reference, only from 2400 to 4000 cm^{-1} to better highlight the OH peak. Background is subtracted and spectra are normalized on the higher peak.

As concern the 25wt.% loading (sample 15), there is the same shift of the C=C encountered in the sample 14. The height of the double bonds peak (once the background is subtracted end the spectra normalized) is equal to 0.1627 (Figure 5.25). According the method previously applied, the estimated conversion is about 58%. It is reminded that also in this case this calculation is only indicative, because the peak of C=C is superposed with the one at 2900 cm^{-1} and its height can be strongly affected. In the same way of the previously sample, selectivity can be estimated. Figure 5.25 represents the spectrum of sample 15 compared to the reference, only from 2400 to 4000 cm^{-1} to better highlight the OH peak. Background is subtracted and spectra are normalized on the higher peak.

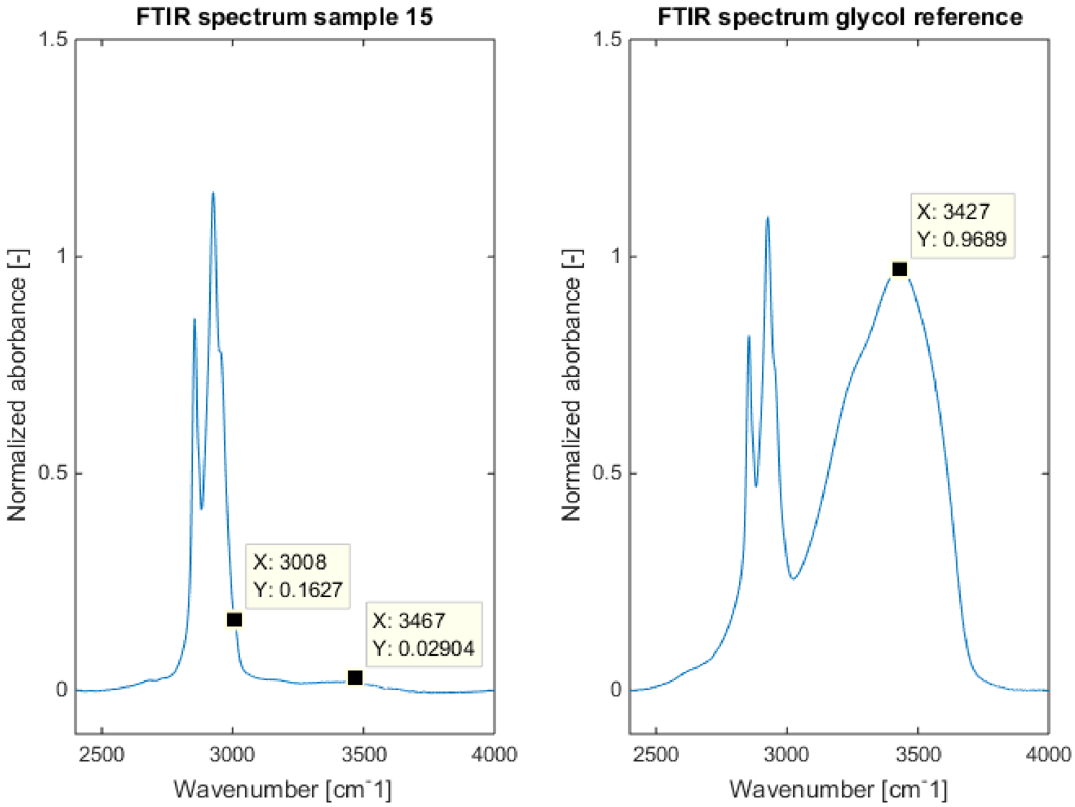

Figure 5.25. *Comparison between spectra of Sample 15 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the -OH peaks permits the estimation of the selectivity. The height of C=C peak permits the calculation of conversion.*

Applying the same approach of sample 14, the estimated selectivity for sample 15is equal to 95%.

As concerns the 40wt.% of resin loading (sample 16), the evaluation of double bonds peak results even more difficult than the previous case. However, the most reasonable value is 0.1065 (Figure 5.26). In this way can be evaluated and it is estimated equal to 73%. At this point also the selectivity can be estimated. Figure 5.26 represents the spectrum of sample 16 compared to the reference, only from 2400 to 4000 cm^{-1} to better highlight the OH peak. Background is subtracted and spectra are normalized on the higher peak.

