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Master Degree Thesis in Chemical and Process Engineering

EPOXIDATION AND THERMAL STUDY OF VEGETABLE OILS IN A CALORIMETRIC REACTOR

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Abstract

The aim of this thesis is the study of the vegetables oils epoxidation in a calorimetric stirred and jacket reactor. Vegetable oils that have been studied are: Soybean oil, Sunflower oil, Rapeseed oil. The reaction of epoxidation has been performed using oil, acetic acid, hydrogen peroxide and sulphuric acid like liquid catalyst.

In the first part of this work, it has been carried out the calibration of the reactor. Thanks to this two values have been obtained, specifically from the cooling transient it has been possible to calculate τ (that indicates the time that thermal transient is exhausted), instead from the steady state it has been possible to calculate U*A (global heat exchange coefficient), eventually thanks to the previous parameters thermal capacity m*cp has been derived. The calibrations have been carried out for all three oils both 600 rpm and 1500 rpm.

After that, the reaction of epoxidation has been carried out, which has been made both with remixing program as well as without remixing program and both at 4 hours and 5 hours. From this, thermal profiles have been obtained to assess the exothermic behaviour of the reaction. Then the FTIR analysis has been performed to derive the selectivity and thanks to the global heat exchange coefficient calculated by calibration, heat of reaction has been calculated. Finally both % of epoxy oxygen by titration of epoxidized oil and the reaction yield have been calculated. All this has been done to compare the differences among these oils and to assess the different behavior and different characteristics.

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INTRODUCTION

In this thesis the study of the epoxidation reaction has been carried out. This reaction has been made for all three oils (soybean oil, sunflower oil, rapeseed oil) using peroxycarboxylic acid which has been obtained in situ, by reacting hydrogen peroxide with carboxylic acid. So that the peroxycarboxylic acid reacts with double bonds of the oil and epoxidized oil has been obtained. To start the reaction so a catalyst have to be added; in this case the liquid acid catalyst was selected, a between sulphuric acid and phosphoric acid, the former was selected because it is more reactive and has been found that speeds up the reaction. As a carboxylic acid, acetic acid has been chosen because if on one side the formic acid is more reactive and therefore allows a faster conversion of the double bonds of the oil, on the other side it causes many side reactions and therefore could break the epoxides leading to the formation of glycols which would be the undesired products of the reaction. So there are different method to carry out the epoxidation reaction:

- Biphasic epoxidation: it is made using hydrogen peroxide, carboxylic acid, oil, sulphuric acid. This method is called conventional method. Practically there is a aqueous phase where peroxycarboxylic acid is formed which have a good solubility into organic phase and in fact it is used like carrier of oxygen, after the latter migrates in the organic phase and it reacts with the double bonds of the oil; in the mean time acetic acid which is formed during the reaction, came back into aqueous phase.

- Acid ion exchange resin (AIER) method: It would be a triphasic epoxidation; it is made using hydrogen peroxide, carboxylic acid and (AIER) that would be an insoluble gel type catalyst in the form of small yellowish organic polymer beads[1]. The peroxycarboxylic acid reacts with the catalyst entering into the pores of the catalyst.

- Enzymatic method: To avoid side reactions and to make the process more environmental friendly, enzyme catalyst are preferred. An example of enzyme catalyst is Immobilized Candida Antarctica lipase. It has been studied that the enzymatic activity may also be lost due to elevated concentrations of hydrogen peroxide or to temperature effects. However, some recent papers have shown that Candida Antarctica B lipase remained stable above 50 °C[1].

- Metal catalyst method: it used to increase the oxirane content and improve the efficiency of epoxidation reaction. Various metal catalysts such as titanium, molybdenum, tungsten can be used. Even in this case hydrogen peroxide reacts with carboxylic acid in situ giving a peroxycarboxylic acid, like catalyst, a mineral acid is used. So there are some drawbacks because the selectivity of the epoxidized products is low, and moreover there are acids by products that should be detrimental for further applications[1].

In this thesis the conventional method was used and the epoxidation reactions were performed for all three oils both at 4 hours and at 5 hours, both without remixing program and with remixing program.

It is important to list the different uses that epoxides and epoxidized oil could have. Thanks to the high reactivity of the oxirane ring , the epoxides can be used as a raw material to create a variety of chemical such as glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers[1]. Epoxidate oils are used like intermediates for the production of alcohols, alkanolamines, polyols for some polymers like polyurethanes and polyesters. Vegetable oil is used like raw material because first of all it is one of the most abundant biological feedstock in nature, and because it has a low toxicity and a inherent biodegradability[1]. The epoxidation reaction was carried out in a calorimetric reactor, a stirred, jacket batch reactor which contains inside a thermocouple. Two other thermocouples are positioned one at the jacket entrance and the other at the jacket outlet. The main purpose is to maintain constant the temperature of the jacket, because in this work an isoperibolic calorimetry has been used. In the reactor there is a transducer that permits the measure of the pressure that have to be constant. After doing the epoxidation reaction, the heat of reaction has been calculated. To calculate the latter, before the calibrations have been carried out. During the calibration both the cooling transient as well as the steady state have been analyzed to calculate respectively τ (time of cooling transient) and U*A (global exchange heat coefficient). Thanks to this two dates it has been possible to calculate m*cp (thermal capacity of the mixture). By the way it is important to remember that the epoxidation is a exothermic reaction. To calculate both a U*A and τ a proper system is developed.

A well determined heat has been generated inside the reactor thanks to an automatic power controller. This system has been design and built *ad hoc* and it is based on ATmega 328 microcontroller. It is important to say that reaction of epoxidation has been carried out without remixing that is the impeller velocity was fixed to 600 rpm, but it has carried out even with a mixing program, that is the impeller velocity has been changed from 600 rpm to 1500 rpm every 20 minutes for 30 seconds. This brought some advantages. After that, it was possible to calculate the heat of the reaction by integrating the temperature profile with

respect to time using Matlab. After making the reaction, the epoxidized oil was used to perform titration analysis and FTIR analysis from which it was possible to calculate % of epoxy oxygen and selectivity respectively. This was done for all three oils both at 4 and 5 hours and both with the remixing and without remixing. Eventually, the yield of the different reactions was calculated. The results obtained were then compared and analyzed, highlighting the differences according to the used oil and the conditions in which the reaction was carried out.

This work is divided in 4 chapter. In the first chapter there is a brief description of the different oils used. The main uses, the composition, the quantity and the structures of fatty acids of each oil and the physical properties are shown. After which a general overview of the epoxidation reaction is given, specifically the conventional method has been studied, highlighting its characteristics. In the second chapter a brief introduction on the calorimetry was made. A distinction between the different calorimeters and the measurement principles on which calorimetry is based have been made. After the instrumentation and the procedures used to perform the calibration, the epoxidation reaction, the titration of epoxidized oil and FTIR analysis have been described. In the third chapter the results of the calibration have been reported, both from the cooling transient (from which τ has been calculated) as well as from the steady state (from which U*A has been calculated). The results were used to calculate the thermal capacity of the mixture in the reactor (m * cp). The final results for the three different oils were then compared to each other. In the fourth chapter, the results concerning the epoxidation reaction were reported both at 4 hours and at 5 hours, and with the remixing and without remixing (temperature profiles were reported both in the reactor and in the jacket as a function of the time); then the results concerning the FTIR analysis were reported, and the selectivity of the reactions with the different oils has been calculated. At the end, the results concerning the titration analysis of the epoxidized oils have been reported, and the yield of the reactions with different oils and in different conditions has been calculated.

Chapter 1

Description of oils and reaction of epoxidation

Vegetables oils are a sustainable and renewable raw material resource extracted from plants and wood; they represent one of the cheapest and most abundant biological feedstock available in large quantities.

These vegetables oils are used like starting material and they offers numerous advantages such as low toxicity and inherent biodegradability[2]. In the last years, the epoxidation of vegetables oil received a great interest from industry. Thanks to the epoxidation reaction the unsaturations present in vegetables oils can be chemically modified to a value added product.

Due to the high reactivity of the oxirane ring, due to the high availability and low cost, epoxides are used as raw material to form numerous chemical products such as: alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds, and polymers like polyesters, polyurethanes and epoxy resins [3].The most important sources of these oils are palm, soybean, rapeseed and sunflower. In this chapter, vegetable oils are presented and in particular Soybean oil, Sunflower oil, Rapeseed oil will be analyzed. After introducing oils studied in this work, the focus will be shifted towards the epoxidation reaction , and above all on the biphasic reaction with a conventional method.

1.1 Vegetable oils

Vegetable oils are widely used for the production of bio based polymers due to their low cost, low toxicity, high availability and potential biodegradability.

As shown in (figure 1.1), the world production of vegetable oil has reached about 180 million tons in 2018. The quantity of vegetable oil produced increases year by year, it increases by about 2,3 million tons per year and it has increased from 155 million tons in 2013 to almost 170/180 in 2018. Palm oil is the most used, with a value that settles around 50 million metric tons, followed from soybean oil (with a value just below 50 million metric tons), rapeseed oil (20 million metric tons) and finally there is sunflower oil (10 million metric tons)[4].
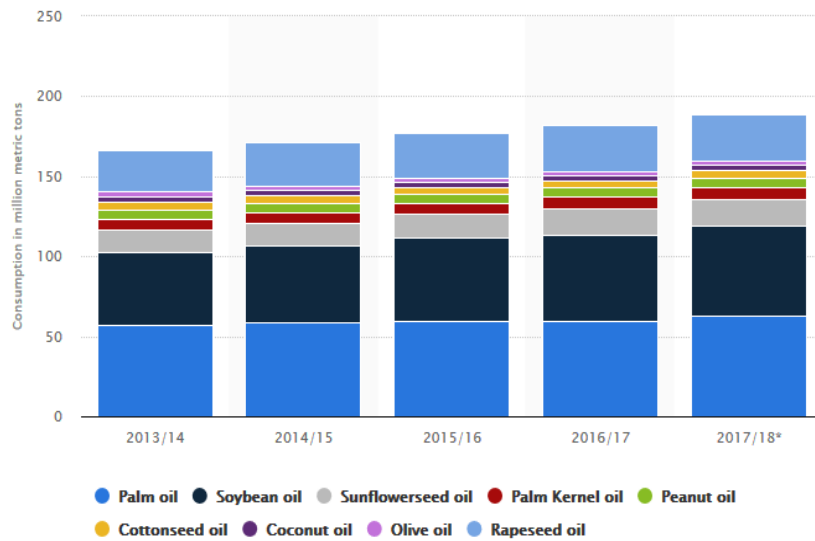
Figure 1.1 *The world total production of vegetables oil*[(4)]

About 80% of world production is used in food industry, while only 20% is used like industrial feedstock for biofuels, coatings, paints, lubricants, plasticizers, surfactants[(5)]. For what concern biofuels, many studies have been conducted, and both positive as well as negative aspects have been found. The pros are: the biodegradability, the absence of sulphur, the low content of carbon monoxide emissions, of particulate matter and of unburnt products; the cons instead are given by the different physical characteristic and from different competitiveness with diesel. The most important disadvantage is given by high viscosity which is the cause of incomplete combustion and of the consequent formation of deposits and wear on the engine.[(6)]

Vegetables oil belong to family of chemical compounds know like fat or lipid.

Lipids are very common in nature; they can derive from marine and natural sources, but they can be found in many cases as by-products in the production of marine and animal plant proteins. Fats, on the other hand, have been used for decades as food, lubricants and fuel. This is because fats have specific physical properties and structure. The chemical structures of lipids is very complex due to the combinations and permutations of fatty acids that can be esterified[(7)].

Vegetables oil are mainly composed of triglycerides, that is three fatty acid chains joined by a glycerol center. The most common types of used fatty acids have a chain length ranging from 4 to 24 carbon atoms, besides they can have from 0 to 3 double-bonds, and the most famous among them are: palmitic acid, linoleic acid, linolenic acid, stearic acid and oleic acid, but how it will be possible to see later, erucic acid is really important for the distinction between rapeseed oil and canola oil.

The figure 1.2 shows the triglycerides and figure 1.3 shows the fatty acids listed above[5], respectively.
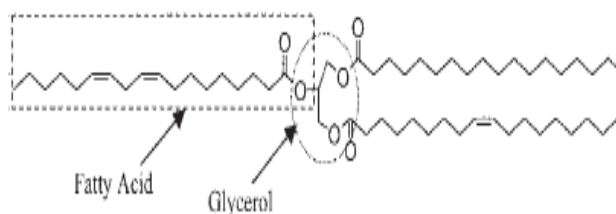
Figure 1.2 *Typical structured of triglyceride*
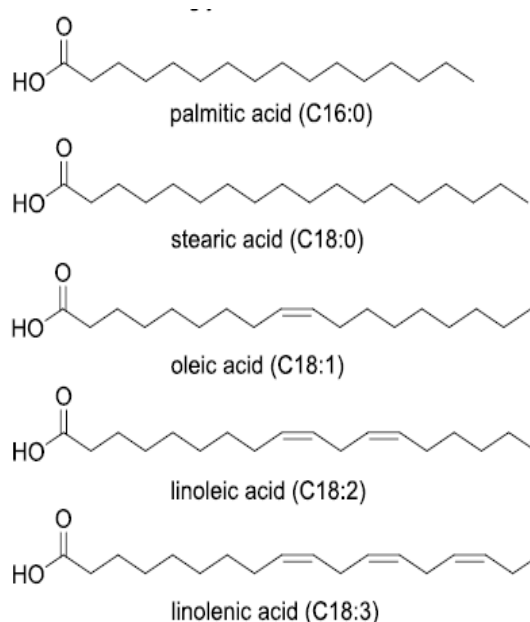
Figure 1.3 *Major types of fatty acid*

The fatty acids can be saturated and unsaturated. The common saturated fatty acids are: palmitic acid (C16:0) and stearic acid (C18:0), the common unsaturated fatty acids are: oleic acid (it called monounsatured acid), linoleic acid and linolenic acid (it called polyunsatured acids), which containing one (C18:1), two (C18:2) or three (C18:3) double bonds respectively[5]. Unsaturated fatty acids are used to create thermosetting polymers application, since double-bonds create reticulated structures, favoring thermal and mechanical resistance, while the saturated fatty acids don't show any reactivity.

The chemical modification of the carboxyl groups and/or carbon unsaturation groups present in the fatty acids, are the base of the industrial exploitation properties of them. Among the various parameters that influence the chemical and physical properties of fatty acid and so

vegetable oils, one of the most meaning is the number of double bonds, or degree of unsaturation, which are measured by the iodine number (I.V.).

Based on the iodine values ,vegetables oil (VOs) can be divided into three types:

- drying oils (I.V. > 130, such as linseed oil);
- semi-drying oils (100 < I.V. < 130, such as soybean oil, sunflower oil and canola oil, rapeseed oil)
- non-drying oils (I.V. < 100, such as palm oil)[5].

Table 1.1 shows the properties and compositions of the fatty acids of the most common and useful vegetables oils.

Table 1.1 *Properties and fatty acid compositions of common vegetable oils*[5]

VO	Saturated		Unsaturated			Double Bonds[a]	Iodine Value[b]
	palmitic	stearic	oleic	linoleic	linolenic		
Canola	4	2	61	21	9	3.9	110-126
Cottonseed	22	3	19	54	1	3.9	90-119
Corn	11	2	25	60	1	4.5	102-130
Linseed	5	4	22	17	52	6.6	168-204
Olive	14	3	71	10	1	2.8	75-94
Palm	44	4	39	10	-	1.8	44-58
Peanut	11	2	48	32	-	3.4	80-106
Soybean	11	4	23	53	8	4.6	117-143
Sunflower	6	4	42	47	1	4.7	110-143

Where: [a]Average number of double bonds per triglyceride; [b]I.V. = grams of iodine consumed by 100 g of oil samples.

1.1.1 Soybean oil

Soybean oil, is a vegetable oil extracted from the seeds of soybean. It is above all used by the food industry (because it is cheap, healthfully and has a high smoke point), in a variety of food products including salad dressings, sandwich spreads, margarine, but it is also used as renewable raw material to produce a variety of non-food products including bio diesel, inks,

plasticizers, crayons, paints. It is the second largest source of vegetable oil in the world after palm oil. Soybeans owe their dominance of the oilseed market to the value of their protein, which is much greater than that of other oilseeds[8]. Soybean oil has a low stability to oxidation due to high content of Linoleic acid; this because a great quantity of unsaturated fatty acids decreases the oil stability to high temperature. The typical composition of soybean oil is presented in table 1.2.

Table 1.2 *Constituents of soybean oil* [9]

Component	Soybean
Triglycerides (%)	93-99.2
Phospholipids (%)	-
Crude Oil	up to 4.0
Free Fatty Acids (%)	0.3 - 1.0
Unsaponifiables (%)	0.5 - 1.6
Tocopherols (ppm)	1700 - 2200
Chlorophylls (ppm)	Trace
Sulfur (ppm)	-

Soybean oil is mainly made up of triglycerides (about 99%), taking as a basis 100% you get: 15 % of saturated fat (palmitic and stearic acid), 23 % of monounsaturated fat (oleic acid) and 58 % of polyunsaturated fat (linoleic and linolenic acid), as shows in the table 1.3.

Table 1.3 *Percentage of fatty acids in soybean oil*[10,11]

Saturated fatty acids		Monounsatured fatty acid	Polyunsatured fatty acids	
Stearic acid	Palmitic acid	Oleic acid	Linoleic acid	Linolenic acid
4	11	23.4%	53.1%	7.8%

Instead it is possible to find the following acids in very small amounts in soybean oil : 0.1% Myristic acid, 0.1% Margaric acid, 0.3% Arachidic acid and 0.3% Bhenic acid (monosataruted fatty acids); 0.1 % Palmitoleic acid(monounsatureted fatty acids). [12]
Table 1.4 lists the most important physical properties of soybean oil.

Table 1.4 *Physical properties Soybean oil*[12,13]

Characteristics	Typical	Range
relative density (20°C) g/ml	0.923	0.919 to 0.925
Refractive index (25°C)	1.4728	1.470 to 1.476
Iodine value	126	110 to 143
Saponification number	192	189 to 195
Specific heat, 20°C (J/g)	1.874	1.874 to 2.7878
Pour point	-12	-12 to -16
Melting point (°C)	-22	-20 to -23
Solidification point (°C)	-	-16 to -10
Cloud point (°C)	-9	-
Smoke point (°C)	245	245 to 250
Viscosity(cSt)	34	
Flash point(°C)	324	320 to 330
Fire point(°C)	360	358 to 360

1.1.2 Sunflower oil

In antiquity, sunflower seeds were used as medicines for bruises, snake bites and cuts. The extraction of sunflower oil used for food took place for the first time in Russia around 1830.

Sunflower oil, obtained from sunflower seeds (*Helianthus annuus)*, is used both in the kitchen and as an emollient in cosmetics. Its world production in 2018 is about 18 million tons and it is the fourth most produced oil in the world.

Sunflower oil is light amber colour, has a distinctive but not altogether unpleasant flavor and odor, which is easily removed by deodorization.

In the past years, the cultivation of sunflower oil has increased, because its oil has a great quality and is useful for both human and to produce biodiesel. Sunflower oil is an important edible source thanks to its ability to grow anywhere, it could grow even in regions without irrigation. Oil with a high level of oleic acid is used for feeding, especially for frying, because it resist better to high temperatures, while oil with a high level of linoleic acid is preferred by the paint or fuel industry. Standard sunflower oil crops contain high amounts of linoleic acid, moderate amounts of oleic acid and low amounts of linolenic acid. Sunflower seeds contain a high amount of oil (40–50%) which is an important source of polyunsaturated fatty acid (linoleic acid) of potential health benefits [14]. The great quantity of unsaturated fatty acids make this oil really sensible to oxidation and rancidity.

The typical composition of sunflower oil is presented in table 1.5.