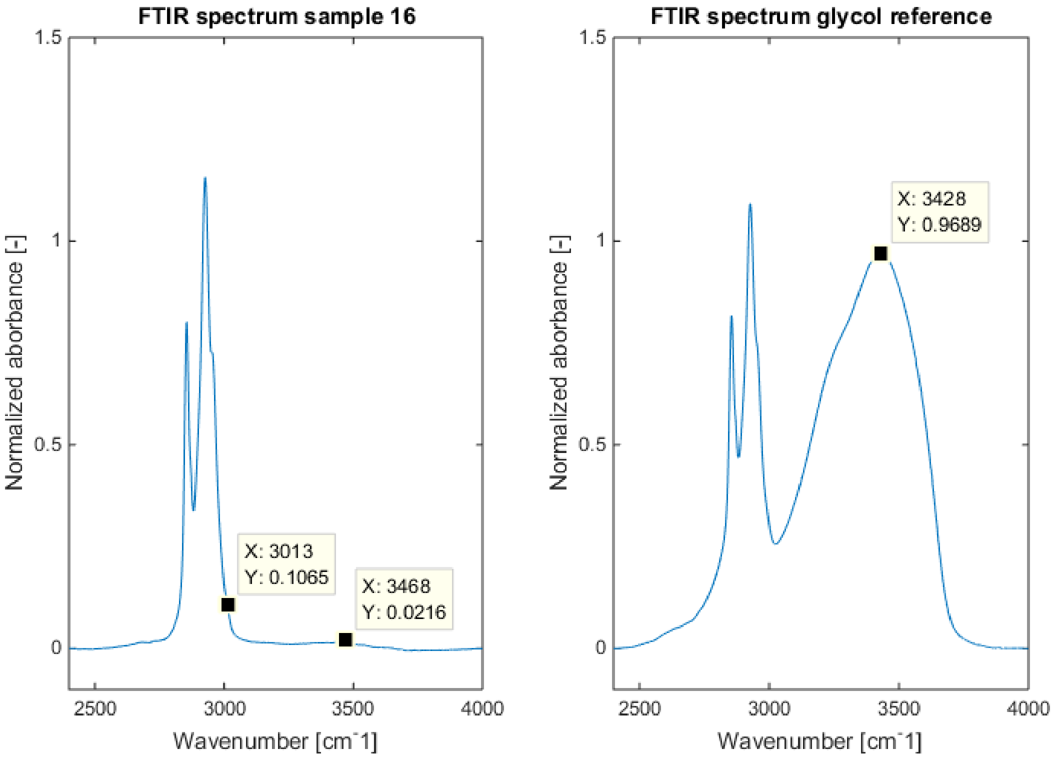

Figure 5.26. *Comparison between spectra of Sample 16 and the glycol reference. Both the spectra are normalized once the background is subtracted. The height of the -OH peaks permits the estimation of the selectivity. The height of C=C peak permits the calculation of conversion.*

Applying the method previously used, the estimated selectivity for sample 16 is equal to 97%. All these results indicate two important evidences. The first is that ion exchange acidic resin shows a good catalytic activity towards the epoxidation. As a matter of fact, all the samples demonstrate that, after 4 hours, at least a part of the oil is converted and epoxides are produced. It is reminded that, without resin or acid, no conversion is observed. In conclusion, ion exchange resin works well. If the conversion after 4 hours is plotted vs the resin loading, the graphic in Figure 5.27 can be obtained.

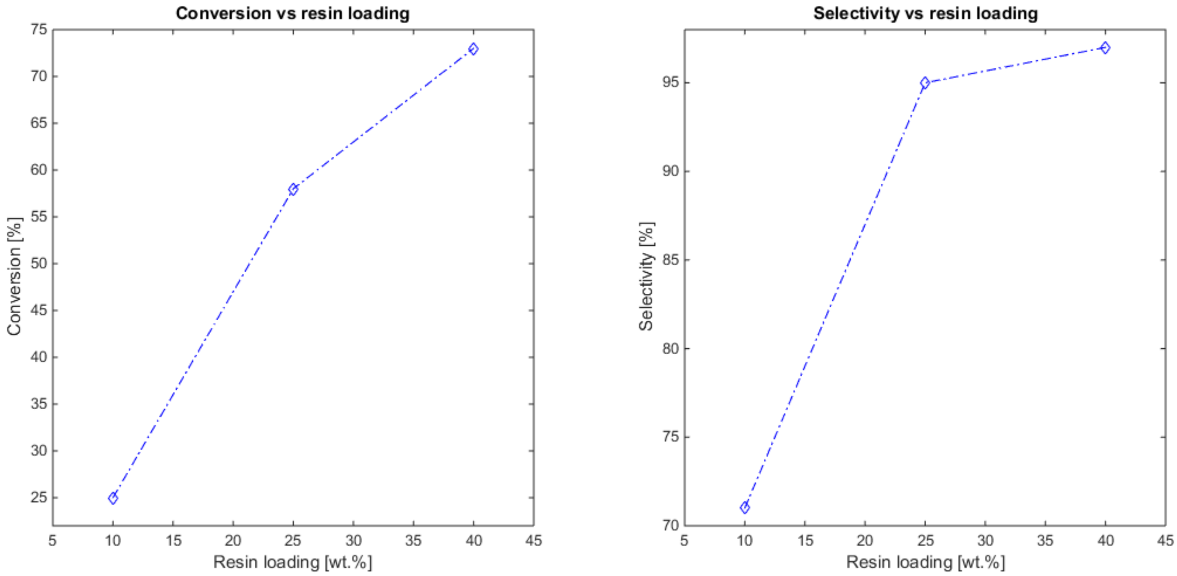

Figure 5.27. *Conversion and selectivity vs. resin loading. Amberlite IR120 resin. Loading at 10, 25 and 40wt.% correspond to Samples 14, 15 16.*

As can be seen in Figure 5.27 the conversion increases when the loading of resin is increased. This trend is less than linear and shows a saturation behaviour. In fact, passing from 25 to 40wt.% of resin, the conversion does not increase in the same way as occurs from 10 to 25wt.%. Moreover, it is reminded that the fact that the double bonds peak is shifted towards the C-H peak (2900cm^{-1}) could slightly overestimate the quantity of double bonds. This means that the conversion is slightly underestimated and the oil could be more converted than this estimation. The second consideration is that selectivity is much lower (77%) if the loading is low (10wt.%), whereas it increases to 96-95% when the loading is higher (25-40wt.%). This can be due to the fact that when the reaction is slow (10% of catalyst) the epoxides that has been formed are opened to glycols because the two reactions of epoxidation and epoxy-ring opening have comparable rates. If the loading is increased, the epoxidation is boosted and its rate is higher than the rate of the side reaction. Probably, If the resin loading is further increased beyond 40%, the strong acidic behaviour of the resin could catalyse the side reaction and selectivity could low.

Definitively, the 25wt.% loading is chosen as the best compromise because a larger amount of the resin does not improve so much the conversion and the selectivity. Moreover, in this way a lot of resin is saved with respect to the case of 40wt.% loading.

As concerns the temperature profiles, the profiles of samples 14, 15 and 16 are represented in Figures 5.28, 5.29, 5.30.

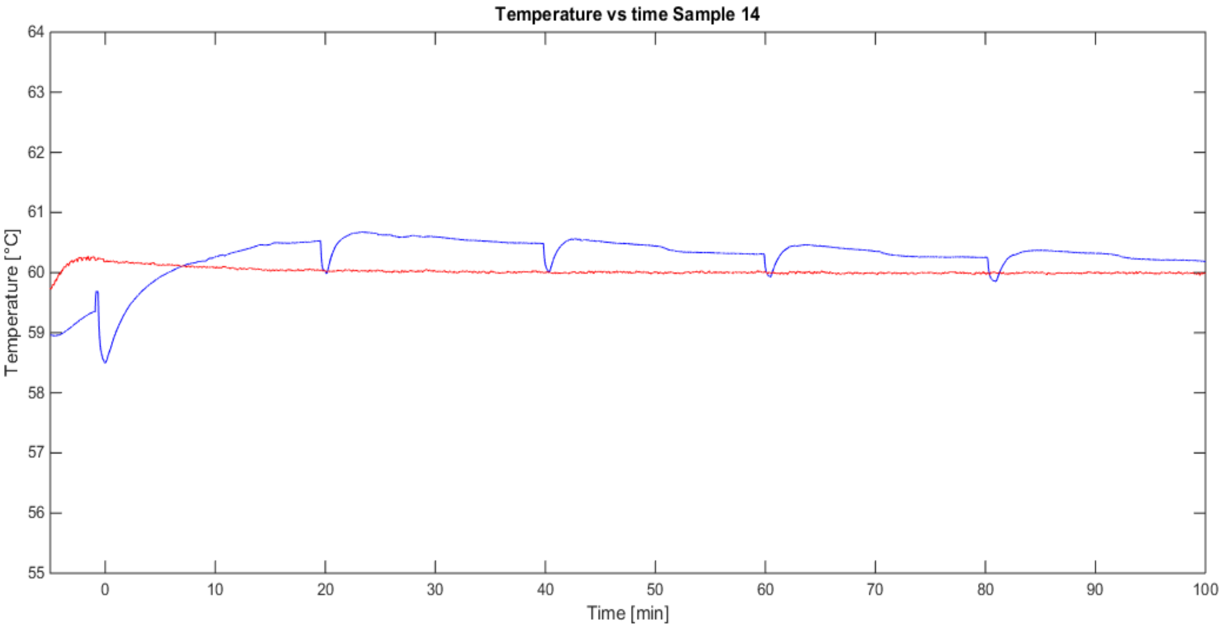

Figure 5.28. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 14 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Amberlite IR120 10wt.% respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

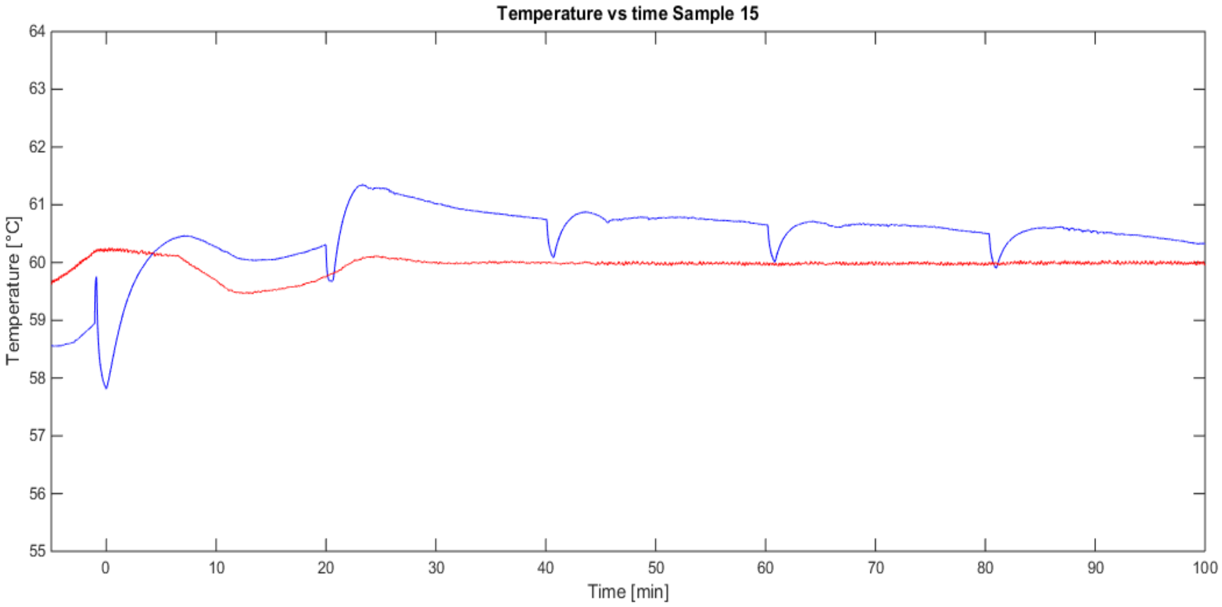

Figure 5.29. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 15 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Amberlite IR120 25wt.% respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