Table 1.5 *Constituents of sunflower oil*[15]

Component	Soybean
Triglycerides (%)	93.0 – 99.0
Phospholipids (%)	-
Crude Oil	-
Free Fatty Acids (%)	0.03-0.06
Unsaponifiables (%)	<1.5
Tocopherols (ppm)	440 - 1520
Chlorophylls (ppm)	Trace
Sulfur (ppm)	-

Sunflower oil is mainly made up of triglycerides (about 99%), taking as a basis 100% you get: 11.5 % of saturated fat (palmitic and stearic acid), 18.7 % of monounsaturated fat (oleic acid) and 68.3% of polyunsaturated fat (linoleic and linolenic acid), as shows in the table 1.6.

Table 1.6 *Percentage of fatty acids in sunflower oil*[16]

Saturated fatty acids		Monounsatured fatty acid	Polyunsatured fatty acids	
Stearic acid	Palmitic acid	Oleic acid	Linoleic acid	Linolenic acid
4.5%	7 %	18.7%	67.5%	0.8%

Then in very small quantities sunflower oil has : 0.1 % Myrisitc acid, 0.7 % Behnic acid and 0.4%Arachidic acid (saturated fatty acids); 0.1 % Gadoleic acid and 0.1% Palmitoleic acid (monounsaturated fatty acids);

There are different types of sunflower oil such as: oil with a high content of linolenic acid,(and so low content of oleic acid), oil with an medium content of oleic acid, about 69%, and oil with a high content of oleic acid, about 82%;

The different value of monounsatured fatty acids (acid oleic) is strongly influenced by both genetics and climate. Sunflower oil also contains lecithin, tocopherols, carotenoids and waxes. The phosphatides (0.1–0.2%) present in the oil are lecithin (38.5%) and cephalin (61.5%); they occur in combination with protein and carbohydrates.[17]

The table 1.7 shows the physical properties of sunflower oil.

Table 1.7 *Physical properties of Sunflower oil*[18,19,20,21]

Characteristics	Typical	Range
relative density (20°C)g/ml	0.921	0.919 to 0.923
Refractive index 25°C	-	1.461 to 1.468
Iodine value	122	120 to 136
Saponification number	-	188 to 193
Specific heat (J/g)	-	2.5 to 175
Pour point °C	-24	
Melting point °C	-	-18 to -20
Solidification point °C	-17	-
Cloud point °C	-9.5	-
Smoke point(°C)	234	-
Flash point(°C)	316	-
Fire point(°C)	341	-
Viscosity(cSt)	36-37	

1.1.3 Rapeseed oil

Rapeseed oil is a vegetable oil obtained from (*Brassica napus*)[22]. Initially it was used to illuminate the streets, as food it did not find much consensus because of the risks to human health connected with the high presence of erucic acid present at concentrations between 30 % and 60%, in order to avoid this and allow them to be used for food, a series of the original plant were developed.

The rapeseed oil was used like fuel for automotive, and appropriately treated it can be transformed into biodiesel and used as a biofuel for diesel engines. In the cosmetic industry, rapeseed oil is used as an emollient for the skin both with high Erucic acid as well as high oleic varieties. Rapeseed oil is the third most produced oil in the world, with about 20 million tons of tons in 2018, and is mainly produced in China, Canada, and United States.

Regarding the various mutations obtained from the original plant *Brassica*, in the 1968 was product first variety with a low tenor of Erucic acid (<5 %) called *Oro*. Then in 1974 was produced the second variety with a low tenor both Erucic acid that glucosinolate, from this variety, the Canola was then produced (from Canadian Oil Low Acid) with Erucic acid less than 2% and less than 30 micromoles of glucosinolates per gram of deoiled and dried paste.[14] In 1998 the Stellar variety was made with a low Erucic acid content and a high Oleic acid content, and with a few polyunsaturated acids (Linoleic acid <3%). Later, over the oil with a low tenor of Erucic acid, oil with a high tenor of Erucic acid were produced especially for the

industry of lubricant[14]. These are all the mutations obtained from the rapeseed oil with a different concentration of fatty acids .[23]

- *EAR* rapeseed oil with low erucic acid content, (Canola);
- *HEAR* rapeseed oil with high erucic acid content (standard Rapeseed oil);
- *HOLL* rapeseed oil with high oleic acid and low linolenic acid;
- *VHOA* rapeseed oil with a very high oleic content;
- *LEHL* Low erucic and high lauric canola oil;
- *VGLN* rapeseed oil with a very high γ-linolenic content;

The typical composition of Rapeseed oil is presented in table 1.8.

Table 1.8 *Constituents of rapeseed oil*[9]

Component	Soybean
Triglycerides (%)	91.8- 99.2
Phospholipids (%)	-
Crude Oil	up to 4
Free Fatty Acids (%)	0.3 - 2
Unsaponifiables (%)	0.5 - 1.2
Tocopherols (ppm)	700-1000
Chlorophylls (ppm)	trace
Sulfur (ppm)	-

Rapeseed oil is mainly made up of triglycerides (about 99%), taking as a basis 100% of oil you get: 6 % of saturated fat (palmitic and stearic acid mostly), 70 % of monounsaturated fat (oleic acid, Erucic acid and Gadoleic acid) and 14% of polyunsaturated fat (linoleic and linolenic acid), as shows in the table 1.9.

Table 1.9 *% of fatty acids Rapeseed oil*[23]

Saturated fatty acids		Monounsatured fatty acid	Polyunsatured fatty acids	
Stearic acid	Palmitic acid	Oleic acid	Linoleic acid	Linolenic acid
1%	4%	14.8%	14.1%	10.1%

Then we have: 1 % Arachidic , 0.3 % lignoceric and 0.8% Bhenic acid(monosaturated fatty acids); 0.3% Palmitoleic ,   10 % Gadoleic and 45.1% Erucic acid (monounsaturated fatty

acids); Just the amount of Erucic acid, remarks the difference between Rapeseed oil and Canola oil, as the latter is a derivative of Rapeseed oil but with a very low quantitative of Erucic acid about 0.2% as mentioned previously.

The table 1.10 shows the physical properties of Rapeseed oil.

Table 1.10 *Physical properties of rapeseed oil* [19,20,21,24]

Characteristics	Typical	Range
relative density (20°C)g/ml	0.915	0.914 to 0.9117
Refractive index 25°C	-	-
Iodine value	111	97 to 115
Saponification number	-	168 to 181
Specific heat (J/g)	-	1.900 - 20
Pour point °C	-18	-
Melting point °C	-9	-
Solidification point °C		0 to -15
Cloud point °C	-5	-
Smoke point(°C)	-	226 to 234
Flash point(°C)	317	278-282
Fire point(°C)	344	-
Viscosity(cSt)	37	-

1.2 The reaction of epoxidation: features and possible ways

Epoxidation is a method that consists in the oxidation of fatty acids by introducing in correspondence the unsaturations present in the chain, an oxygen atom, thus creating epoxidated fat acid.
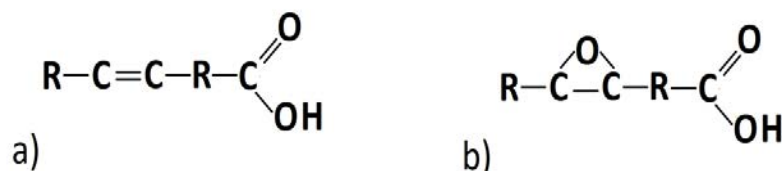

Figure 1.4 *a) An unsaturated fat acid, b) An epoxidated fat acid* [25]

On an industrial level, it is often performed in situ using the performic acid method which is already industrially performed in a large scale. However, catalyst acids (such as sulphuric acid) are essential for this process and these acidic components lead to several drawbacks:[26]

1) side reactions because of acid catalysed epoxide ring opening, with the formation of alpha glycols;
2) separation of acidic by products is difficult;
3) abundant neutralized salts which have to be disposed are produced;
4) corrosion problems due to the strong acids in the process.

For these reasons, selectivity to the desired products hardly exceeds 80 % in industrial plants. The epoxidation of vegetable oils, for example soybean ,sunflower and rapeseed oil, is industrially carried out by reacting the double bonds of the oil with a peroxycarboxylic acid ,generally peroxyacetic acid or peroxyformic acid (the order of reactivity of some of the peracids is *m*-chloroperbenzoic > performic > perbenzoic > peracetic), generated in situ by reacting concentrated hydrogen peroxide with acetic or formic acid in the presence of a mineral acid as a catalyst. The peroxcarboxylic acid formation occurs in the aqueous phase according to the following reaction [22] :

$$Formic\ acid + Hydrogen\ Peroxide \longrightarrow Performic\ acid + Water \qquad (1.1)$$
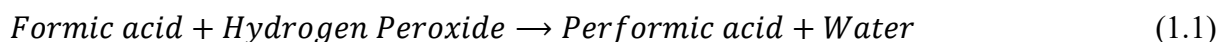
Subsequently, performic acid migrates into the organic phase and spontaneously :

$$Performic\ acid + Vegetables\ oil \longrightarrow Epoxidized\ vegetsbles\ oil + Formic\ Acid \quad (1.2)$$

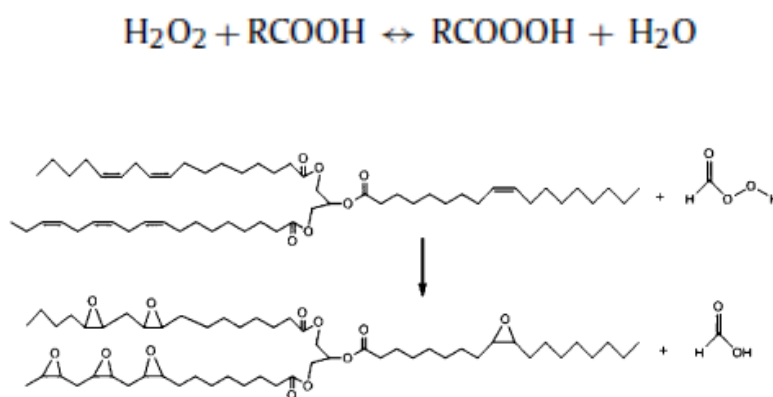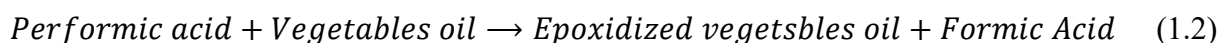$$H_2O_2 + RCOOH \leftrightarrow RCOOOH + H_2O$$

Figure 1.5 *Graphical representation of the epoxidation of a vegetable oil using a peroxycarboxylic acid*[22]

And so oil reacts with peroxycarboxylic acid and obtain epoxidized oil with carboxylic acid in organic phase. This reaction is highly exothermic (H = −55 kcal/mol for each double bond) and an excessive increase of the temperature in the industrial reactors is prevented by adding a limited amount of a mixture of H_2O_2 and formic or acetic acid to the mixture of oil and acid catalyst .The reaction normally requires 8 h to be completed, keeping the temperature between 60 and 75 ∘C.

There are four known technologies to produce epoxides from olefinic type of molecules. According to Dinda *et al*[27] following classification it is possible to have:

- epoxidation with percarboxylic acids, the most widely used in industry, can be catalyzed by acids or by enzymes, where the only by- product is water ;

- epoxidation with organic and inorganic peroxides which includes alkaline and nitrile hydrogen peroxide epoxidation. Like catalyst a transition metal is used;

- epoxidation with halohydrins , using hypohalous acids (HOX) and their salts;

- epoxidation with molecular oxygen using silver like catalyst.

In this work, we used the first approach cited above, both for soybean oil, as well as for rapeseed oil and sunflower oil.

1.2.1 Biphasic epoxidation: H_2O_2, acetic acid and H_2SO_4

The epoxidation process in this work is carried out in batch reactor, the process could be described through the following steps:

i) formation of peroxycarboxylic-acid in water phase;

ii) peroxycarboxylic acid transfer in organic phase;

iii) epoxidation reaction with formation of epoxidized oil and release of organic acid;

iv) decomposition of the obtained epoxidized oil both in oil phase at the phase border.

Following Santacesaria et al. (2011), two different phase can be considered. The first reaction occur in aqueous phase (inorganic phase) where formic or acetic acid and hydrogen peroxide react together and give peroxycarboxylic acid which has a good solubility into organic phase, and so it is used like a carrier oxygen. On the contrary, peroxide hydrogen is not soluble in organic phase. Thanks to the mass transfer between two phases, peroxycarboxylic acid is transferred in the organic phase, and the second reaction occurs, which happens between performic or peracetic acid (acid peroxycarboxylic) and the double bonds contained in the

oil, promoted by acid catalyst(H_2SO_4). In this scheme, the mass transfer between the two phases of substances involved in the process is essential[3].

A scheme of the reactions is reported in Table 1.11[15], where n (=1,2,3) are mono-enes, di-enes and tri-enes; Epox(n) is the epoxide group deriving from the mono-enes, di-enes and tri-enes, DEG is the decomposed oxirane group obtaining by different compounds: H_2O_2, FA (formic acid), PFA (performic acid), H_2O, or more in general by H_3O^+ group and indicated with H. There are different side reactions, but, according to the same authors the ring opening reactions mainly occur at the water–oil interphase. In this case, the reaction scheme can be simplified by considering only one ring opening reaction promoted by the protonic attack of the epoxide rings at the interphase followed by the formation of a carbocation that can promptly react with hydrogen peroxide, water, formic and performic acids.[22]

Table 1.11 *Scheme of the biphasic epoxydation reactions* [3]

Aqueous phase	
$H_2O_2 + HCOOH \rightarrow HCOOOH + H_2O$	(1)
$H_2O_2 \rightarrow H_2O + 0.5\ O_2$	(2)
Organic phase	
$HCOOOH + C=C(n) \rightarrow Epox(n) + HCOOH$	(3)
$Epox(n) + H^+ \rightarrow DEGH$	(4)

It has been found that the reaction can be approximated at first order, instead side reaction is of the second order[6], and it could be represented in one step instead that two steps[7].

It is evident that the global process is divided into four stage: there are two reactions and two mass transfer. Epoxidation reaction requires that peroxycarboxylic acid, formed in the aqueous phase, migrates in the organic phase reaction (3). In the meantime, reaction (3) gives carboxylic acid that returns back to the aqueous phase. Partition equilibria for these two compounds allow the development of both the reactions (1) and (3), provided that the interface surface area is large enough to warrant a mass transfer faster than the reaction demand. All this is shown in figure (1.6). Thanks to epoxy ring opening, some by-products can be created like for instance α glycol (reaction 4); of course a product with high value of oxirane and low content of α glycol is desired.
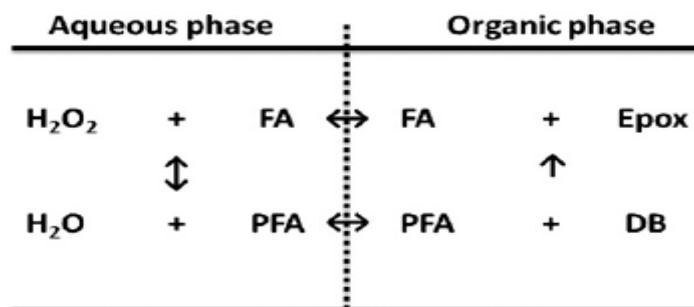
Figure 1.6 *Scheme of global process that involve both two reactions as well as two mass transfer*[22]

In according some studies, the peroxycarboxylic acid formation is the rate determining step in the epoxidation, instead there are other studies for instance that are done by *Santacesaria et al.*[22] which indicates that the epoxidation that occurs in the organic phase is five times slower than the oxidation of carboxylic to peroxycarboxylic acid.

1.2.2 Choice and concentration of: acid catalyst, carboxylic acid hydrogen peroxide.

For what concerns the use of acid catalyst, during the years many studies have been done. For instance *Santacesaria et al.* make epoxidation reaction using like acid catalyst both H_2SO_4 and H_3PO_4. They will show that sulfuric acid is more active that phosphoric acid like it is possible to see in figure 1.7[22].
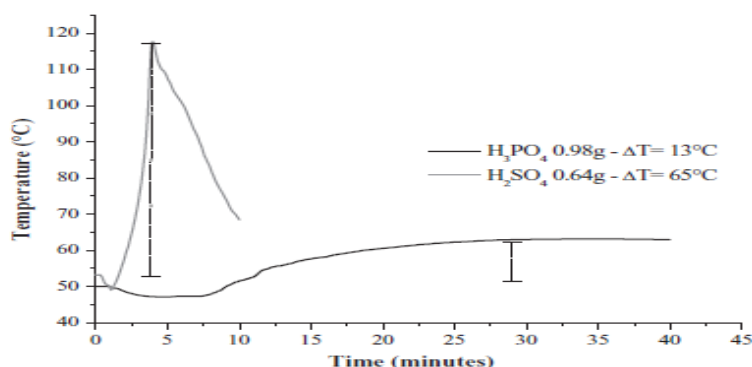

Figure 1.7 *Thermal profile using both H_2SO_4 as well as H_3PO_4*[22]

From which it is possible to note that using H_2SO_4 an increase of the temperature of more than 60 °C was observed, on the contrary, using H_3PO_4 the increase was only 13°C. So it was possible to conclude that the epoxidation with of H_2SO_4 is faster than epoxidation with H_3PO_4 and so the reaction is favored for what concerns the kinetics. Anyway in literature it has been

found that the process is favored by acid conditions, generally with a pH between 3.5- 6.5. According to *Dinda et al*[27] in this way both acids (especially sulphuric acid) have a great catalytic activity as it has been possible to see above, and it boosts the formation of oxirane. Finally it is important to say that it is important to choose a right amount of the fraction of the inorganic acid. This because if on one hand a low amount of acid doesn't permits a good catalysis of the reaction, on the other hand a large amount of acids causes the open of the oxirane and so it causes a decreases of commercial value of the product. In according to *Dinda et al*[27] mass fraction of sulfuric acid (98%) greater than 3% promotes this side-reaction so the right value is 2%. In this work a concentration of 3% has been chosen.

It is important to say that acid catalyst is important because it prevents the acetic acid dissociation, which could be dangerous for the formation of the peroxycarboxylic acid and the oxirane, and prevents the spontaneous decomposition of the peroxycarboxylic acid[25].

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 to same authors.

In 2008 *Dinda et al*, worked epoxidation kinetics of cottonseed oil using a hydrogen peroxide, using like carrier oxygen a carboxylic acid for example acetic acid or formic acid, (they found that acetic acid is better than formic acid like a carrier oxygen), and they used a liquid acid catalyst i.e. HCl, H_2SO_4 HNO_3 discovering that H_2SO_4 was be most efficient and effective[1]. *Goud et al.* led to the reaction of mahua oil using hydrogen peroxide. They said that the economic value of mahua oil could be increased by converting oil to epoxidized mahua oil. They used acetic acid like as carrier oxygen, and hydrogen peroxide like donar oxygen, and and as a catalyzer they used sulphuric acid because latter is the better catalyst for this process conduct a 50-60°C , and that producing a high conversion of double bonds to oxirane groups[1].

In 2010, *Jia Lian Kun et al*. worked by epoxidation reaction on the synthesis of vegetable oil based polyether polyols. In this work the oil epoxidation was carried out by generating performic acid, obtained from the in situ reaction between hydrogen peroxide and formic acid. They used HBF_4 (40% wt). They deduced that by using acid catalysts such as H_2SO_4 many secondary reactions were ignored, such as the opening of oxirane rings with diols, hydroxy esters, estelloids[1].

For what concerns carboxylic acid, the most used are: acetic acid and formic acid.

Acetic acid is more used because formic acid is corrosive, so it could create runaway reactions because the temperature reached would be too high, but it could cause many side reactions and therefore open the oxirane[27]. Anyway it is important to say that formic acid is more reactive than acetic acid, and it permits a fast conversion of the double bonds of the oil.