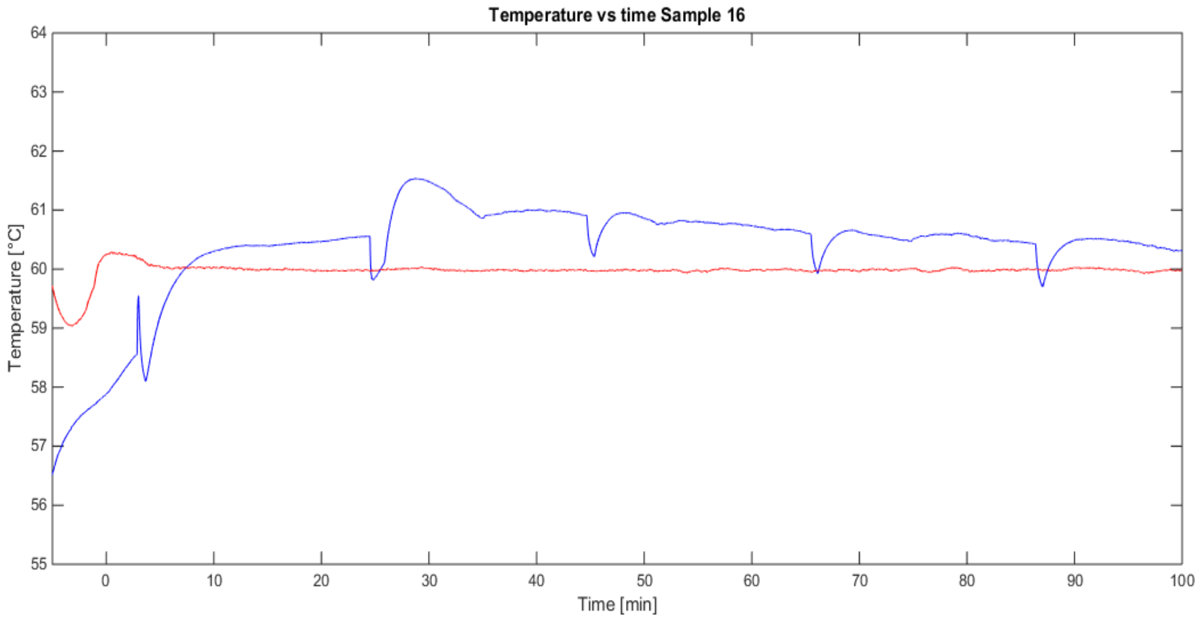

Figure 5.30. *Temperature profile vs time inside the reactor (blue) and at the inlet of the jacket (red) of Sample 14 visualized up to 100 mins. Acetic acid:double bonds equal to 0.5:1 and hydrogen peroxide:double bonds equal to 1.5:1. Amberlite IR120 40wt.% respect to oil. Impeller speed 500 rpm. Remixing at 1500 rpm for 30s at interval of 20 mins.*

From the previous temperature profiles, it can be seen that the temperature at the beginning is equal to 60.67°C, 61.35°C and 61.53°C for sample 14, 15, 16. With these data the thermal power generated at the beginning can be calculated. Thermal power is equal to 8.8W, 14.7W and 16.2W. These results are plotted in Figure 5.31.

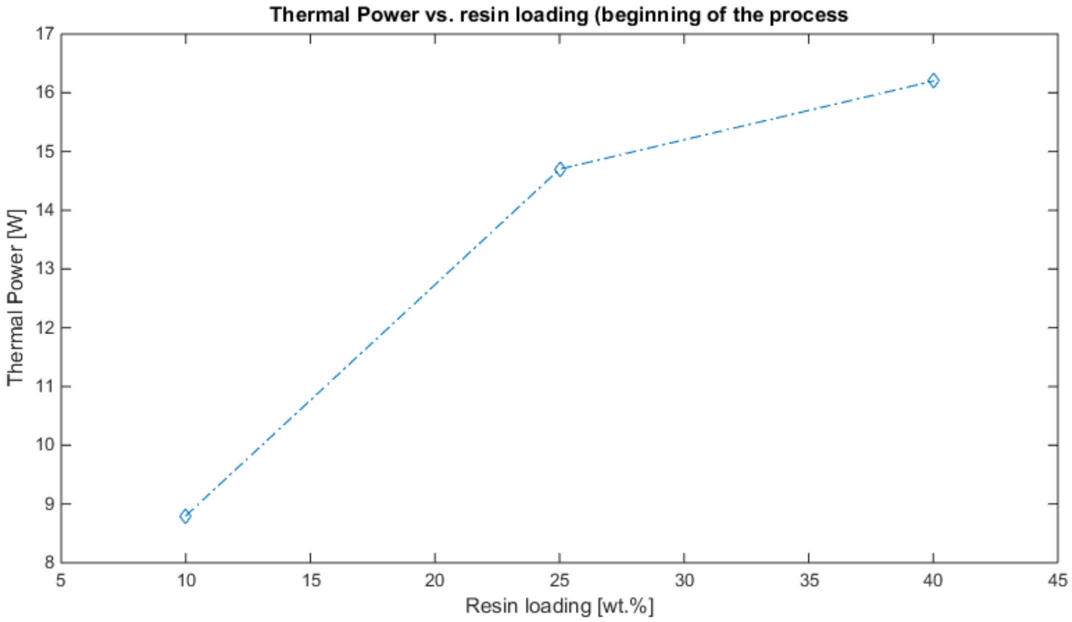

Figure 5.31. *Thermal power generated in the early stages of the reaction vs resin loading. Loading equal to 10wt.%, 25wt.% and 40wt.% correspond to samples 14, 15 and 16.*

As can be seen in Figure 5.31. the thermal power generated by the epoxidation at the beginning of the process does not increases linearly but less than linearly. This means that the rate of reaction in the early stages of the process increases with the loading of resin thanks to its catalytic activity. However, the activity per unit of mass of the catalyst becomes weaker and weaker when the loading of catalyst is increased. This fact totally confirms what previously stated about conversion (Figure 5.27).

An equivalence in terms of catalytic activity can be find between resin and sulfuric acid. Approximatively 1g of sulfuric acid has the activity of 10 g (one order of magnitude) of resin. This evaluation is carried out basing on the data of power.

All these data are summed up in Table 5.3.

Table 5.3. *Main result obtained varying the resin loading. The best compromise is highlighted with red colour.*

Amberlite *IR120* resin	10wt.%	25wt.%	40wt.%
Sample	14	15	1
Conversion after 4h (estimated)	25%	58%	73%
Selectivity after 4h (estimated)	71%	95%	97%
Thermal power generated at the beginning	8.8W	14.7W	16.2W

In conclusion, acidic ion exchange resin demonstrates a good catalytic activity towards epoxidation. Selectivity and conversion that can be obtained are very good. The best compromise is 25wt.% with respect to the oil. The conversion at 4 hours is noticeably lower than the case of sulfuric acid (conversion nearly total) since the resin is less active. However, this is a good result since the typical time duration of the conventional process using liquid acid is around 6-8 hours. Moreover, it is reminded that, in the industrial conventional process, phosphoric acid is often used. Even if phosphoric acid is not tested in this work, on the base of the data of Santacesaria *et al.* ([5]), the activity of the resin is at least comparable or even better than phosphoric acid. These good results indicate that ion exchange resin can be successfully used as a good solution in an industrial process.

5.7 – Estimation of the heat of reaction

Since the heat exchange coefficient is well known (§4.3), the heat of reaction can be estimated. The sample taken into account is sample 8. This is the sample without remixing that could create great problems when the calculation is performed. The conversion is assumed to be nearly total (§5.2).

The temperature profile is integrated in *Matlab* once the steady state temperature is subtracted. The integration is performed from the instant 0 to the end of the reaction (4 hours) by trapezoidal integration. The obtained result is -105.6kJ. Since in the reactor 105.6g of oil are loaded and 100g of oil contain 0.518 mols of double bonds, the total number of double bonds are 0.547mols. This results lead to the estimated heat of reaction equal to -193kJ/mol. This value is very close to the results of De Quadros *et al.*(4) and Santacesaria et *al.*(5), 196kJ/mol and -230kJ/mol respectively. This result is considered affordable and sufficiently accurate.

Table 5.3 summarizes this result.

Table 5.4. *Heat of reaction determined in this work and by De Quadros et al* (4)*. and Santacesaria et al* (5)*.*

	This work	De Quadros et al.	Santacesaria et al.
Heat of reaction	-193 kJ/mol	-196 kJ/mol	-230 kJ/mol

5.8 – Notes on the conservation of the epoxidized oil

Several articles (6) suggest extracting the oil with diethyl ether in such a way the acqueous phase and the organic one are well separated. In this way the aqueous phase is well separable. The ether can be removed from the oil by simple warm up to 50-60°C. In this case instead, the product is stored in fridge in glass becker with its aqueous phase that segregates on the bottom. However, it is noticed that after several weeks some bubbles of oxygen are formed and the *Parafilm* covering is inflated. These means that some reactions take place. For the sake of correctness, sample 9 so conserved is analysed after one month of storage in fridge. The result is presented in Figure 5.32.

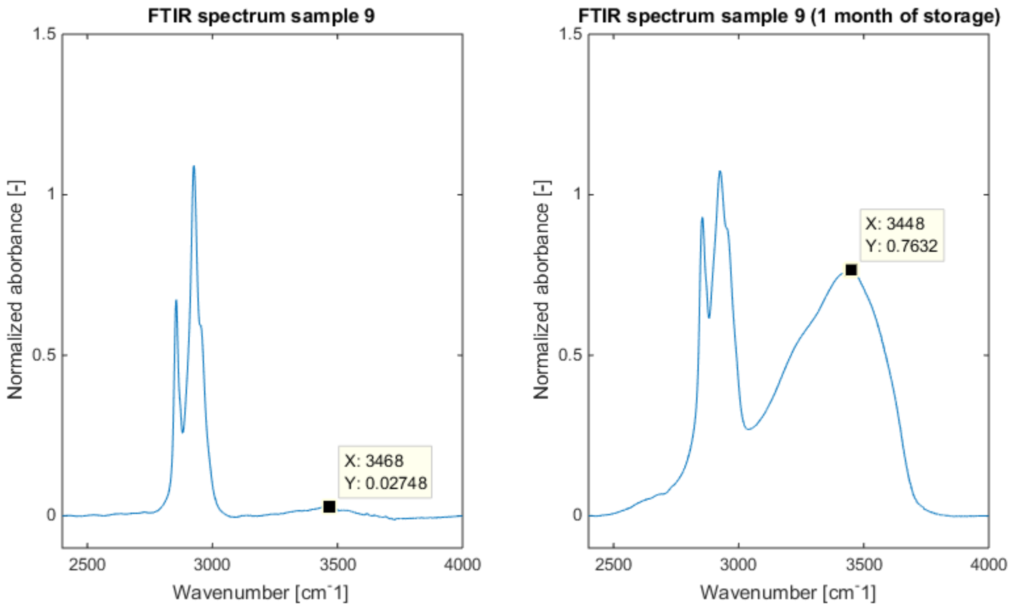

Figure 5.32. *FTIR spectra of sample 9 immediatly after the production (left) and after one month (right). Spectra visualized from 2400 to 4000 cm*$^{-1}$.