Regarding the molar ration between acetic acid and double bond of the oil according to *Dinda et al*[27], the right value is 0.5:1, this because low concentrations of acetic acid does not

allow a good transfer of oxygen to the oil, instead high concentrations of acetic acid would cause the formation of motions by-products such as alpha glycols.

For instance *Cai et al.* (2008), worked on the kinetics of epoxidation of sunflower oil, soybean oil and corn oil catalysed from H_2SO_4 with a peroxyacetic acid. They found that using a peroxyacetic acid, soybean oil have a lowest activation energy, and the highest rate of conversion. [1]

Regarding the temperature and concentration of hydrogen peroxide, the classic process uses a temperature of 60° and a concentration of hydrogen peroxide of 34 wt%, because in this way it is possible to obtain higher double bond conversion and high epoxide productivity[6].

Even in this case a optimal ratio between hydrogen peroxide and double bond of the oil exists. According to *Dinda et al*[27] the right ratio is 1.5:1 and 2:1, this because a high value of hydrogen peroxide could cause the cleavage of the oxirane, instead on the contrary, low value could not be sufficient for the epoxidation. During the tests anyway, it has been found that the best value of hydrogen peroxide was 50%wt, but as it could cause explosion, this precautionary value has been chosen[27].

It has been studied that high value of temperature cause high velocity of conversion but a low selectivity so the reaction would be favorite from the kinetic point of view, so many by products could create because the ring opens; on the contrary instead low value of temperature guarantee a high selectivity but low velocity in conversion. For this reason the optimal value of temperature is 60°C[27].

For what concerns the enthalpy of the main reaction according to *Santacesaria et al*[22] is equal to -230 KJ/mol, even if in literature there isn't a great clarity regarding this topic. This value has been obtained using acid formic. As concerns kinetics parameters the value found are 76 and 66 KJ/mol. This dates regarding the reaction carried out by acetic acid.

The aim of this work is to conduct the epoxidation reaction starting from three different oils and compare the results obtained. This comparison will allow to understand which oil has the best performance for industrial use.

In this work is important understand the amount of oil that has been epoxidized, and how many by-products have formed, and to do this we use 3 different parameters:

1. *Double Bonds* conversion= $\frac{[D.B.]start-[D.B.]end}{[D.B.]start} * 100$ \hfill (1.3)

Where $[D.B.]$ indicates the concentration of double bonds, the value of which depends on the iodine number, It indicates the number of double bonds that have react.

2. Relative conversione to oxirane= $\frac{OO\ exp}{OO\ the} * 100\%$ \hfill (1.4)

Indicates how many epoxies were formed; OO_{exp} indicated value of the oxirane oxygen experimental, while OO_{the} indicated value of the oxirane oxygen theoretical.

3. Relative conversion to α glycol$=\frac{G\ exp}{G\ the} * 100\%$ (1.5)

Give an indication of how secondary reactions have influenced the main product; 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.

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Chapter 2

Calorimetric methods and material

In this chapter it will be briefly explained what is meant by calorimetry, then the different techniques of calorimetry will be shown, the instrumentation used and the parameters calculated through this technique. Later, the batch reactor used in this work and all the necessary equipment for calculating the heat exchanged will be illustrated. In the second part of this work the various experimental methodologies and materials used in calorimetric reactor calibration, in epoxidation reaction, in titration of epoxidized oils, and in FTIR analysis will be described.

2.1 Calorimetric methods

Calorimetry is the technique used for measuring heat which in turn can be generated (exothermic process), consumed (endothermic process) or simply dissipated by a sample. There are different ways to measure heat, from the simple thermometric method (temperature measurement) during the years more accurate and detailed techniques have been designed, which allow users to collect data and maintain samples in conditions that were previously not possible. The advantage of calorimetric methods over the other physical-chemical and analytical tools is their applicability to any kind of process that produce heat. The calorimeters can be used to measure the pH adding a simple electrodes inside them, or they can be used to calculate the consumption of oxygen etc. The calorimetric methods, together with other techniques such as thermal analysis are useful as they construct tables and databases, from thermochemical and termophysical data, and thus improve the understanding of the constitutive properties of the material together with other derived techniques (thermal analysis).

Nowadays it is not possible to measure directly the heat, but only the effects caused by its flux from a body to another or its accumulation in a definite system can be measured. Among different effect it could have thermal effect (temperature changes, phase changes) or non-thermal effects (changes of volume, pressure and so on).

A calorimetric system is a measuring apparatus essentially constituted of [1] :

- A calorimetric vessel(CV) which contains the system or the substance that absorbs or produces heat during a spontaneous or induced process.

- A surrounding (S), that can be a thermostat or a furnace; It is put in contact with the calorimeter, it supplies or absorbs heat from the calorimeter and then transfers it to the external environment;
- Thermal resistance (Rh), composed by all the materials lying through (CV) or (S).

The most important characteristics of a calorimeter are[1] :

- **Accuracy:** The difference between the value of the measurement and the true value of the heat released.
- **Sensitivity**: The ratio between the change of the measured signal and that the heat released.
- **Uncertainty**: Range around the mean value measured. Without systematic mistakes the true value should be within this range.
- **Repeatability** : the value among different measurements that have been done with the same instrument, method, operator at different time interval.
- **Reproducibility** : It is useful to estimate systematic mistakes. It indicates the agreement among different values of a parameter. If the measurements have been done in different conditions , with different methods and instruments.
- **Linearity** : It shows how the calibration factor can be accurately represented by a horizontal straight line.
- **Stability** : It indicates the fluctuations of the instrument base line over a considerable period.

2.1.1 Safety parameters

There are 4 parameters categories of measuring in calorimetry that have to be checked : Temperature, Pressure, heat and time. Temperature and pressure are taken into account because they could create a problem of runway reaction, anyway the pressure is the most important parameters, because if it increases too much, the equipment could be damaged.

For what concerns the **Temperature** some parameters that can be considered are[2,3]:

- Process temperature (**T**);

- Maximum Temperature Synthesis Reaction (**MSTR**). This parameter indicates the maximum temperature that can be reached in an adiabatic calorimeter, considering only the desired reaction synthesis;
- Exothermic start temperature (**T_{onset}**); it indicates the temperature at which exothermic process starts; this value depends of the instrument sensibility;

- Increases of adiabatic temperature (**ΔT$_{ad}$**). This parameter indicates the increase in adiabatic temperature;
- Decomposition temperature (**T$_d$**);
- Self Accelerating Decomposition Temperature (**SADT**); It depends on the cooling constant, and it indicates the temperature at which the heat generation rate is equal to the thermal capacity of the system;
- Maximum Self Heating rate;

Instead , for what concerns **heat/ power** , this parameters have to be considered:

- Power released ($\dot{Q}_r$); it indicates the power released in a specific time;
- Maximum power released ($\dot{Q}_{r\ max}$);
- Developed heat (Q_r); It indicates the heat released from the system in all the time necessary to make the reaction occurs, it would be the integral the heat over the time. For a total conversion ,it indicates the heat of reaction;

Finally for what concerns the **time**, it is possible to consider the following parameters:

- Time to Maximum Rate ($T_{MR\ ad}$); It indicates the time necessary to reach the maximum self-heating rate, in adiabatic conditions;
- Induction time; It is the time after that, a exothermic phenomenon occurs, in adiabatic conditions;

2.1.2 Measurement principles in calorimetry

In calorimetry there are different measurements principles, which can be used depending on type of instruments that is used[2]. The main goal of these measurements is to calculate $\dot{Q}_{flow}$ i.e the thermal power :

- **Heat balance:** $\dot{Q}_{flow}$ is calculated through a energy balance on the jacket of the reactor following this equation (2.1)

$$\dot{Q}_{flow} = \dot{m}_j * cp_j * (T_{jin} - T_{jout}) \tag{2.1}$$

  Where $\dot{m}_j * cp_j$ are calculated through calibration of the reactor, instead T_{jin}, T_{jout} are the measured variable and they represent the temperature of the service fluid at the inlet and the outlet of the jacket respectively. It is the most used criterion in reaction calorimetry.

- **Heat flow :** $\dot{Q}_{flow} = U * A * \Delta T \tag{2.2}$

Where ΔT is measured variable, U*A,(global heat exchange coefficient) is obtained through calibration.

- **Calvet principle:** This method used mostly for what concerns microcalorimetry (that is calorimeter with a volume of 1ml) like in DSC (differential scanning calorimetry), but it is even used in reaction calorimetry. The measured variable is the difference in temperature between external and internal walls inside which the sample is placed; this difference is calculated thanks to the thermocouples. Knowing then geometry, thickness and thermal conductivity of the second wall it is possible to calculate $\dot{Q}_{flow}$.

- **Heat compensation:** This principle is used both for DSC and for reaction calorimetry. In the first case, the maximum temperature difference between sample and reference is measured; the sample and the reference are put in two different ovens; It is important to keep this difference close to zero. In the second case, instead, the heat transfer between the sample and its surroundings must be as constant as possible; moreover, thanks to a heating element inserted inside the sample, the sample temperature must be kept close to the set point. In both cases $_{flow}$ it is calculated as the difference between the power supply and the power of the baseline.

- **Isoperibolic balance:** This criterion is used in reaction calorimetry. It is important to keep the system in quasi- isothermal condition; the vessel is put among the system and jacket that is keep in a isothermal condition. The heat transfer coefficient between vessel and jacket is calculated by calibration, using an electrical calibrated heater. $\dot{Q}_{flow}$ is calculated thanks to a energy balance on the vessel .

- **Adiabatic balance:** It is used in adiabatic calorimetry where ΔT adiabatic have to be calculated. In this case $\dot{Q}_{flow}$ is not calculated because its value is zero. It is important instead a parameter called Phi Factor (Φ). The closer to zero this value will be, the more adiabatic the system will be.

2.1.3 Operating modes

The calorimeters behave differently depending on the conditions adopted:

- **Isothermal condition:** This test is mainly used in a reaction calorimetry. The sample is keep at constant temperature. The dates obtained are: heat released over time, the induction time and the duration of the reaction peak.

- **Adiabatic condition:** This test is carried out maintaining the system in adiabatic condition, that is no heat have to be dispersed. During this test different parameters can be calculated like for instance temperature and pressure trend over the time.

- **Isoperibolic condition:** This test is used above all in a reaction calorimetry; the temperature of the surrounding environment(such as the temperature of fluid in the jacket) have to be constant**.**

- **Oscillating temperature condition:** This test permits to calculate m*cp and U*A of the system ; it is used mostly in a reaction calorimetry causing a sinusoidal changing in the jacket temperature.

- **Temperature scanning:** A ramp temperature is applied by to the sample. With this test is possible to calculate the temperature at which exothermic reaction starts, the heat capacity and heat released.

2.1.4 Volume Classification Criterion

An important criterion of subdivision between calorimeters is given by the volume[2]. In this category there are:

- **Microcalorimters** : Instruments with a small volume(1 μl) are included; To this category belong: **DSC(Differential Scanning Calorimetry)** is a method that compares the heat absorbed or generated between a sample and the reference, both subjected to the same temperature regime;
  DTA (Differential Thermal Analysis) is a method that compares the difference of the temperature between sample and reference, both subjected to the same temperature regime.

- **Minicalorimeters :** Instruments that have a volume of the order of ml like for instance **Calvet calorimters or TSU**. They have the similar functioning principle of microcalrimeters but they are more sensible.

- **Reaction calorimetry**: Instruments that have a volume between 0.3 and 10 L; They are a little dimension reactor and moreover they have a **jacket and a mixing system**.

2.1.5 Isothermal, Adiabatic and Isoperibolic Calorimetry

For what concerns the operating mode three main groups can be identified: Isothermal calorimetry, Adiabatic calorimetry and isoperibolic calorimetry. In reaction calorimetry, the calorimeters can be assumed to be similar to agitated and jacketed reactors and so the energy balance is the same.

The equation that represents the energy balance of the calorimeter is[4]:

$$\dot{Q}_{acc} = \dot{Q}_{reac} + \dot{Q}_{he} + \dot{Q}_{loss} + P_{stirr} + \dot{Q}_{comp} \tag{2.3}$$

Where:

$\dot{Q}_{acc}$ is the accumulate heat over the time

$$\dot{Q}_{acc} = m_{reac} * cp_{reac} * \frac{dTreactor}{dt} \qquad (2.4)$$

Where ($m_{reac}*Cp_{reac}$) is the thermal capacity of the system, T_r is the temperature inside the reactor.

$\dot{Q}_{reac}$ is the heat flow developed during the reaction:

$$\dot{Q}_{reac} = r * V_L(-\Delta H_{reac}) \qquad (2.5)$$

Where r indicates the rate of the reaction, V_L indicates the volume of the reagents and ($-\Delta H_{reac}$) indicates enthalpy variation of the reaction.

$\dot{Q}_{he}$ indicates the flow of heat exchange between reactor and jacket:

$$\dot{Q}_{he} = U * A * (T_{reac} - T_{jack}) = m_j *cp_j *(T_{jin} - T_{jout}) \qquad (2.6)$$

Where U is the global thermal exchange coefficient, A is the exchange surface, T_{reac} is the temperature of the reactor and T_{jack} is the temperature of the jacket. But it is also equal to the thermal power acquired or lost by the service fluid expressed by the product between the service fluid flow rate (m_j) ,its specific heat (cp_j) and the temperature difference between input and output (T_{jin}- Tj_{out}).

$\dot{Q}_{loss}$ indicates heat disperse towards external environmental.

$$\dot{Q}_{loss=} (U * A)_{ext} * (T_{amb} - T_j) \qquad (2.7)$$

P_{stirr} is the power of the agitation , Q_{comp} is the flow of heat compensation.

2.1.5.1 Isothermal calorimetry

This type of calorimetry is the most widespread, because it permits to calculate different parameters like rate of reaction, and the global heat transfer coefficient which is fundamental for the calibration of the reactor; besides this type of calorimeters are used on an industrial scale. The condition of isothermicity is guaranteed if the vessel temperature is continually equal to that of the surrounding environment. Tcv (t) = Ts (t). However the resistance cannot actually be nil and the kinetics of heat conduction is a relatively slow process. They can be of two types depending on how the internal T of the reactor is controlled:

- **Heat compensation calorimeters:** They have a reactor, a external jacket which maintain constant the temperature inside it; A heating element is placed in the reactor, in order to maintain constant the temperature of the reaction environment . The heat of reaction is calculated by solving equation (2.3) making the following assumptions: $\dot{Q}_{acc}$ null, the $\dot{Q}_{he}$ and $\dot{Q}_{loss}$ are considering constant together with T_{reac} and T_{jack}

which were constant at the beginning, and so the heat of the reaction is equal to $\dot{Q}_{comp}$ at different time intervals. These calorimeters are used rarely, because the heat exchange between reactor and jacket is not constant in many applications, and so it is not possible to assume $\dot{Q}_{he}$ constant[4].

- **Heat flow calorimeters:** In turn, these calorimeters are subdivided according to the parameter that is changed for temperature control, because in this case the temperature control does not take place on the reacting mixture or no heating element is inserted into the reactor. There are three category. The most used *is calorimeter with temperature control of the jacket* thanks to which it is possible to calculate the global heat transfer coefficient through a flow balance . According to type of calculation that is used to find the global thermal heat exchange, two under categories can be identified. The first one includes *heat flow calorimeters*[4], where The following equation is used :

$$\dot{Q}_{flow} = U * A * \Delta T \tag{2.8}$$

Where as it will explain after U*A can be calculated through calibration of the reactor and ΔT is given by instrument.

The other category includes *heat balance calorimeters*[3], where the global balance permits to calculate convective thermal power inside the jacket through the following equation:

$$\dot{Q}_{flow} = \dot{m}_j * cp_j * (T_{jin} - T_{jout}) \tag{2.9}$$

An example of isothermal calorimeters is provided by ice calorimeter or (Lavoiser calorimeter). Lavoisier calorimeter consists of 3 containers one inside the other. In the external container there is melting ice which create an isolant layer to avoid that heat of the outer environment can melt the ice placed into the second container. The second container contains ice and besides it has a pipe on its bottom in such a way the water that is produced by the heat released by the substance (which is placed in the innermost container) can flow out the calorimeter. The internal container is made by metal walls so doing the heat exchange between ice and substance is easier. First of all a calibration of the calorimeter have to be made; the latter have to be carried out under the same conditions as the calorimetric measurements. Another more recent and more used example of isothermal calorimetric is given by Bunsen calorimeter.

2.1.5.2 Adiabatic calorimetry

It is defined as adiabatic if there is no heat exchanged between CV and S. This condition can be obtained statically through a great value of the resistance(Rh), or dynamically   by

continuously equalizing the T of the Thermostat (Ts) to that of the sample and its vessel (Tcv). In the last case the temperature sensor is put in the vessel and Tcv is the temperature of the sample. Adiabatic calorimeters are often used for determining specific heats ,especially at low temperatures.

An example of adiabatic calorimeters is given by Mahler bomb, which is composed by a iron reactor that can resist to high pressures; it is used to study combustion reactions where a reagent is added at high pressures. The reactor is put in a large basket full of distilled water. Inside the bomb a specific amount of sample is burned. The combustion is brought about a spark which is obtained passing the current through an electrod put inside the reactor. As soon as the heat is produced by the reaction, a little increase of temperature occurs. This one is measured by a thermometer put inside water bath. Before doing all this, the thermal capacity of the calorimeter is calculated thanks to an experiment where a specific quantity of substance is burned with a known combustion heat .These process is adiabatic, because the heat is transferred directly to the water and to the walls of the calorimeter in contact with it. Practically there isn't heat exchange with the environment.

2.1.5.3 Isoperibolic calorimetry

The third category contains all the calorimeter that are neither isothermal nor adiabatic. In these calorimeters the thermostat is at Ts = cost but different from that of the Tcv Vessel. Thanks to this type of calorimeter it is possible to obtain similar information to isothermal calorimetry; in this case the jacket temperature is constant.. In this work a reaction calorimetry has been used and so the measurement principle used is the isoperibolic balance and isoperibolic conditions have been adopted.

At the end it is possible to say that adiabatic calorimeter have a great resistance to heat transfer between reactor and environment, and so it is possible to consider this system as a isolated system; on the contrary isothermal calorimetry have a low resistance to heat transfer between reactor and environment which guarantee the stationary condition.

2.2 Calorimetric reactor

In this work, reactions of epoxidation of soybean oil, sunflower oil, and rapeseed oil, have been conduct in a calorimetric reactor (figure 2.1), through which calorimetric analysis is performed, and pressure and temperature values have been recorded.
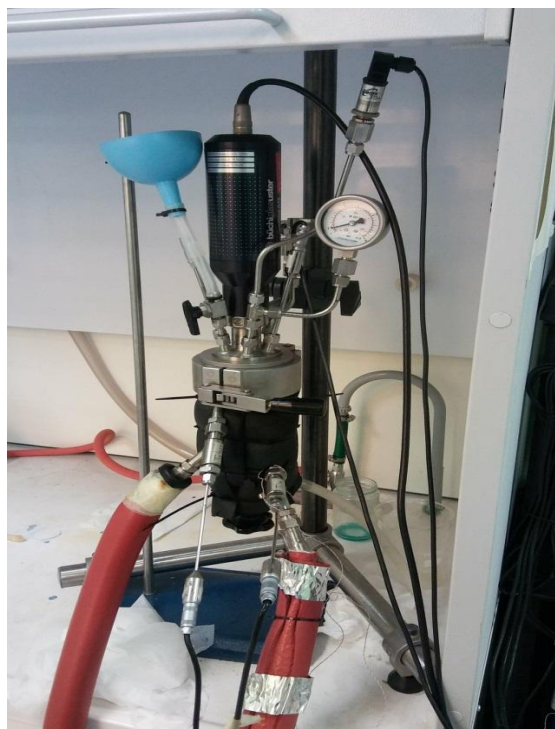
Figure2.1 *Calorimetric reactor*

The latter is a batch reactor, stirred and jacketed tank by *BüchiGlasUster*. The Huber thermocryostat, which in this work is set at a T = 60 ° C, check both internal temperature, that is the temperature of the bath that contain thermoregulation liquid inside it, as well as a external temperature to the machine. The service fluid to the calorimeter jacket is silicone oil and can be heated or cooled (depending on the updated temperature set point value).It is important so, to maintain a constant temperature in the jacket.(Figure 2.2

Figure 2.2 *Thermocryostat by Huber*

For the measurement of pressure and temperature have been used different instruments: There is a transducer in the reactor, a manual pressure gauge which only intervenes in case of transducer failure, and then there is also a rupture disk that guarantees the reactor safety; for what concerns the measurement of the temperatures, instead there are 3 thermocouples Pt100 which have been installed inside the reactor, at the inlet and at the outlet of the jacket.