It is evident that epoxy ring opening take place in a noticeable way. This is quite obvious since the presence of water, hydrogen peroxide, acetic acid and a strong acid as the sulfuric acid promote the formation of glycols. However, in order that this fact occurs, such a considerable interval time has to pass (one month).

It is reminded that this fact does not affect the results previously exposed, since they were analysed immediately after their production. This evidence only highlights the necessity of a good purification of the organic phase before long time storage otherwise degradation takes place.

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4. Quadros, J.V.Jr., R. Giudici (2015). Epoxidation of soybean oil at maximum heat removal and single addition of all reactants. *Chemical Engineering and Processing*, **100**, 87-93.
5. Santacesaria, E., R. Tesser, M. di Serio, R. Turco, V. Russo, D. Verde (2011). A biphasic model describing soybean oil epoxidation with H_2O_2 in a fed-batch reactor. *Chemical Engineering journal*, **173**, 198-209.
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Conclusions

In this work of thesis, a study on the epoxidation of soybean oil is carried out using peroxyacetic acid in a calorimetric reactor, comparing conventional and non-conventional methods. The objective of this work is the study of the epoxidation of soybean oil using peroxycarboxylic acid and hydrogen peroxide in absence of any acidic catalyst (base case) or in presence of an acidic liquid or solid catalyst. The case that employs a liquid catalyst (sulfuric acid) represents the classical conventional method. The use of ion exchange resins as a solid catalyst represents a non-conventional and innovative method. In order to reach the objective, first of all, a deep safety study on the conditions (temperature and pressure) at which runaway reactions takes place is performed in TSU reactor. This step is necessary since the presence of hydrogen peroxide can originate high temperature and pressure that could be very dangerous. Moreover, the process of epoxidation and the effect of the presence of the two catalysts is studied using a calorimetric reactor. An optimization of the operating process variables in both cases is carried out. The heat exchange coefficient of this reactor is determined using a system designed and built *ad hoc*. The obtained product is evaluated in terms of conversion and selectivity. In conclusion a thermal study is carried out, in order to estimate the heat of reaction.

As regards the preliminary safety study, it is carried out using a *Thermal Screening Unit*, an instrument made of a small reactor capable to contain a couple of milliliter collocated in an electric oven. The mixture under test are two: one made of hydrogen peroxide and acetic acid and the other made of hydrogen peroxide, acetic acid and of soybean oil. The tests demonstrate that, in the case of the first mixture, the uncontrolled decomposition (runaway) of hydrogen peroxide starts from about 90°C. While at 70°C no thermal overshoots are presents, at 100°C the decomposition is totally uncontrolled and high pressure and temperature can be reached (43.24 bar, 213.7°C). This evidence is confirmed both by the isothermal and the ramped tests. Moreover, both at 70 and 90°C the pressure increases linearly, the rate of decomposition is nearly constant and it increases with the temperature. This rate is equal to is equal to 0.00577mmol/min and 0.04917 mmol/min for the two temperatures respectively. In the case of the second mixture, the runaway phenomena starts from 125°C, about 30°C higher than the previous case. This means that the oil damps the reaction of decomposition. This is also confirmed by the fact that, if an isothermal test is performed at 70°C for 150 mins, the pressure that can be reached is equal to 3.68bar and 1.41 bar in the absence or presence of oil respectively.

As concerns the determination of the heat exchange coefficient, the determination is carried out generating a well determined thermal power inside the reactor using a ceramic heater and an automatic power controller designed and built *ad hoc*. The accuracy on the generated power is about 1-3%. The heat exchange coefficient is determined studying both the transient and the steady state. With this two information, it is possible to calculate both the heat exchange coefficient and the effective heat capacity, which includes also the capacity of the impeller and the losses. While in the literature this coefficient is calculated only on the base of the transient and the theoretical heat capacity (given by the mixture only), in this case a more complete and accurate study is carried out. In fact, the heat capacity is equal to 8.630 W/K, whereas the effective and the theoretical heat capacities are equal to 861.6 J/k and 488.4J/K respectively. This great difference is justified by the presence of steel impeller. This fact demonstrates the correctness of this procedure. As a matter of fact, if only the transient is studied, an error of about 50% should be committed on the exchange coefficient.