The pressure and temperature data are then sent to a PC where there is a software LabView (National Instrument), where the values and graphical trends of T and P are displayed in real time. The Rushton turbine, which is a radial flow impeller used for many mixing applications, is used to mix. This turbine create a good emulsion between organic phase and aqueous phase, but it could give problem of segregation. The impeller is connected to the electric motor, which in turn is controlled by an apparatus that allows its regulation (Figure 2.3). This last one allows to position the first knob (starting from the left) on external or internal If the knob is put on the internal, the second knob have to be chosen to regulate the rotation speed of the impeller, if instead the first knob is positioned on the external, the rotation speed of the impeller is set using the lab view software

Figure 2.3 *Equipment that regulates the rotation speed*

2.2.1 Equipment for the determination of the global heat exchange coefficient

For the determination of the thermal capacity of the mixture, the information both on the steady state and cooling transient have been obtained. From the steady state the global heat exchange coefficient (U*A) has been calculated, instead from the cooling transient the time of the cooling (τ) has been found.

$$\frac{T(t)-Tjacket}{T(t_0)-Tjacket} = e^{-\frac{U*A}{m*cp}(t-t_0)} = e^{-\frac{t-t_0}{\tau}} \tag{2.10}$$

from which τ is derived;

$$Q = U * A * (T - T_{jacket}) \tag{2.11}$$

From which U*A is derived;

So knowing τ and U*A, the thermal capacity of the mixture inside the reactor can be calculated. U*A is the global heat exchange coefficient [W/°K], τ is the time in [s], m*cp is the thermal capacity [J/°K].

To do this, during the calibration of the reactor, an electrical heater together with an automatic power controller have been used, respectively (figure 2.4) and (figure 2.5). Firstly the measure was made only through ceramic heater, but the problem was that during the test internal resistance and consequently the adsorbed electrical power can change. In this way it was really difficult to supply a well constant thermal power. Moreover the possibility to change the thermal power supplied has been considered to observe the consequence on the global heat exchange coefficient. For his reason the ceramic heater is used together with an automatic power controller, which carried out the check through a regulator feedback. The feedback controller was only called into question in the event of an error: e = Pset point - Preal. The P set point was gradually changed every 15 minutes starting from 10 W up to 25 W, while the Preal was calculated using the following formula:

$$P = V * I \tag{2.12}$$

where the current and voltage values are calculated using an ammeter and a voltmeter, connected with cables to the automatic power control.

Figure 2.4 *Electrical heater*

Figure 2.5 *Automatic Power Controller*

This system is made of many units [3]:

- An element that measures both the voltage applied to the resistor as well as the current that flow inside it;
- An element that calculates the power applied at all times at the resistor;
- An element that converts the output signal into an analog signal;
- An actuator which causes the resistor to have the same pressure desired by the microcontroller.

The system is based on a platform called *Genuino* (*Arduino*) that mounts an ATmega 328 microcontroller.

2.2.2 Equipment for the separation and titration

For the epoxidation reaction, the batch reactor described above was used. After obtaining the solution, it is necessary to separate the epoxidized oil from the aqueous solution (water and acetic acid) and to do this ethyl ether and a solution with a bit of water plus $NaHCO_3$ were used. Then to remove the ether in such a way as to have only oil, a thermostatic bath (Jualabo), (figure 2.6) and a pump (figure 2.7) have been used. Finally, the titration to calculate the epoxidized oil % has been carried out. To do this a burette, phthalate acid potassium, a solution with acetic acid and about 2 ml of bromidric acid and crystal violet in addition to oil obtained in advance from separation have been used.

Figure 2.6 *Thermostatic bath*

Figure 2.7 *Pump*

2.3 Experimental methodologies

After describing the equipment used in this work, in this paragraph a brief description about the various methodologies used in the calibration, in the epoxidation, in the titration and FTIR will be done.

2.3.1 Calibration calorimetric reactor

For the calculation of heat exchange coefficient and thermal capacity different tools have been used: a calorimetric reactor, a thermocryostat of *Huber* for to set the temperature at 60°C (described above) , a solution of acetic acid 98% ,hydrogen peroxide 34%, and in the first case soybean oil, in the second case sunflower oil, and in the third case rapeseed oil. The oils have been bought by supermarket (Despar).

The amount of total solution was 205,6 gr, and it was composed: 100 gr vegetables oil(soybean oil or sunflower oil or rapeseed oil), 16,78 gr of acetic acid and 88.82 gr of hydrogen peroxide. In this case sulfuric acid has not been used because with the introduction of the latter the epoxidation reaction begins, as it will seen later.

First of all, the temperature of 60 °C of the Huber and the impeller speed of 600 rpm were set, then the solution was introduced with oil, acetic acid and hydrogen peroxide. After that it was expected for about an hour before the steady state was reached..

Once the ceramic heater has been put in the reactor, it is connected to the automatic power regulator, and the power is set. Different power have been used: 10w 15w 20w 25w, the duration of test is about 15 min, which is the time when the transient is run out.

Then repeat everything by setting the impeller rotation speed to 1500 rpm.

The data and the graphs have been elaborated through accurate algorithm in *Matlab.*

The calibration was done at both 600 rpm and 1500 rpm, for all three oils studied in this work (soybean, sunflower and rapeseed). For example the power at 10 watt for 15 minutes has been set, after that, the controller has been turned off, and waited for 15 minutes, the time required for the cooling transient.

2.3.2 Epoxidation in the calorimetric reactor

In the epoxidation of vegetables oil have been used : calorimetric reactor, thermocryostat of *Huber*, acetic acid 98%, hydrogen peroxide 34%, sulfuric acid (like catalyst) and vegetable oil.(soybean, sunflower and rapeseed).

The epoxidation is carried out with 205, 6 gr of solution thus formed: 100 gr of oil(in the first case soybean, in the second case sunflower and in thirds case rapeseed), 16,78 gr of acetic acid, 88,82 gr of hydrogen peroxide , and finally it is added 3 gr of sulphuric acid diluted with a bit of hydrogen peroxide.

The following proportion was followed: acetic acid:hydrogen peroxide:double molar ratio bonds equal to 0.5:1.5:1.

First of all, the temperature of thermocryostat at 60 °C has been set, after the oil was add in the reactor, the reactor has been closed , and the speed of impeller at 600 rpm has been set; it was expected for about an hour before the steady state was reached..

In the meantime, the thermal transient is exhausted, the solution of acetic acid and hydrogen peroxide was prepared, and the solution has been heated for about 10 minutes at 65 °C in a thermostatic bath (by Julabo). Finally, a hot solution of acetic acid and hydrogen peroxide with sulfuric acid has been poured into the reactor simultaneously via a funnel. Firstly, the epoxidation reaction was carried out for both soybean oil, and sunflower and rapeseed oil with a impeller speed of 600 rpm. After which, for all three oils, a mixing program was used. Through the mixing, initially the rotation speed of the impeller has been set to 600 rpm, then after 20 minutes the velocity of impeller has been increased to 1500 rpm for 30 seconds, and after the velocity of 600 rpm has been set again. This cycle has been repeated for 4 and 5 hours.

2.3.3 Separation between solution with epoxidized oil(organic phase)
and acetic acid plus water(aqueous phase)and titration

In this phase of our work the separation between oil and a aqueous solution of acetic acid plus water have been done.

After carrying out the epoxidation reaction in the first case for 4 hours and in the second case for 5 hours, both without remixing and with remixing, the reactor has been opened and the solution has been discharged into a beaker. The latter was then placed for about 20 minutes in the fridge to make it cool.

The new cooled solution was ready for separation. To make the separation, ethyl ether, pipette to prevail the oil, a solution of $NaHCO_3$ plus H_2O previously prepared, and a funnel have been used.

Through a pipette, a certain amount of solution was then taken, which in turn was placed inside the separating funnel; immediately afterwards a bit of ether was added and the washing with the $NaHCO_3$ solution plus water was carried out three times. The washes were carried out until the litmus paper, with which the PH is measured, did not take on a green color.

Once this point has been reached, ie after having removed water and acetic acid, the solution containing epoxidized oil and ether was put into test tubes and subsequently in a thermostat bath at 55 ° C until there is no disappearance of the bubbles, and therefore of the ether.

Subsequently the epoxidized oil was titrated to find the % epoxy oxygen. Titrations were carried out for all three epoxidized oils, at 4 hours and 5 hours both in the case without remixing and in the case with remixing.

To carry out the titrations, about 0.3 grams of epoxidized oil were weighed together with 10 ml of acetic acid, few milliliters of hydrogen peroxide, 4 drops of crystal violet and a magnetic stir bar inside a small beaker, which in turn was placed on a heated and stirred plate. The burette was then filled with acetic acid and the titration was carried out, until the turning point, ie the contents in the beaker, passed from violet to light green. Before making the titration, the acetic acid standardization was carried out. To carry out this, a solution was prepared with about 75 ml of acetic acid and about 2 ml of bromidric acid, all of which was then poured into a flask, after another amount of acetic acid has been addedd until to arrive to 100 ml. At the same time about 0.400 gr of phthalate acid potassium were measured and the contents were poured into an Erlenmeyer flask together with 10ml of acetic acid, inside which a magnetic stir bar and the para film was placed, the whole was then placed on a heated and stirred plate to make dissolve the phthalate. After 4 drops of crystal violet have been addedd. The standardization was carried out until to the solution into the flask changed its color from yellow to matt green. After that the titration was carried out. Successively the FTIR tests were carried out on the epoxidized oil sample.

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Chapter 3

Results calibration

In this chapter, we will show the results obtained by calibrating the calorimetric reactor with all three oils (soy, sunflower, rapeseed). The test were performed both at 600 rpm that at 1500 rpm, and information has been obtained about the heat exchange coefficient and effective heat capacity.

3.1 Determination of the global heat transfer coefficient of the calorimetric reactor

The objective of our measurement is calculated the thermal power $\dot{Q}$. Two equation of balance have been used:

- **Heat balance**: $\dot{Q}_{flow} = \dot{m}_j * cp_j * (T_{jin} - T_{jout})$ $\qquad$ (3.1) or (2.1)

  Where m_j*cp_j* are calculated through calibration considering the heat losses from the jacket. T_{in} is the temperature the fluid inside the jacket, and T_{out} the temperature out the jacket.

- ***Heat Flow***: $\dot{Q}_{flow} = (U * A) * \Delta T$ $\qquad$ (3.2) or (2.2)

  Where U*A (global heat exchange coefficient, given by the product between the exchange coefficient and the exchange area) are calculated through calibration. By using a isoperibolic calorimetry equation 3.2 has been used in this work.
  Considering equation (2.3) this formula (3.2) has been obtained doing the following assumptions: $\dot{Q}_{reac}$ is null because there aren't reactions; $\dot{Q}_{loss}$ can be neglected because the heat losses are really little (they are considered in equation (3.1 ore 2.1); $\dot{Q}_{comp}$ and P_{stirr} are neglected because they are irrelevant. It has been used this formula instead that the (3.1) because the goal is to calculate (U*A).

For the calculate of the heat exchange coefficient in this work was used a proper method described in the chapter 2. Through an automatic power controller a thermal power is generated inside the reactor and the temperature is recorded. In this work information both cooling transient as well as steady state have been obtained.

From the cooling transient is possible estimate the τ, that is the time that the thermal transient takes to run out, while of the steady state is possible obtain information regard the global heat exchange coefficient U*A. Finally it has been possible to calculate the thermal capacity m*cp knowing τ and U*A.

3.1.1 Global heat transfer coefficient: study on the cooling transient at 600 and 1500 rpm for soybean, sunflower and rapeseed oil

Starting from the energy balance of the batch reactor:

$$\frac{dH}{dt} = Q \tag{3.3}$$

by rearranging it and considering that there is no reaction the equation (3.4) is obtained

$$m * cp * \frac{dT}{dt} = -(U * A * (T - T_{jacket})) \tag{3.4}$$

which after some simplifications leads to the follow equation (3.5)

$$\frac{dT}{T - T_{jacket}} = -\frac{U*A}{m*cp} * dt \tag{3.5}$$

Finally after integrated latter, the equation 3.6 or 2.1 is obtained

$$\frac{T(t) - T_{jacket}}{T(t_0) - T_{jacket}} = e^{-\frac{U*A}{m*cp}(t - t_0)} = e^{-\frac{t - t_0}{\tau}} \tag{3.6 or 2.6}$$

Now applying the logarithm to both side the equation (3.6) or (2.6), it is possible to obtain the equation (3.7). This last one have the same form of the straight line equation, equation (3.8).

$$\ln(T(t) - T_{jacket}) = -\frac{U*A}{m*cp} * (t - t_0) + \ln(T(t_0) - T_{jacket}) = \tag{3.7}$$
$$-\frac{t - t_0}{\tau} + \ln(T(t_0) - T_{jacket})$$

$$y = -\frac{1}{\tau}x + q \tag{3.8}$$

Through the equation 3.6 is possible obtain from the cooling transient the time constant τ, that equal to $\frac{m*cp}{U*A}$. It is possible to verify this dimensionally because U*A is expressed as [W/°K], and m*cp is expressed as [J/°K], so through simplifications , it is possible to obtain a time in [s].

Applying a different power every 15 minutes, starting from 10 watts and reaching 25 watts, the different values of temperature of the cooling transient have been recorded for the soybean, sunflower and rapeseed oil, both at 600 rpm that 1500 rpm. Subsequently the logarithm was applied to the temperature difference obtained through the experimental data. The purpose of this study is to calculate τ by studying the cooling transient, so firstly ΔT_{exp} has been calculated with the data collected from the cooling ,after using Matlab the ΔT_{calc} was calculated. The latter has been obtaining by linear fitting starting from the initial estimation values of τ and q, and making them until the segments constituted by the found values of ΔT_{exp} and ΔT_{calc} were superimposed as much as possible.. Furthermore, the mean quadratic deviation and the adaptation coefficient were calculated to verify the accuracy of the fitting. Below the graphs related to the cooling transient and the fitting made for **soybean oil** at 10W ,15W, 20W, 25W at **600 rpm** have been reported.
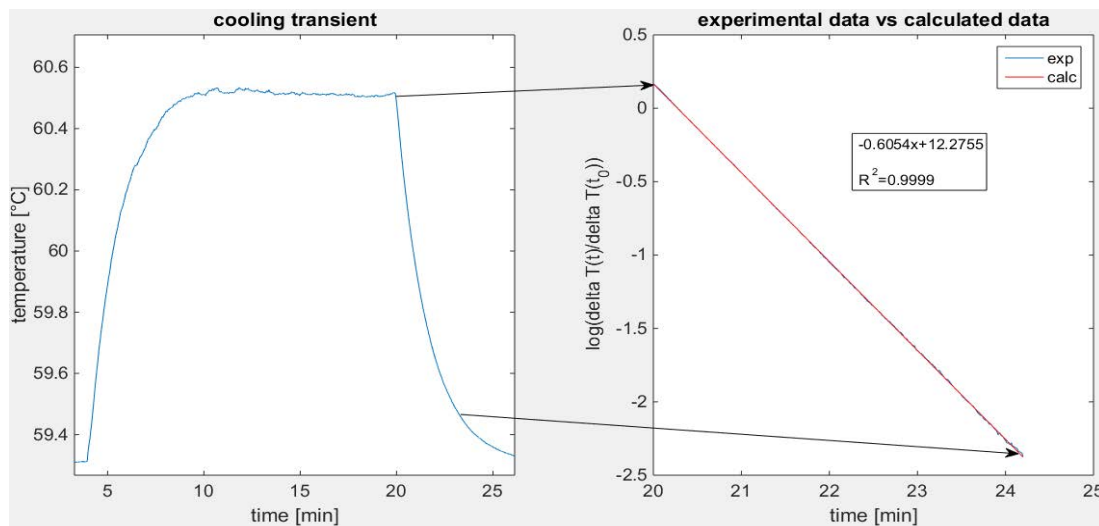
Figure 3.1 *The graph on the left shows the T inside the reactor vs time at power of **10W**, instead the right graph shows the linear fitting at **10 W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
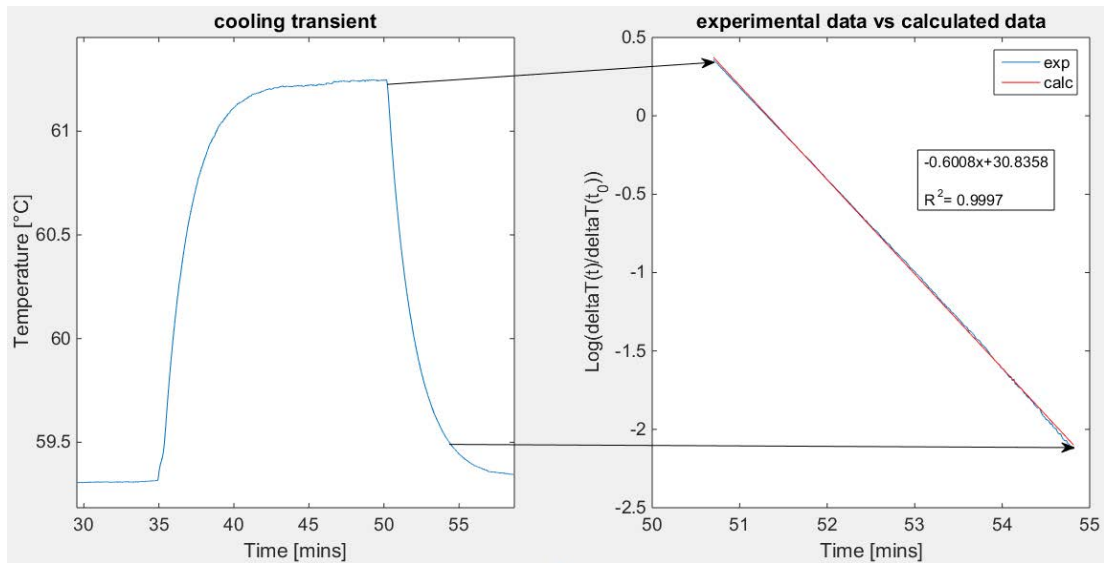
Figure 3.2 *The graph on the left shows the T inside the reactor vs time at power of **15W** , instead   the right graph shows the linear fitting at **15W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated,*
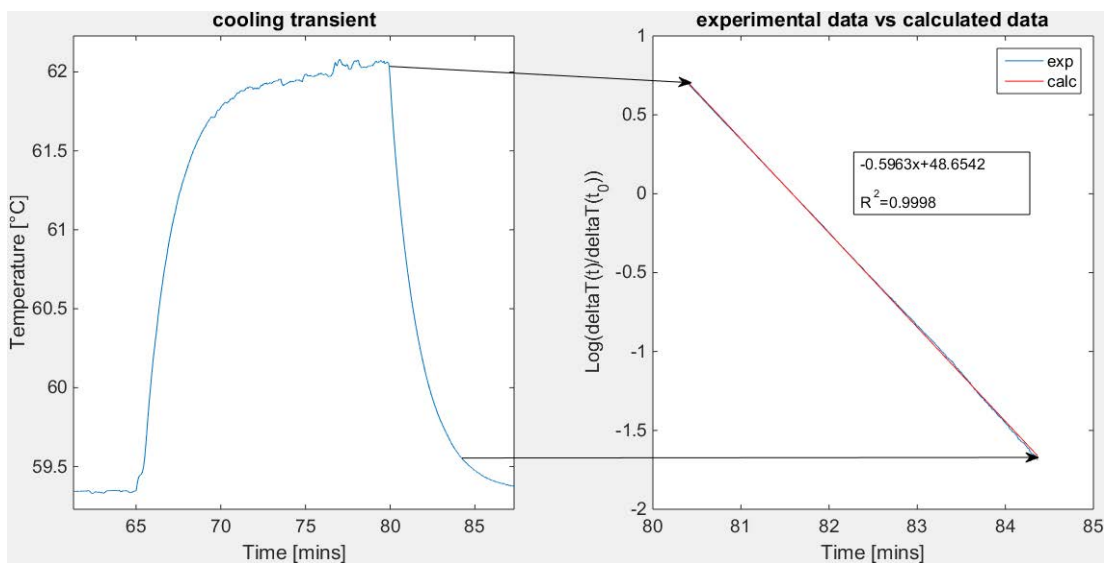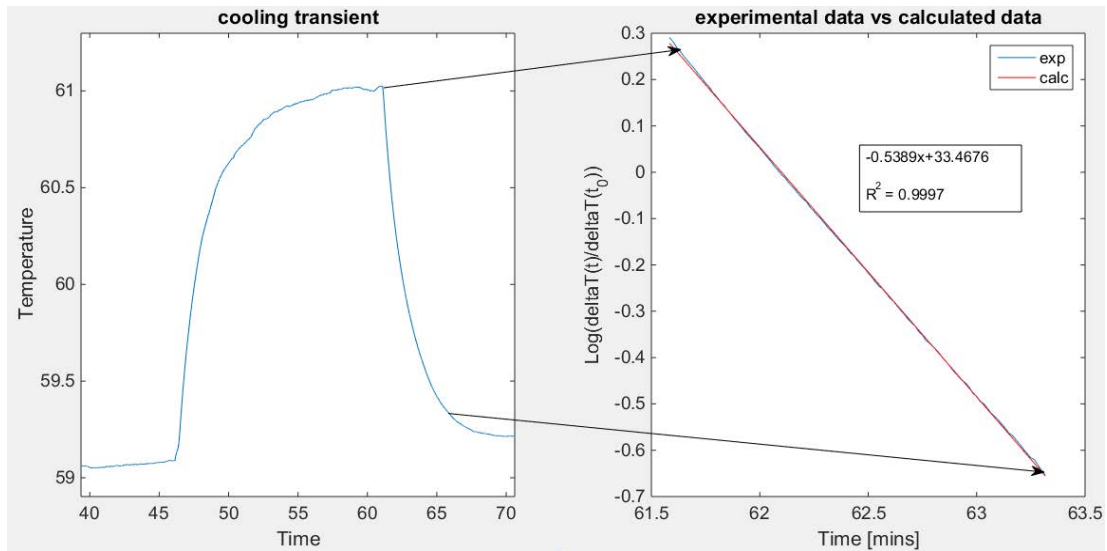

Figure 3.3 *The graph on the left shows the T inside the reactor vs time at power of **20W** , instead the Right graph shows the linear fitting at **20W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
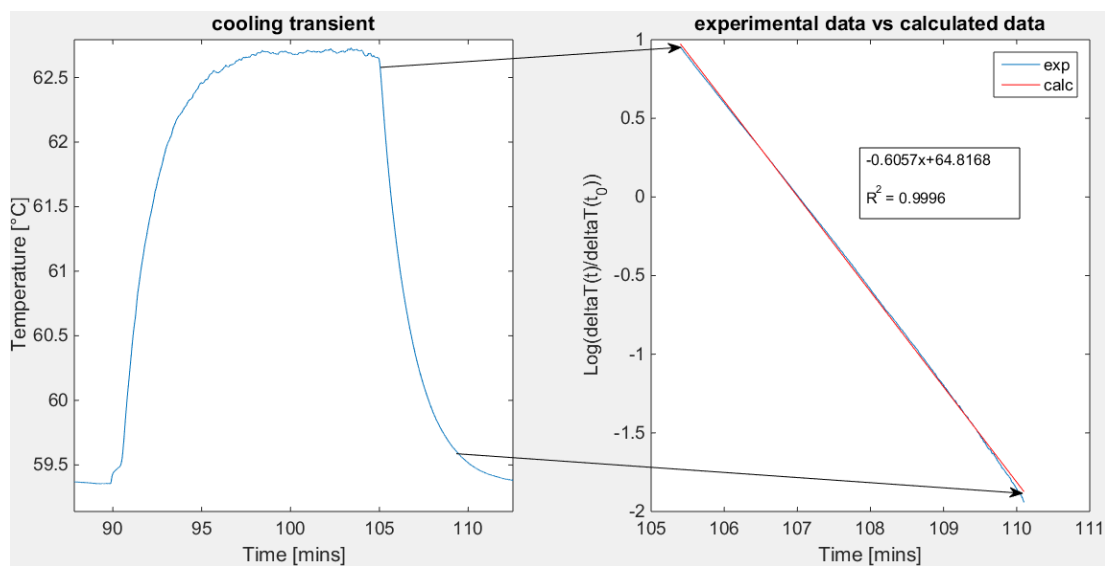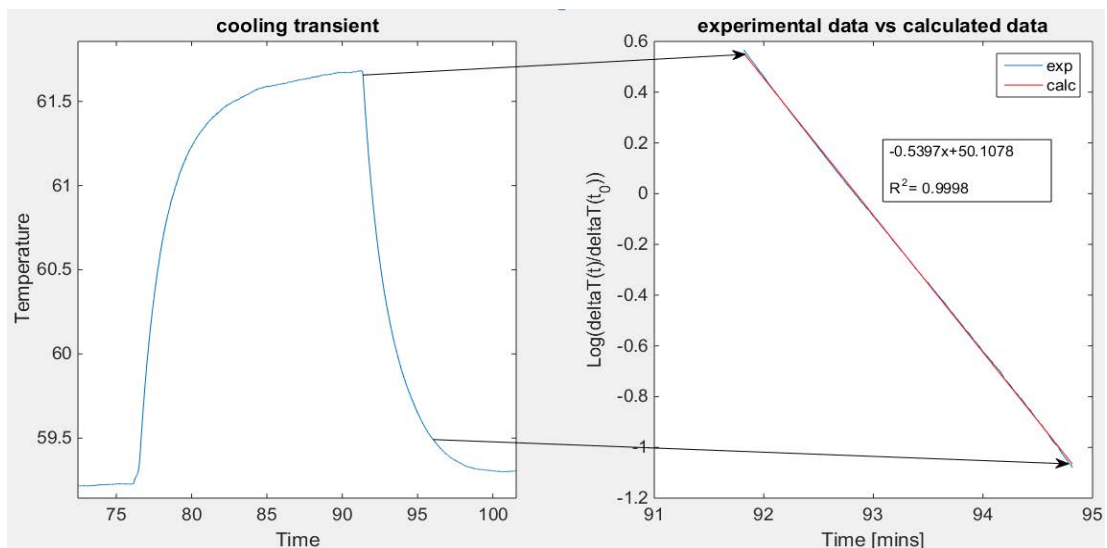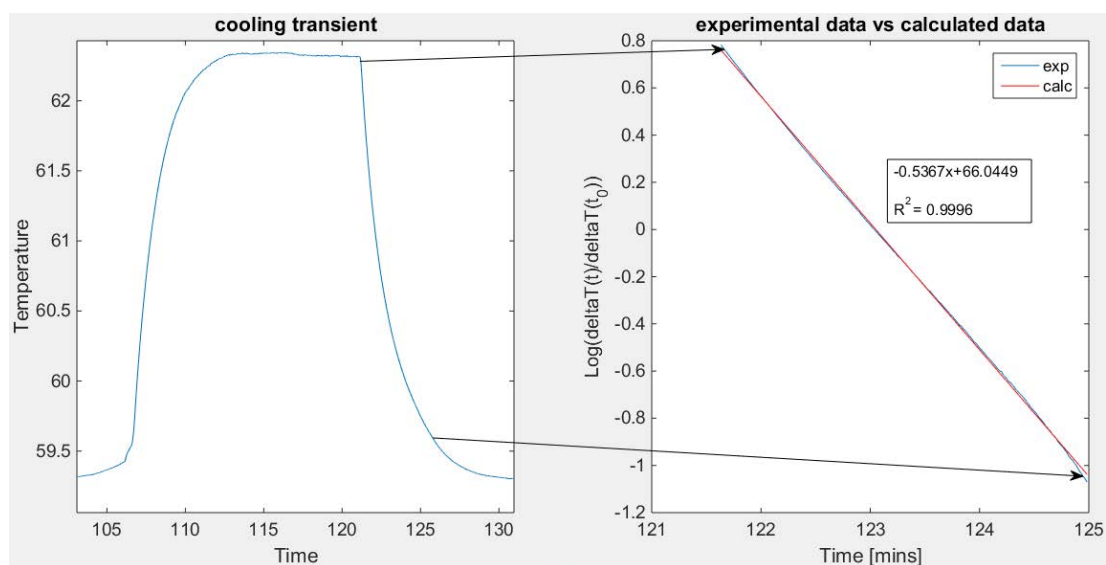
Figure 3.4 *The graph on the left shows the T inside the reactor vs time at power of **25W** , instead the right graph shows the linear fitting at **25W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

The table below shows the tau values expressed in seconds and minutes for **soybean oil** at 10W, 15W, 20W, 25W at **600 rpm**

Table 3.1 *Value of τ at different power, and mean value of τ at 600 rpm for soybean oil*

Power[W]	$\tau^{-1}[\min^{-1}]$	$\tau[\min]$	$\tau^{-1}[s^{-1}]=\frac{U*A}{m*cp}$	$\tau[s]=\frac{U*A}{m*cp}$
10	0.60	1.65	0.01	99.10
15	0.60	1.66	0.01	99.86
20	0.59	1.67	0.01	100.62
25	0.60	1.65	0.01	99.05
mean value	**0.60**	**1.65**	**0.01**	**99.66**

From the graphs, and from the table it is possible to note that the time constant (τ) are very similar even if calculated at different powers. This mean that the experimental data are very good, in fact we this is possible to see from the linear fitting, where the fitting coefficient R^2 it varies between 0.996 and 0.999, and the S(average square deviation) it is very small.
Finally, the mean value of time is equal to 99.6635 second, that is the cooling transient it is extinguished in 398-498 second (4-5 τ).

Below the charts of **soybean oil** with an impeller speed of **1500 rpm** at 10W, 15W, 20W, 25W have been shown.

At 10 W it was not possible collect experimental data, because the because the cooling temperature inside the reactor has gone below that at which the heating phase begins due to problems in the measurement.
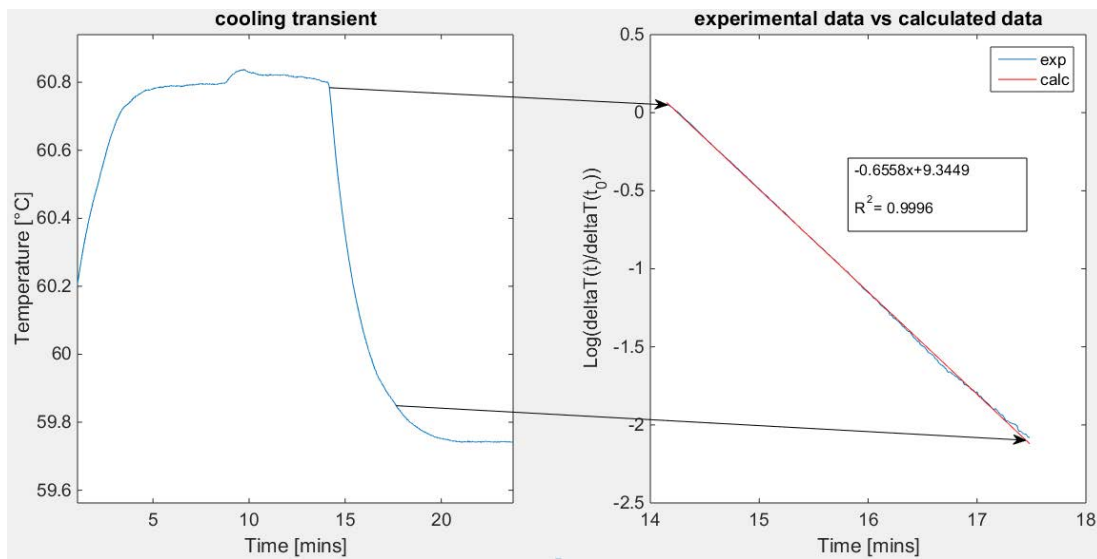

Figure 3.5 *The graph on the left shows the T inside the reactor vs time at power of **15W** , instead the right graph shows the linear fitting at **15W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

Figure 3.6 *The graph on the left shows the T inside the reactor vs time at power of **20W** , instead the right graph shows the linear fitting at **20W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
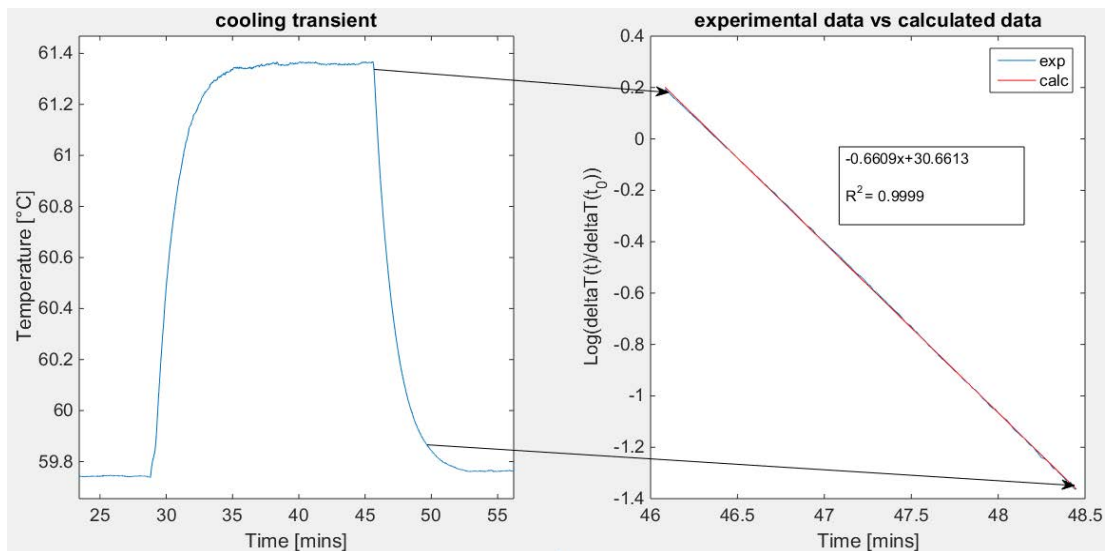
Figure 3.7 *The graph on the left shows the T inside the reactor vs time at power of **25W** , instead the right graph shows the linear fitting at **25W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

The table below shows the τ values expressed in seconds and minutes for **soybean oil** at 10W, 15W, 20W, 25W at **1500 rpm.**

Table 3.2 *Value of τ at different power, and mean value of τ at 1500 rpm for soybean oil*

Power[W]	τ^{-1}[min^{-1}]	τ[min]	τ^{-1}[s^{-1}]$= \frac{U*A}{m*cp}$	τ[s]$= \frac{U*A}{m*cp}$
15	0.53	1.85	0.01	111.33
20	0.53	1.85	0.01	111.17
25	0.53	1.86	0.01	111.79
mean value	**0.53**	**1.85**	**0.01**	**111.43**

Even at 1500 rpm the time constants are quite similar, with R great of 0.999, so a good fitting. The cooling transient is extinguished in 455-555 second (4-5 τ).

The calculation of the τ from the cooling transient was then made taking into account the **sunflower oil**. As previously the tests have been made at 10 W, 15W, 20W, 25W, at **600 rpm**. The graphs have been reported below:
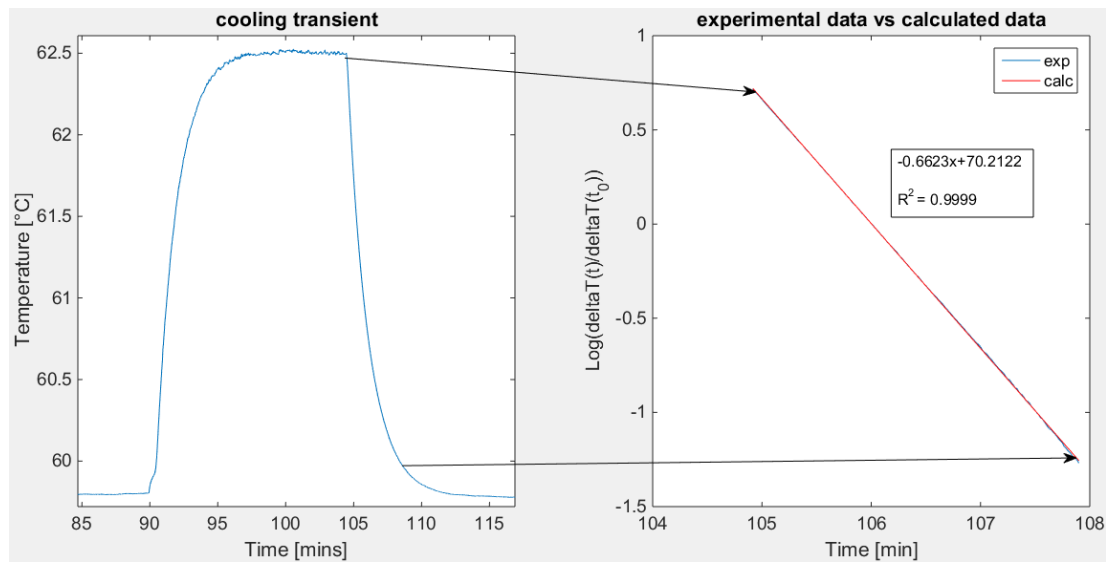
Figure 3.8 *The graph on the left shows the T inside the reactor vs time at power of **10W** , instead the right graph shows the linear fitting at **10W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