Regarding the epoxidation, the process is carried in presence or absence of liquid or solid catalyst and a sensitivity analysis is carried out on the principle process variables. The liquid catalyst is sulfuric acid that is the traditional catalyst and it is chosen for its greater activity than the phosphoric acid. The solid one is the *Amberlite IR120* (Dow Chemical) ion exchange resin, chosen for easier separation than the previous catalyst. Acetic acid is used instead of formic acid since it is much less aggressive towards the instrumentations, even if it is less reactive. Moreover, hydrogen peroxide 34wt.% is used instead of 60wt.% in order to reduce the risk of detonation or runaways. The studied process variables are the presence and the concentration of sulfuric acid or the loading of the resin, the mixing program and the concentration of the acetic acid. The sensitive analysis on the concentration of the hydrogen peroxide is neglected since in the literature appears evident that it has a weak effect. However, hydrogen peroxide is in a slight excess since the hydrogen peroxide : double bonds is equal to 1.5:1. The acetic acid : double bonds is equal to 0.5:1. The process is carried out for 4 hours and the Rushton turbine impeller speed is equal to 500 rpm. The samples are analyzed by FTIR spectroscopy. The results indicate that the process cannot be carried out without any acidic catalyst, since after 4 hours no epoxides are formed and the double bonds are still present. The presence of sulfuric acid (3wt.% with respect to oil) leads to the formation of epoxides, the conversion is nearly total after 4 hours and the estimated selectivity is equal to 77%. The presence of noticeable thermal overshoots demonstrates that the reaction is running and the great catalytic activity of the sulfuric acid is confirmed. In addition, the mixing program assumes a noticeable relevance. In fact, it is noticed that at 500 rpm segregation occurs in the reactor whereas, increasing the speed, degradation of oil takes place even if segregation is reduced. Even if in the literature the mixing regime is studied, in this work the importance of the mixing program is revealed. In fact the solution is to keep the speed impeller equal to 500 rpm and to increase the speed to 1500 rpm for 30 seconds at intervals of 20 minutes (remixing). In this way the reacted oil is take away from the impeller and in this way the product is less exposed to the acid liquid phase that promotes the epoxy ring opening. On the other hand, the 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. In this case, the experimental results indicate that, in presence of 3%wt. of sulfuric acid, the estimated selectivity increases from 77% to 97%. The time required to total conversion decreases from 4h to 3.5h. The previous hypothesis are so confirmed. This a good innovation because mixing program is as important as the mixing regime, which is well taken into account in the literature.

Performing a sensitivity analysis on the concentration of sulfuric acid (2wt.%, 3wt.% and 4wt.%), the time required to total conversion decreases from 4h, 3.5h to 3h respectively, but the selectivity becomes worse from 97% to 90% (3wt.% and 4wt.% respectively). In this way, the great catalytic activity of the sulfuric acid is confirmed and the best compromise is found at 3wt.%. Moreover, the excessive concentration of the acid promotes the epoxy ring opening and the formation of glycols.

As regards the concentration of acetic acid, the acetic acid : double bonds molar ratio is increased from 0.5:1 to 1:1. The time estimated to total conversion decreases from 3.5h to 3 h but the selectivity decreases to 89%. In this case, selectivity decreases for the same reasons of the sulfuric acid. For these reasons, the best compromise is chosen equal to 0.5:1 molar ratio.

Carrying out a sensitivity analysis on the resin loading (10wt.%, 25wt.% and 40wt.% with respect to oil), the good catalytic activity of the resin is demonstrated. In fact, after 4 h, conversion is estimated equal to 25%, 58% and 73% for the three loading respectively. The estimated selectivity is equal to 71%, 95% and 97%. The conversion at 4 hours is noticeably lower than the case of sulfuric acid (conversion nearly total) since the resin is less active.

However, this is a very good result since the typical time duration of the conventional process using liquid acid is around 6-8 hours. Moreover, it is reminded that, in the industrial conventional process, phosphoric acid is often used. Even if phosphoric acid is not tested in this work, on the base of the data of Santacesaria *et al.*, the activity of the resin is at least comparable or even better than phosphoric acid. These good results indicate that ion exchange resin can be successfully used as a good solution in an industrial process.

As concerns the estimation of the heat of reaction, it is equal to 193kJ/mol. This value is similar to the one given by De Quadros *et al.* (196kJ/mol) and Santacesaria *et al.* (230kJ/mol).

In conclusion; the process cannot be carried out in absence of an acid catalyst. The sulfuric acid demonstrates an excellent catalytic activity. The ion exchange resin has a lower activity but works well and the selectivity can be very high. Moreover resin permits an easier separation than the sulfuric acid by simple filtration. The sensitivity analysis on the process variables indicates that the best conditions are 0.5:1 acetic acid : double bonds molar ratio, 3wt.% of sulfuric acid or 25wt.% of ion exchange resin. An important innovation is the importance of a proper mixing program that is fundamental to obtain a good product. The heat exchange coefficient and the effective heat capacity are determined rigorously thanks to the system created *ad hoc*. Thank to these data, the heat of reaction is calculated and it is similar to the one that can be found in the literature.

The perspective of this work consist in the immediate industrial usability of these results, especially the results on remixing. The use of resin can be industrially implemented for its easy separation by filtration. For the sake of correctness, some impurities remain in the product and better system for separation must be dedicated. In the end, if more accurate data on conversion are required, a dedicated titration with hydrobromic acid must be implemented.

Annex

In this annex, the control algorithm in C++ of the automatic power controller and its schematic are reported.

Control algorithm implemented in C++ for an AtMega328 microcontroller.