Figure 3.9 *The graph on the left shows the T inside the reactor vs time at power of **15W** , instead the right graph shows the linear fitting at **15W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
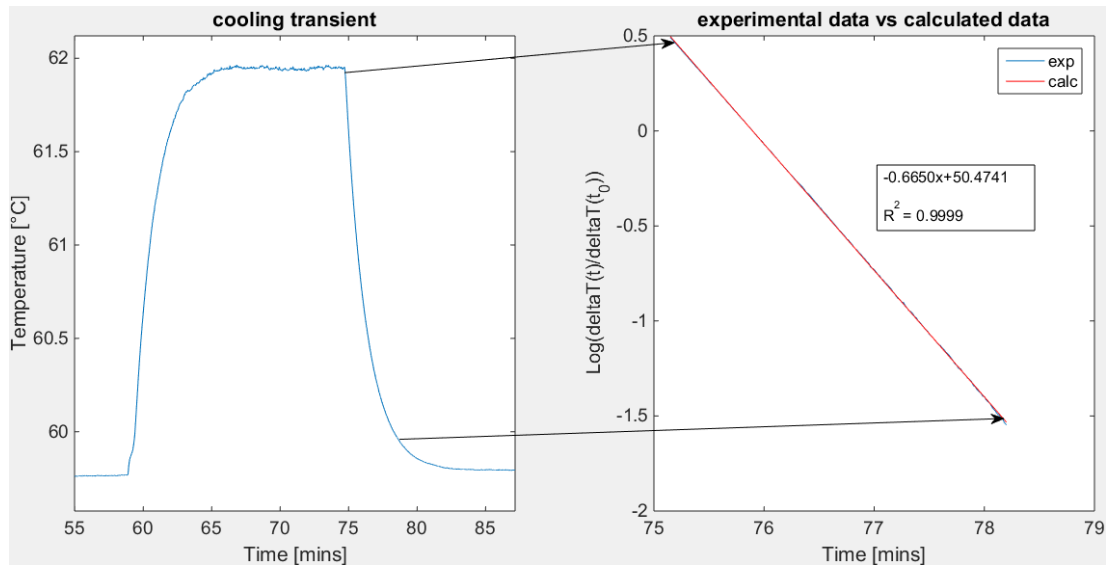
Figure 3.10 *The graph on the left shows the T inside the reactor vs time at power of **20W** , instead on the right graph shows the linear fitting at **20W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
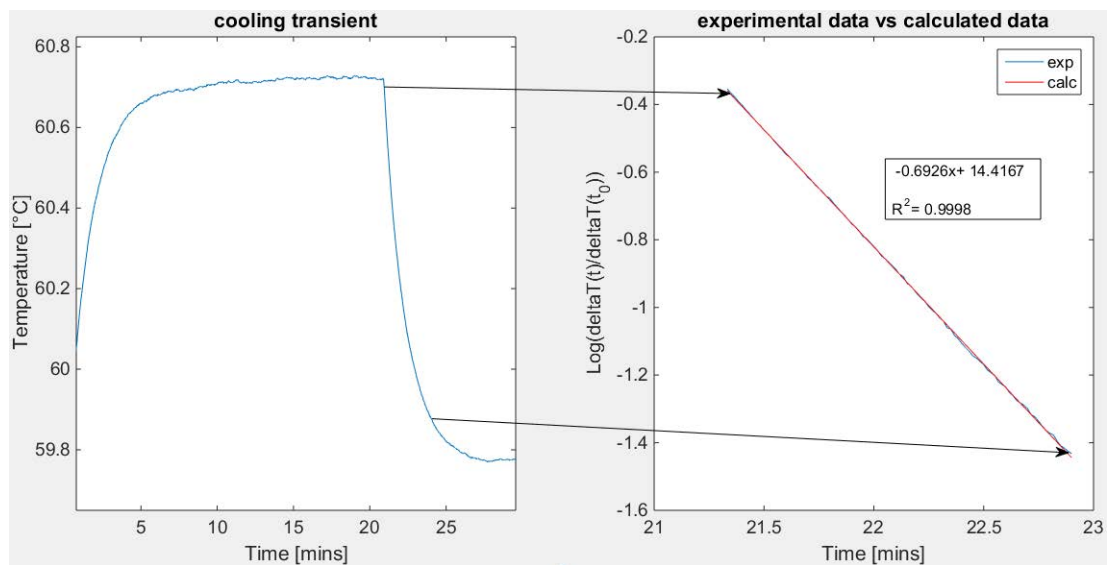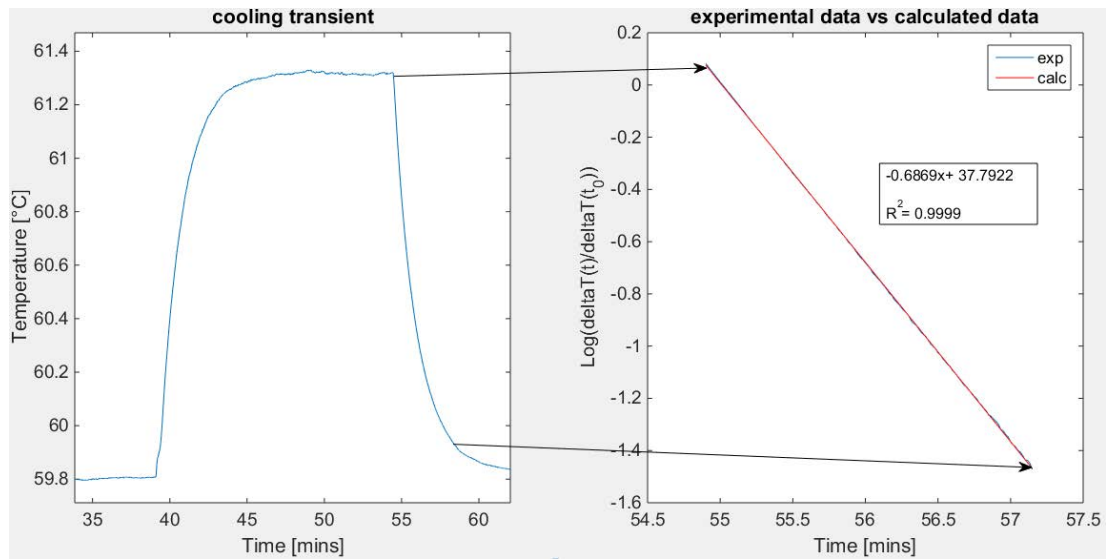

Figure 3.11 *The graph on the left shows the T inside the reactor vs time at power of **25W** , instead the right graph shows the linear fitting at **25W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

The table below shows the τ values expressed in seconds and minutes for **sunflower oil** at 10W, 15W, 20W, 25W at **600 rpm**

Table 3.3 *Value of τ at different power, and mean value of τ at 600 rpm for sunflower oil*

Power[W]	$\tau^{-1}[min^{-1}]$	$\tau[min]$	$\tau^{-1}[s^{-1}]=\dfrac{U*A}{m*cp}$	$\tau[s]=\dfrac{U*A}{m*cp}$
10	0.65	1.52	0.01	91.49
15	0.66	1.51	0.01	90.78
20	0.66	1.50	0.01	90.22
25	0.66	1.50	0.01	90.59
mean value	**0.66**	**1.51**	**0.01**	**90.77**

The mean value of τ is 90.7738, so the cooling transient it is extinguished in about 360-460second. Even in this case the fitting is excellent, since R^2 is greater than 0.999. . Below the charts of **sunflower oil** with an impeller speed of **1500 rpm** at 10W, 15W, 20W, 25W have been represented:
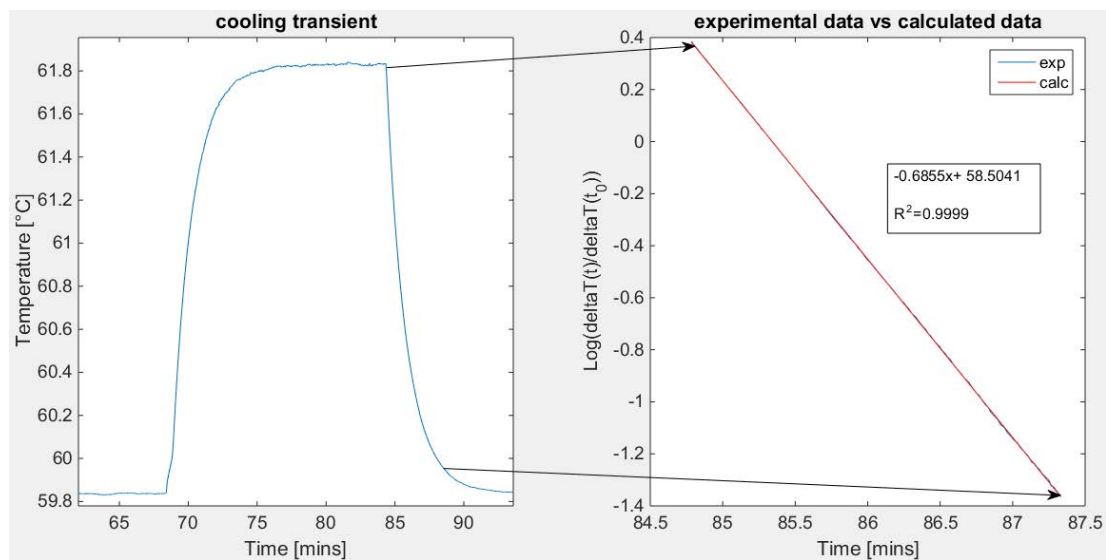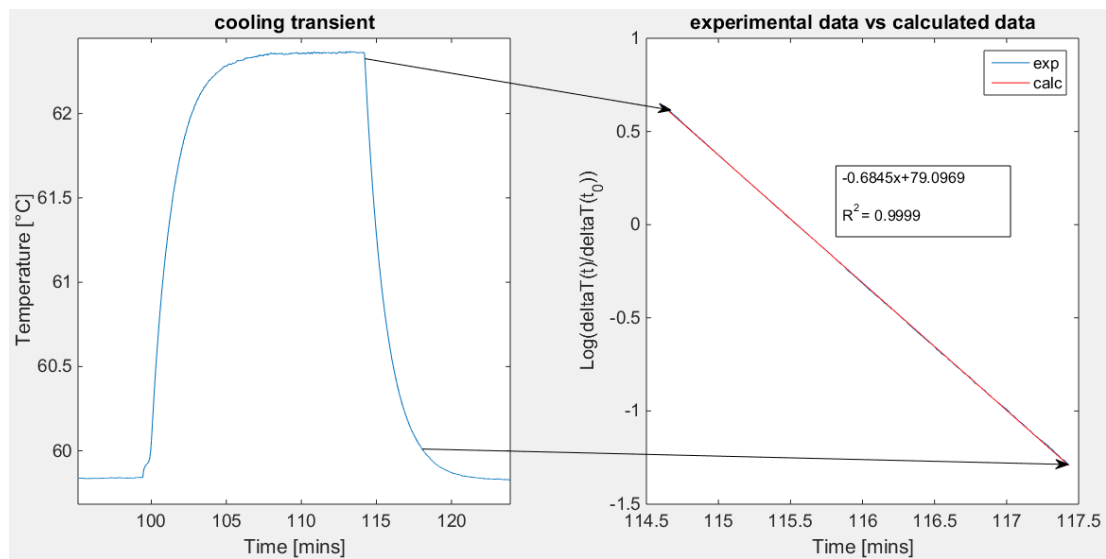

Figure 3.12 *The graph on the left shows the T inside the reactor vs time at power of **10W** , instead the right graph shows the linear fitting at **10W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

Figure 3.13 *The graph on the left shows the T inside the reactor vs time at power of **15W** , instead the right graph shows the linear fitting at **15W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

Figure 3.14 *The graph on the left shows the T inside the reactor vs time at power of **20W** , instead the right graph shows the linear fitting at **20W**, where: blue line is a ln of Δt experimental , and red a ln Δ calculated*

Figure 3.15 *The graph on the left shows the T inside the reactor vs time at power of **25W** , instead the right graph shows the linear fitting at **25W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

The table below shows the τ values expressed in seconds and minutes for **sunflower oil** at 10W, 15W, 20W, 25W at **1500 rpm**

Table 3.4 *Value of τ at different power, and mean value of τ at 1500 rpm for sunflower oil*

Power[W]	$\tau^{-1}[min^{-1}]$	$\tau[min]$	$\tau^{-1}[s^{-1}]= \frac{U*A}{m*cp}$	$\tau[s]= \frac{U*A}{m*cp}$
10	0.69	1.44	0.01	86.63
15	0.68	1.45	0.01	87.34
20	0.68	1.45	0.01	87.52
25	0.68	1.46	0.01	87.65
mean value	**0.68**	**1.45**	**0.01**	**87.29**

The mean value of τ is 87.2904, so the cooling transient it is extinguished in about 350-430second. Even in this case the fitting is excellent, since R^2 is greater than 0.999, so a excellent fitting. Finally the time constant τ, taking into account a **rapeseed oil** has been calculated. Also in this case initially an impeller speed equal to **600 rpm** has been considered**.**
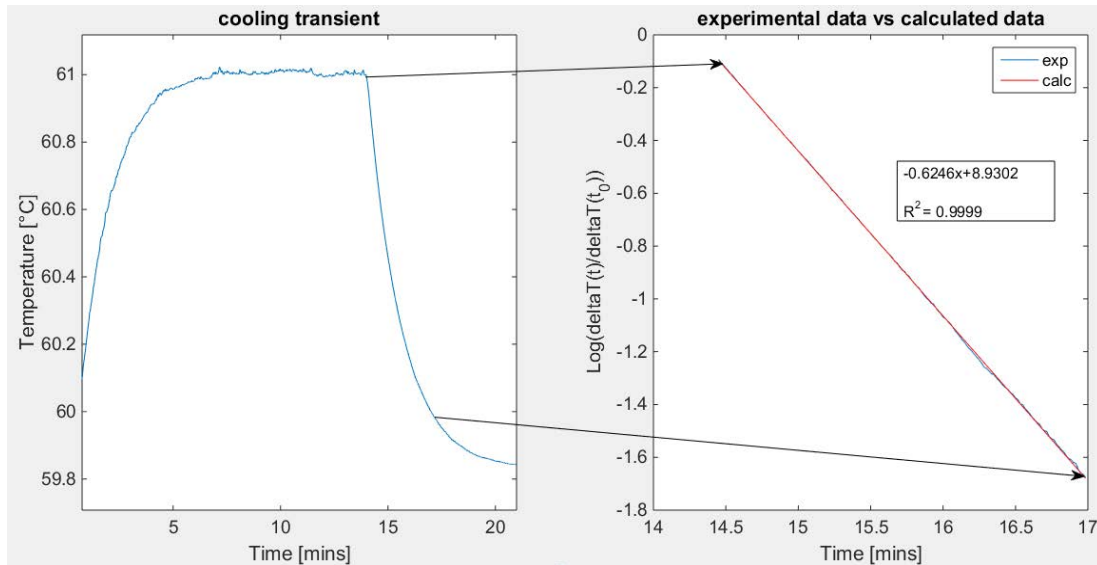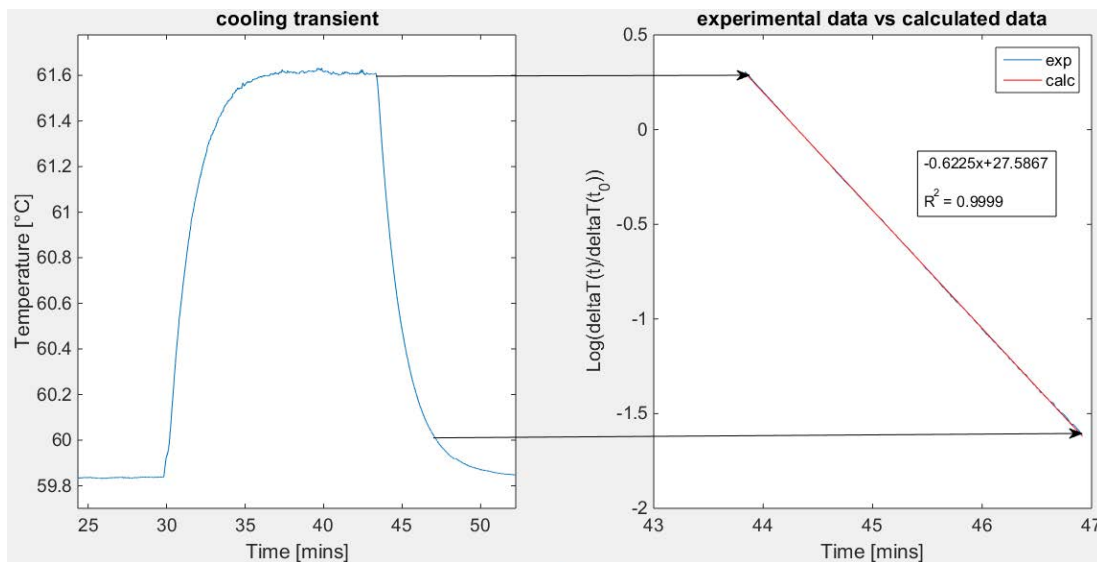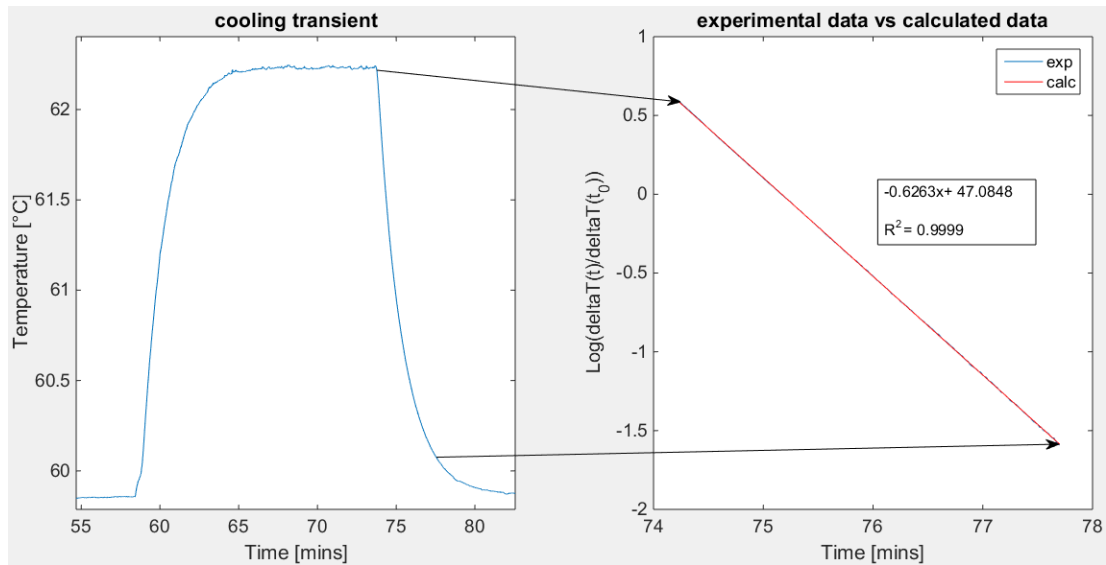

Figure 3.16 *The graph on the left shows the T inside the reactor vs time at power of **10W** , instead the right graph shows the linear fitting at **10W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

Figure 3.17 *The graph on the left shows the T inside the reactor vs time at power of **15W** , instead the right graph shows the linear fitting at **15W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
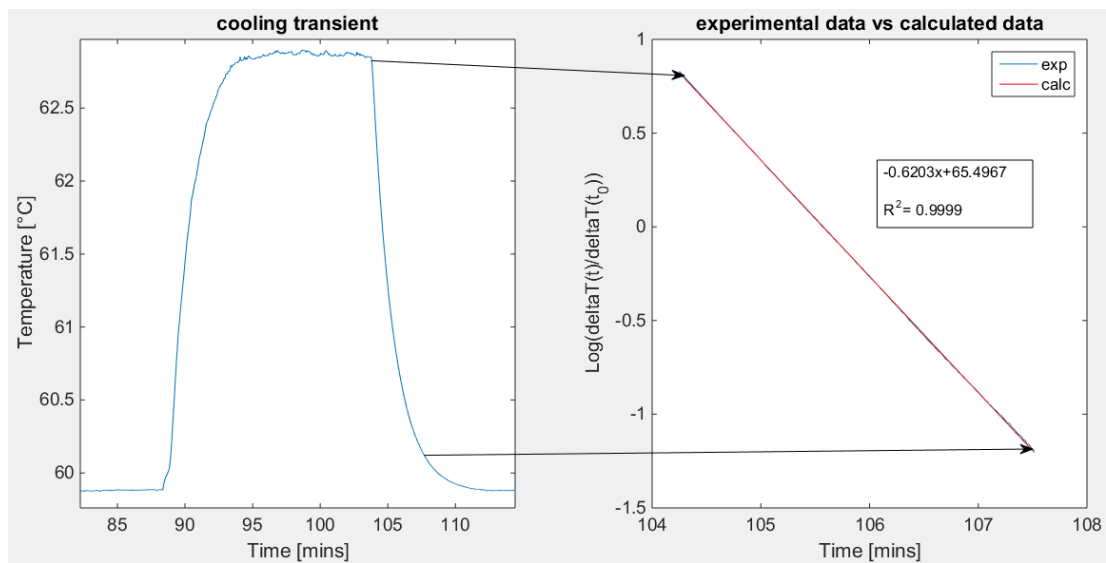
Figure 3.18 *The graph on the left shows the T inside the reactor vs time at power of **20W** , instead the right graph shows the linear fitting at **20W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

Figure 3.19 *The graph on the left shows the T inside the reactor vs time at power of **25W** , instead the right graph shows the linear fitting at **25W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

The table below shows the τ values expressed in seconds and minutes for **rapeseed oil** at 10W, 15W, 20W, 25W at **600 rpm**

Table 3.5 *Value of τ at different power, and mean value of τ at 600 rpm for rapeseed oil*

Power[W]	$\tau^{-1}[min^{-1}]$	$\tau[min]$	$\tau^{-1}[s^{-1}]=\frac{U*A}{m*cp}$	$\tau[s]=\frac{U*A}{m*cp}$
10	0.62	1.60	0.01	96.06
15	0.62	1.60	0.01	96.38
20	0.62	1.59	0.01	95.80
25	0.62	1.61	0.01	96.72
mean value	**0.62**	**1.60**	**0.01**	**96.24**

The mean value of τ is 96.2437, so the cooling transient it is extinguished in about 385-480second. Even in this case the fitting is excellent, since R2 is equal to 0.999. As for all the other oils, even with **rapeseed oil** the τ also at a speed of **1500 rpm** impeller has been calculated.
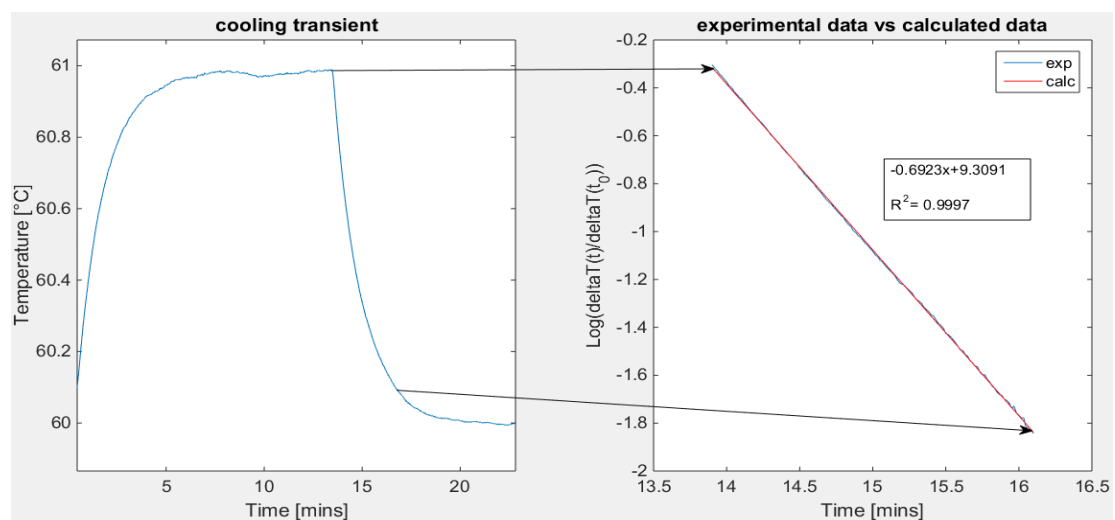

Figure 3.20 *The graph on the left shows the T inside the reactor vs time at power of **10W** , instead the right graph shows the linear fitting at **10W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculat*
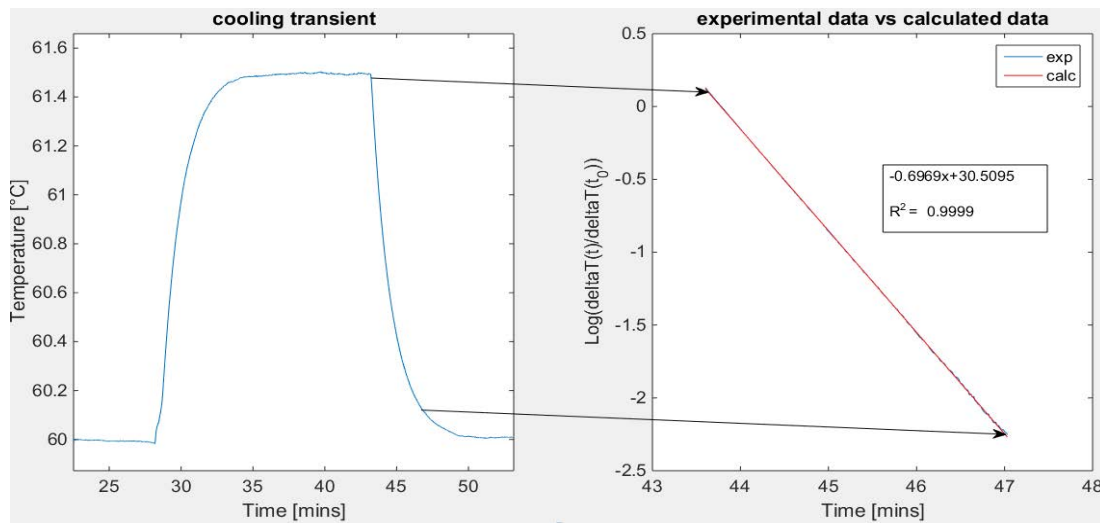
Figure 3.21 *The graph on the left shows the T inside the reactor vs time at power of **15W** , instead the right graph shows the linear fitting at **15W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
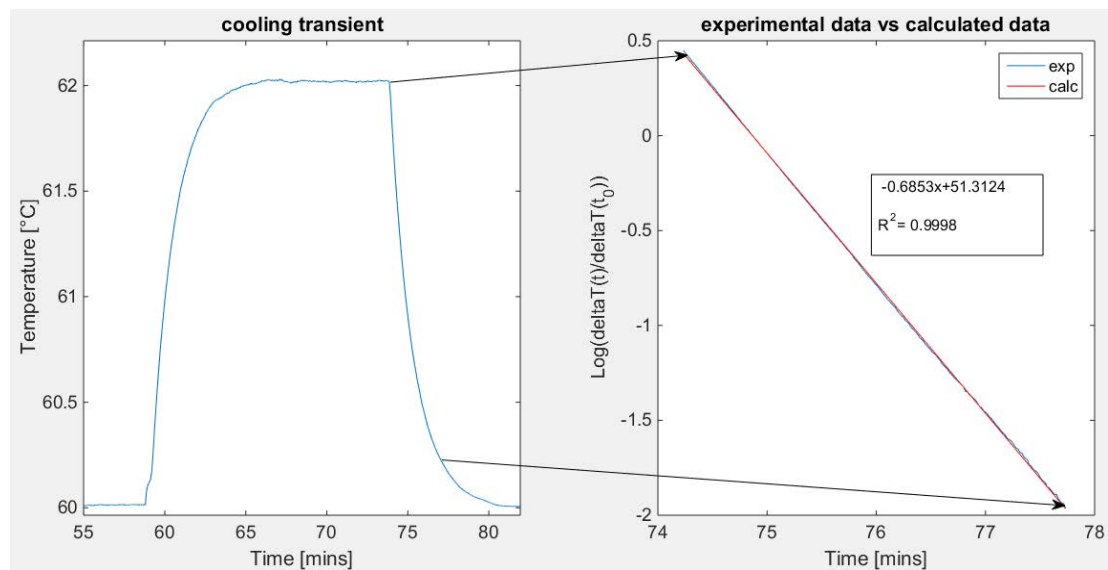

Figure 3.22 *The graph on the left shows the T inside the reactor vs time at power of **20W** , instead the right graph shows the linear fitting at **20W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*
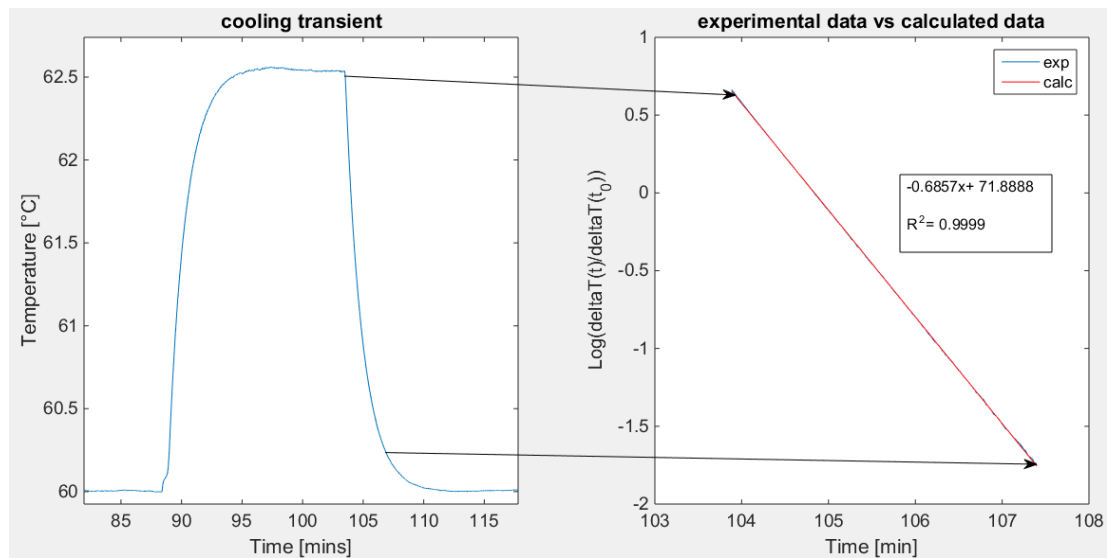
Figure 3.23 *The graph on the left shows the T inside the reactor vs time at power of **25W** , instead the right graph shows the linear fitting at **25W**, where: blue line is a ln of Δt experimental , and red a ln Δt calculated*

The table below shows the τ values expressed in seconds and minutes for **rapeseed oil** at 10W, 15W, 20W, 25W at **1500 rpm**.

Table 3.6 *Value of τ at different power, and mean value of τ at 1500 rpm for rapeseed oil*

Power[W]	τ-1[min-1]	τ[min]	τ-1[s-1]$=\frac{U*A}{m*cp}$	τ[s]$=\frac{U*A}{m*cp}$
10	0.69	1.44	0.01	86.66
15	0.69	1.43	0.01	86.09
20	0.68	1.45	0.01	87.55
25	0.68	1.45	0.01	87.50
mean value	**0.69**	**1.44**	**0.01**	**86.95**

The mean value of τ is 86.9544, so the cooling transient it is extinguished in about 348-435second. Even in this case the fitting is excellent, since R^2 is greater than to 0.999.

The table 3.7 summarizes the mean value of tau at 600 and 1500 rpm for all three oils.

Table 3.7 *Mean value of τ, at 600 rpm and 1500 for soybean oil, sunflower oil ,rapeseed oil*

	Soybean oil	Sunflower oil	Rapeseed oil
Mean value τ[sec] at 600 rpm	99.66	90.77	96.24
Mean value τ[sec] at 1500 rpm	111.43	87.29	86.95

From a first analysis it has been possible to see that the cooling time is lower for both sunflower oil and rapeseed than soybean oil. This is highlighted both at 600 rpm and at 1500 rpm.

Another things that has been possible to note is that the cooling for the sunflower oil and rapeseed oil at 1500 rpm, is faster than cooling at 600 rpm. For the soybean oil instead, the cooling at 600 rpm is faster than cooling at 1500 rpm.

3.1.2 Global heat transfer coefficient: study on the steady state at 600 and 1500 rpm for soybean, sunflower and rapeseed oil

The global heat exchange coefficient U depend from three different ways of transport energy: conduction, convection and radiation, through follow equation:

$$\frac{1}{U} = (\frac{1}{h_{irr}} + \frac{1}{h_{conv}} + \frac{s}{k}) \qquad (W/^{\circ}k*m^2) \tag{3.9}$$

where h_{irr} and h_{con} are respectively the heat exchange coefficients for irradiation and convection, and s/K indicates the ratio between thickness and thermal conducibility.

For the calculate of the convection coefficient in forced convection, first of all it is important to distinguish between laminar flow and turbulent flow through the Reynolds number.

$$Re = \frac{v*\rho*L}{\mu} \tag{3.10}$$

Where:.

- V= mean velocity (m/s);
- ρ= fluid density (kg/m^3)
- L= characteristic size (m);
- μ= dynamic viscosity;

In this work the flow is turbulent. For the calculate of h_{conv} define a new dimensionless number, that is the number of Nusselt:

$$Nu = \frac{h_{conv}*L}{\lambda_f} \tag{3.11}$$

Where:
- λ_f = thermal conductivity (W/m°K)

In turn, the Nusselt number is a function of:

Nu= f(Re, Pr) (3.12)

Where:

$$Pr = \frac{cp*\mu}{k} \tag{3.13}$$

- cp= specific heat (J/kg°K)
- k= thermal conducibility (w/m°K)

So in forced convention and with turbulent flow the Nusselt number is equal to:

$$Nu = a * Re^b * Pr^c \tag{3.14}$$

Then for determination of h_{conv} firstly the Reynolds number and Prandtl number have been calculated , after the Nusselt number and h_{conv} have been calculated.
Starting from equation 3.4 and rearranging it, the equation 3.15 has been obtained.

$$Q = U * A * \Delta T \tag{3.15}$$

Where , ΔT are known values, and it is possible to obtain information about U*A and m*cp.
For find the global heat transfer coefficient U*A a *Matlab* code has been used. First of all the experimental values of T(the temperature of the steady state) vs power supplied (10W,15W,20W,25W) have been graphed, after through linear fitting T_{calc} has been obtained using the following formula 3.16:

$$Tcalc = \left(\frac{1}{U*A} * \left(Q - Q_{supplied}\right)\right) + Tjackett \tag{3.16}$$

varying U*A and Q. The value of the global exchange coefficient that has been taken, was that for which the values of experimental T and T_{Calc} were very similar, therefore the values that gave an excellent fitting have been take into account. On steady state tests were performed at 600 rpm and 1500 rpm for all three oils.

Below are summarise the value of power and T experimental and U*A calculated at 600 rpm and 1500 rpm for all three oils, with the linear fitting graphics
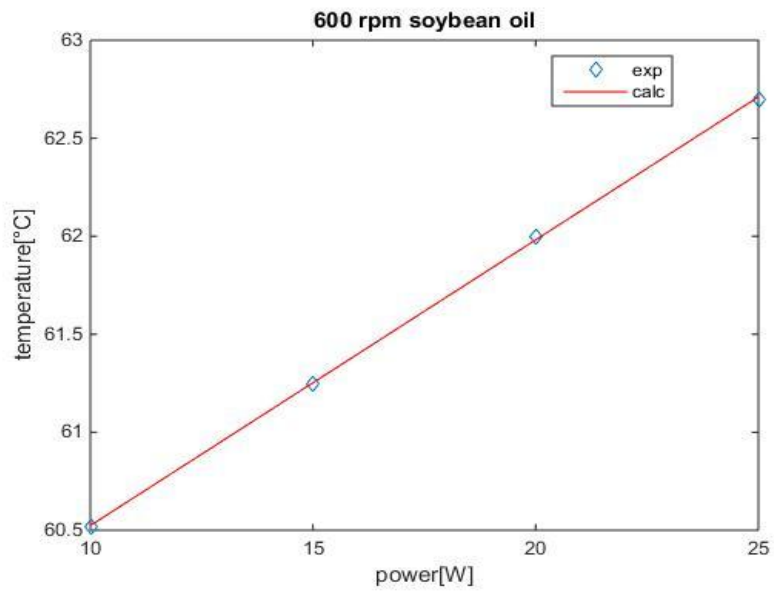

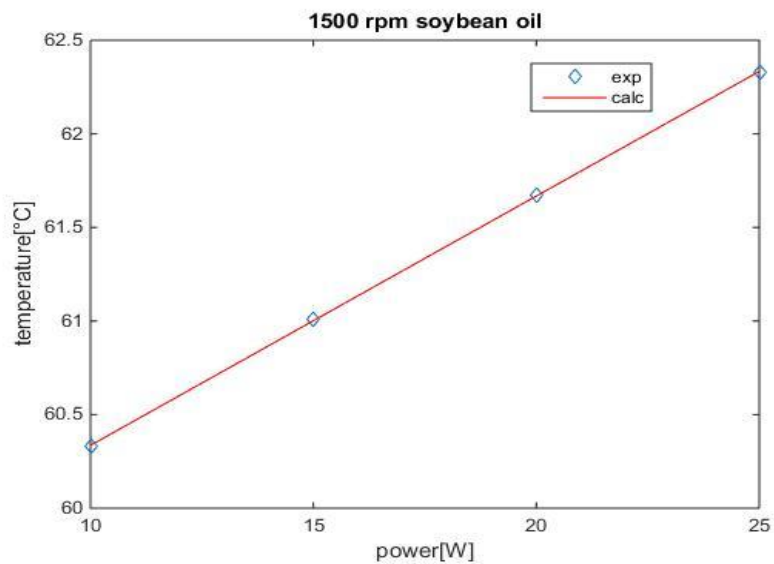**Figure 3.24** *Linear fitting at steady state for soybean oil at 600 rpm*

Figure 3.25 *Linear fitting at steady state for soybean oil at 1500 rpm*

Table 3.8 *Global Heat transfer coefficient U*A at 600 and 1500 rpm for **soybean oil***

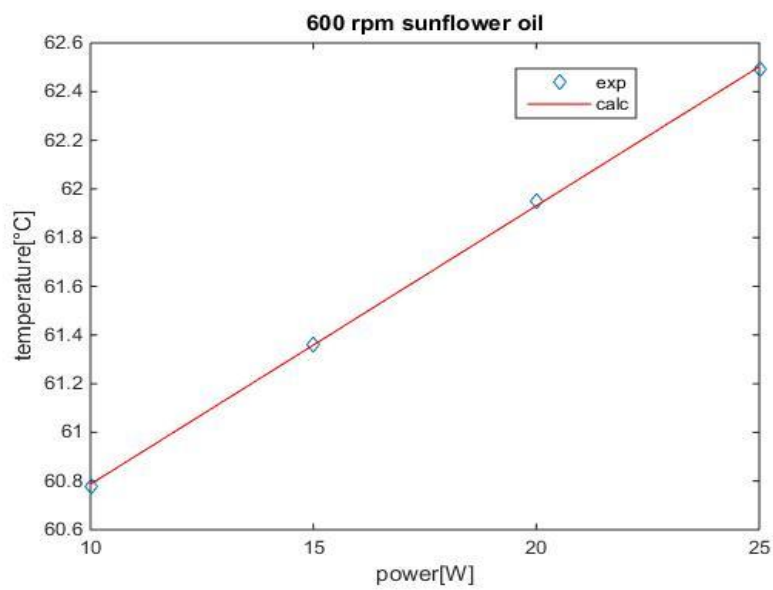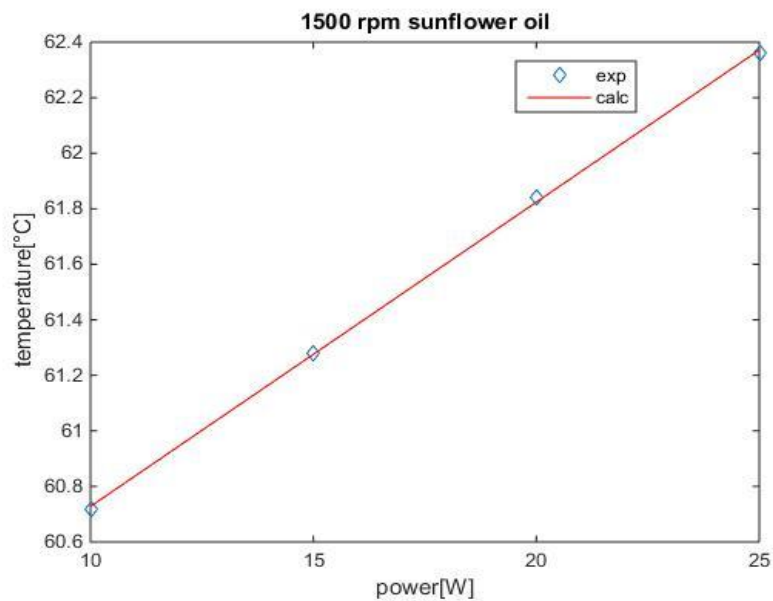|	U*A[W/°K]
Soybean oil at 600 rpm	6.85
Soybean oil at 1500 rpm	7.51