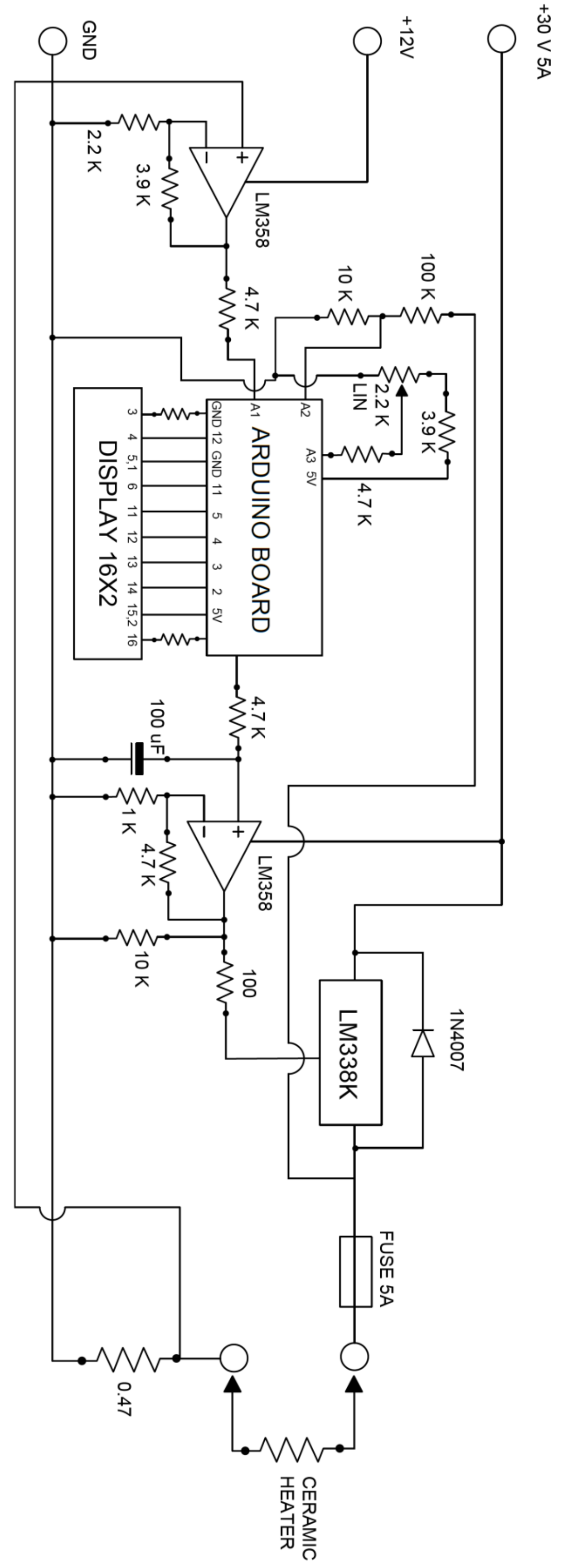
```
//INIZIALIZZAZIONE

#include <LiquidCrystal.h> //Libreria per pilotare il display LCD

#define pot A3 //pin potenziometro potenza

#define pinVh A2 //pin lettura Vh

#define pinVl A1 //pin lettura Vl

#define pin338 10 //pin controllo LM338

int val = 0;

float deltaV=0;

float corrente = 0; //corrente sonda

float potenza =0; //potenza sonda

int valVh = 0; //Valore in uscita dal convertitore Adc pin A2

int valVl = 0; //Valore in uscita dal convertitore Adc pin A1

int valpot = 0; //Valore in uscita dal convertitore Adc pin A3

int potenzaSet = 0;

int b = 60;

int d = 0;

int precedente = 0;

int istantaneo = 0;

LiquidCrystal lcd(12,11,5,4,3,2); //Inizializzazione della libreria con i pin
del display LCD

//IMPOSTAZIONE DEL LOOP

void setup()

{

  lcd.begin(16, 2); //Impostazione del numero di colonne e righe del display
LCD

  //lcd.setCursor(0, 0); //Sposto il cursore sulla prima riga (riga 0) e
sulla prima colonna

  //lcd.print("V.:"); //Stampo il messaggio 'Temp.:' sulla prima riga
```

```
  //lcd.setCursor(0,1); //Sposto il cursore sulla prima riga (riga 0) e sulla prima colonna

  //lcd.print("Pot:"); //Stampo il messaggio 'T.Set:' sulla prima riga


  pinMode(10,OUTPUT);

  Serial.begin(9600);

  analogReference(EXTERNAL);

}

//LOOP DI LETTURA E REGOLAZIONE INVERTER

void loop()

{

  analogWrite(pin338, b);

  valVh = (analogRead(pinVh));

  valVl = (analogRead(pinVl));

  valpot = (analogRead(pot));

  istantaneo = millis();


  deltaV= 0.03474609375*valVh*0.98;

  corrente = 0.002548828125000*valVl;

  potenza = deltaV*corrente;

  potenzaSet = valpot*33/654 + 3;

  Serial.println(potenza);

  if ((potenza - potenzaSet) > 2 && b > 1)

  {

    b = b - 1;

  analogWrite(pin338, b);

  d = 10;

  }

  if ((potenza - potenzaSet) < -2 && b < 254)

  {

    b = b + 1;

  analogWrite(pin338, b);

  d = 10;

  }
```

```
  if ((potenza - potenzaSet) > 0.001 && (potenza - potenzaSet) < 2 && b > 1)
  {
    b = b - 1;
  analogWrite(pin338, b);
  d = 300;
  }
  if ((potenza - potenzaSet) < -0.001 && (potenza - potenzaSet) > -2 && b < 254)
  {
    b = b + 1;
  analogWrite(pin338, b);
  d = 300;
  }
  if ((istantaneo - precedente)> 500)
  {
   lcd.clear();
  lcd.setCursor(0, 0); //Sposto il cursore sulla prima colonna e sulla seconda riga
  lcd.print("Ps:");
  lcd.setCursor(3, 0);
  lcd.print(potenzaSet);
  lcd.setCursor(8, 0);
  lcd.print("Pr:");
  lcd.setCursor(12, 0);
  lcd.print(potenza);
  lcd.setCursor(0, 1); //Sposto il cursore sulla prima colonna e sulla seconda riga
  lcd.print("Vr:");
  lcd.setCursor(3, 1);
  lcd.print(deltaV);
  lcd.setCursor(8, 1);
  lcd.print("Ir:");
  lcd.setCursor(12, 1);
  lcd.print(corrente);
  precedente = istantaneo;
```

```
  }
 delay(d);
 }
```

The schematic of the automatic power controller is here presented.



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