Figure 3.26 *Linear fitting at steady state for sunflower oil at 600 rpm*

Figure 3.27 *Linear fitting at steady state for sunflower oil at 1500 rpm*

Table 3.9 *Global Heat transfer coefficient U*A at 600 and 1500 rpm for **sunflower oil***

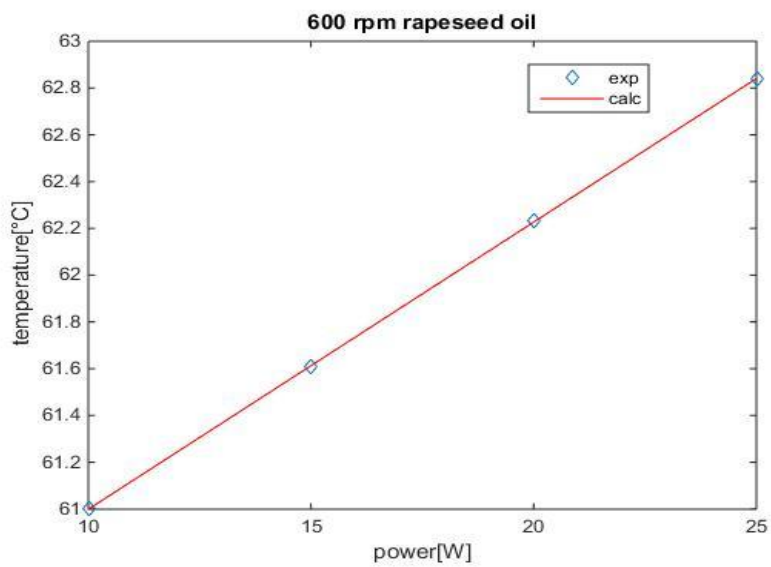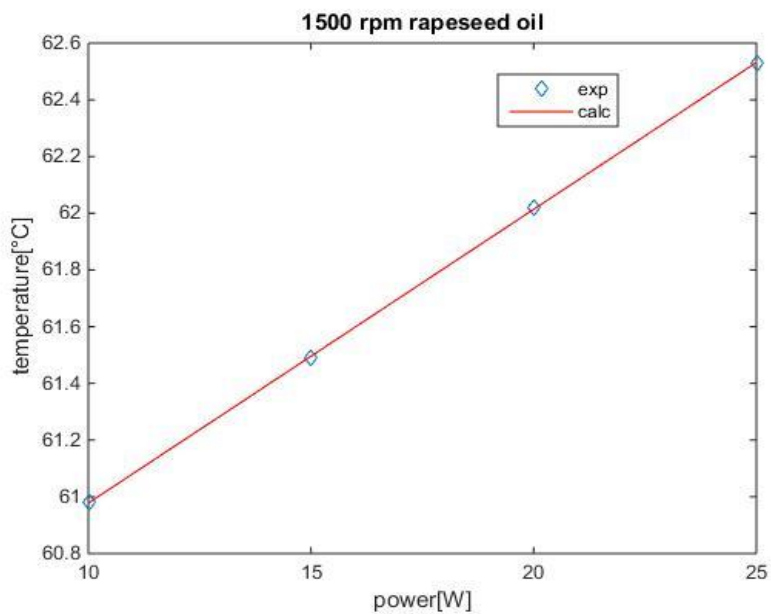|	U*A[W/°K]
Sunflower oil at 600 rpm	8.74
Sunflower oil at 1500 rpm	9.12

Figure 3.28 *Linear fitting at steady state for rapeseed oil at 600 rpm*

Figure 3.29 *Linear fitting at steady state for rapeseed oil at 1500 rpm*

Table 3.10 *Global Heat transfer coefficient U*A at 600 and 1500 rpm for **rapeseed oil***

	U*A[W/°K]
Rapeseed oil at 600 rpm	8.14
Rapeseed oil at 1500 rpm	9.65

Knowing now the τ, calculated previously from the cooling transient, knowing the global heat exchange coefficient U*A just calculated, the heat capacity of the mixture inside the reactor (m * cp) has been calculated through following formula:

$$m * cp = \tau * U * A \tag{3.17}$$

The values of U*A and of the thermal capacity m*cp where then shown in the following table 3.11.

Table 3.11 *U*A and m*cp for all three oils at 600 rpm and 1500 rpm*

	Soybean oil	Sunflower oil	Rapeseed oil
U*A [W/°K] At 600 rpm	6.85	8.74	8.14
U*A [W/°K] At 1500 rpm	7.51	9.12	9.65
m*cp [J/°K] at 600 rpm	683.52	793.47	783.53
m*cp [J/°K] at 1500 rpm	836.99	796.43	839.11

For what concerns an impeller speed of 600 rpm, it has been possible to see that:
The global coefficient of heat exchange (Equation 3.6) depend on the number of Nusselt which in turn is a function of the Prandtl number and the Reynolds numbers, so for a careful analysis it would be useless to start from the calculation of these dimensionless numbers. To calculate the aforementioned numbers the physical properties of the oils have to be considered, namely: density, viscosity, specific heat. The calculation shows that soybean oil has the highest Reynolds number because it has the highest density and lowest viscosity, followed by sunflower oil and rapeseed oil. For what concerns the number of Prandtl instead, the highest value is found in sunflower oil, followed by rapeseed oil and soybean oil. Finally it is possible to calculate the Nusselt number and therefore the global heat exchange

coefficient. From the calculation it is possible to see that (as obtained by matlab) the sunflower oil has the highest overall heat exchange coefficient and is therefore the one that presents an exchange by better convection, followed by the rapeseed and finally by the soybean; it so has the best thermal capacity of the reaction mixture ,therefore it exchanges the greater quantity of heat. All this is related to the case of impeller speed equal to 600 rpm.

Considering the case at 1500 rpm, it can be immediately noticed that both for soybean oil and for rapeseed oil there is a considerable difference in the value of the global exchange coefficient compared to the 600 rpm case, same thing can't say for sunflower oil. By increasing the impeller speed, the heat exchange improves and this can be seen by looking at the values of U * A and m * cp for all three oils. It is noted that the highest value of the global heat exchange coefficient in this case concerns rapeseed oil probably because increasing the rotation speed of the impeller the oil undergoes a degradation, and the sunflower oil is the one that has degraded more than the other two oils. It is in fact noted that in this case, the sunflower oil has the lowest thermal capacity of the reaction mixture and the cooling time is equal to that of rapeseed oil, therefore the amount of heat exchanged is similar to the case at 600 rpm.

From the value of the thermal capacity of the mixture it is clear that the oil has a greater quantity of heat exchanged, going from 600 rpm to 1500 rpm and soybean oil, which however has the highest cooling time due to the large amount of heat exchanged and in relation to the value of the global coefficient. From the results it can be deduced that the increase in the speed of the impeller has brought greater advantages for soybean oil because passing from 600 rpm to 1500 it increased its thermal capacity of 150J/°K. Important advantage have been recorded even for rapeseed oil, which has the highest value of the global exchange coefficient, so it is the oil in which the best exchange by convection occurs, and it has the lowest value of the cooling time, besides having the highest value of the thermal capacity (similar to soybean) it exchanges the greatest quantity of heat.

Anyway the oil that presents a great betterment passing from 600 rpm to 1500 rpm is the soybean.

Chapter 4

Results epoxidation

In this chapter the results of epoxidation, for all three oils, Soybean, sunflower and rapeseed oil will be represented. The reaction of epoxidation was carried out both for four hours and five hours. Then a mixing program has been used, which included increasing the rotation speed for impeller for 30 seconds from 600 to 1500 rpm, every 20 minutes. The mixing program was used for all three oil both 4 hours and 5 hours. For the estimation of selectivity and conversion have been determined the amount of residual double bonds, the number of the glycols and the epoxides formed. To do this a FTIR analysis has been used, which permits of understand if epoxides are presents, and highlights double bonds and glycols (by- product). FTIR is a simple method, but it doesn't permit to calculate in a right way the amount of the epoxides presents. The precise method to estimate the amount of epoxides is to use hydrobromic acid and some pH indicators , but it is a complicated and expensive method. For this reason the FTIR analaysis is sufficient for this work.

In this regard it is possible to see that presence of glycols is associated to a wide peak of about 3500 cm^{-1}. Epoxides present a peak about 825-830 cm^{-1} whereas the peak of double bonds is around 3010 cm^{-1} [1]. Afterwards a titration of epoxidized oil for find the % oxidized epoxide has been made. At last the heat of reaction has been calculated for all three oils, taking into account the amount of energy released during the reaction and the number of moles of the oils.

4.1 Epoxidation with soybean oil

The proportions used for this work ,have been described in chapter 1: Acetic acid: double bonds molar ratio is equal to 0.5:1 and hydrogen peroxide: double bonds is equal to 1.5:1. So the follows quantities have been used: 100 gr of the soybean oil, 16.74 gr of acetic acid, 88.82 gr of hydrogen peroxide and 3 gr of sulphuric acid has been added at the same time for a total of solution of 205,6 gr.

4.1.1 Epoxidation for 4 hours: thermal profile and effect of mixing program ,FTIR analysis

In figure 4.1 it is possible to see the thermal profile for soybean oil, with a reaction of epoxidations carried out for 4 hours , the velocity of impeller is equal to 600 rpm.
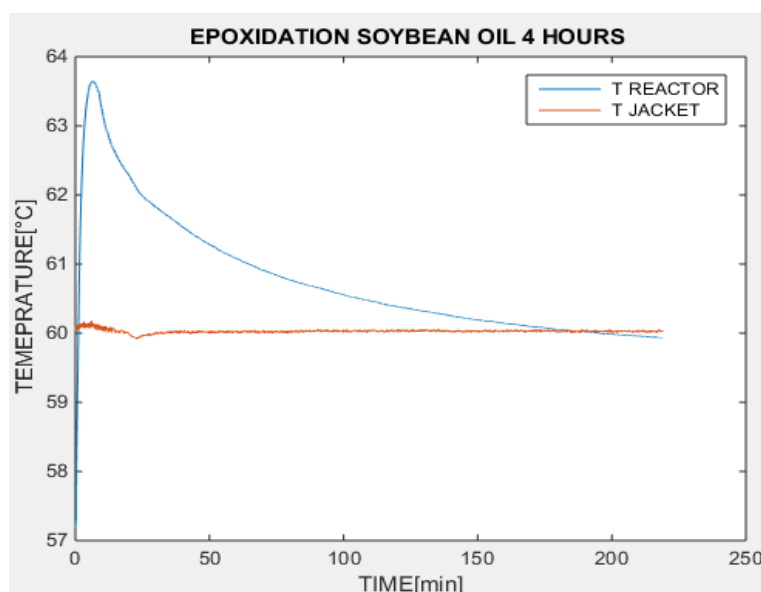

Figure 4.1 *Thermal profile (temperature vs time) soybean oil for an reaction of epoxidation conducted for 4 hours, with a velocity of the impeller of 600 rpm.*

From the thermal profile, it is possible to note that the epoxidation reaction has occurred and this is confirmed by the great thermal overshoot about at 63.5 °C, furthermore, this big overshoot confirm also the great character exothermic of the reaction, because exothermic reaction occur with an increase in the temperature, because there is a decrease of potential energy, an increase of kinetics energy and consequently there is a increase of the velocity and so the temperature increase. A good result that it also is possible to see is that there is only one temperature overshoot, after about 4 hours in fact all the reactants have reacted and the conversion is close to 100%.

After that the mixing program has been used, this because, for a by-phasic system, mixing and mass transfer between phases is very important. This has been seen through some studies[1] where initially the impeller speed has been fixed to 600 rpm and after two hours the speed has been set to 1500 rpm for one minute, all for a total of 4 hours. So doing a problems of segregation has been seen. This because the impeller doesn't work with all mass of oil, but there is a little bit of oil segregates and unreacted, and so when the impeller velocity is set to 1500 rpm the reacted oil is taken away from the impeller and the segregated oil reacts with

the aqueous phase and this could bring another peaks, that is another exothermic reaction happens. In this case, it is important to find the right compromise, this because, if the velocity of impeller is very low a good mass transfer is not obtained, instead of the impeller speed is very high ,the reaction become kinetically controlled, because the determining step is rate of reaction instead that mass transfer, and moreover if the impeller speed is too high, epoxides are more exposed to aqueous phase and glycols can be formed. For resolve this problem, different solutions could be used. First of all the impeller speed could be increased at 1500 rpm for 4 hours, but this is not convenient because this leads at the degradation of the oil. Another solution could be change the impeller, for instance the pitched blade one(4PB) or the 4-blade flat blade (4FB) turbine or the sawtooth impellers could be used. The first one (4 PB) is an axial impeller and it guarantees a good balance between flow and shear; It is the prefer impeller for liquid–liquid dispersion in conjunction with Rushton turbine (6BD). The inconvenient is that this impeller creates a bad emulsion between two phases, even if it works using all the volume. The (4FB) is a radial impeller. It is used if the impeller is placed low in the vessel to provide agitation during the pompout. The Sawtooth impeller is used to create a stable liquid-liquid emulsion. Another solution could be install two Rushton Turbine[1] , but this impellers are not available. As just told previously, the impeller used in this work is (6PB) that is a radial impeller. The latter could give a problem of segregation but at the same way it guarantee a good emulsion. The final solution is to maintain the same impeller speed for 20 minutes at 600 rpm, and then change the speed from 600 to 1500 rpm for 30 seconds. The mixing program has some advantages, for example it causes the product to be less exposed to the acidic aqueous phase, and therefore fewer glycol formations; another advantage is that it increases the reaction speed, because unreacted oil is taken from the impeller and is put into the aqueous phase where it reacts, then gradually with the various remixes the amount of unreacted non-segregated oil is less and less in the area where the impeller reacts.

In figure 4.2 the thermal profile for soybean oil obtained with a mixing program has been shown:
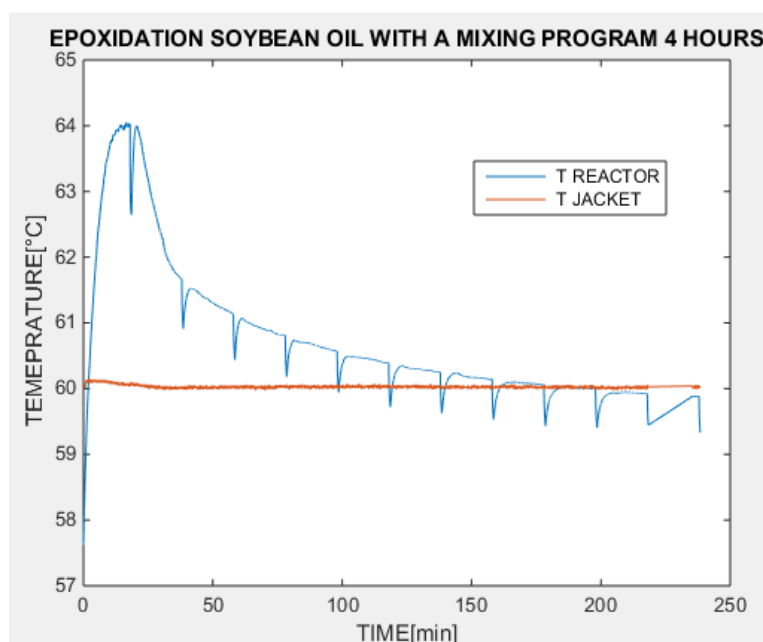
.

Figure 4.2 *Thermal profile (temperature vs time) soybean oil for reaction of epoxidation with a mixing program*
for 4 hours

The thermal profile indicates an exponential decrease as the time increase. There isn't degraded oil. In occasion of each remixing the temperature suddenly decreases because the heat exchange coefficient increases because the turbulence increases; after that the temperature increase again because the reaction is exothermic. The fact that the reaction speed is higher than the previous case (ie, more reactants are transformed into products in this case in epoxidized oil in the unit of time) is established because increasing the interface thanks to a betterment of the mass transfer, the oil that without remix didn't react, now it reacts with aqueous phase so the amount of the oil uncreacted decrease and the velocity of the reaction increase. It can be concluded that remixing speed up the process even because a less time is necessary for the thermal transient to run out. The FTIR analysis of the soybean oil without remix is represented in the figure 4.3
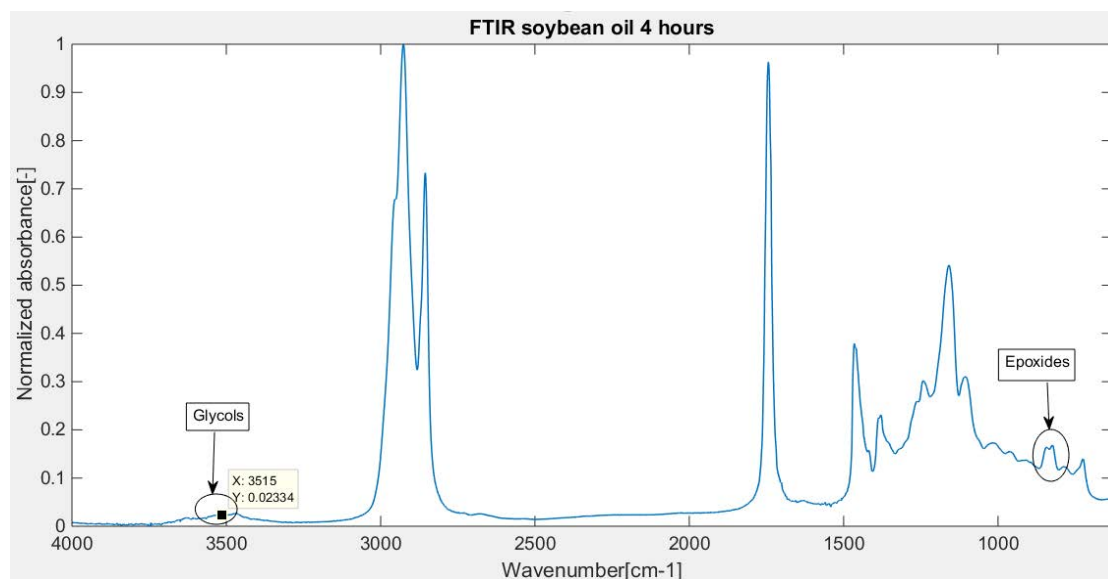
Figure 4.3 *FTIR spectrum of soybean oil. Process carried for 4 hours at 600 rpm*

From the following graph it is possible to note that the epoxidation reaction occurred as there is a peak relative to the presence of epoxides. There is a very little peak relative to glycols so they are surely present as by-products. The peak relative at double bonds C=C is absent, then it is possible to say that a big amount of C=C reacted.

As it was possible to see from the thermal profile without remix the conversion is total, so it is possible to calculate the selectivity through the follows equation 4.1 (if the conversion is near 100%)

$$selectivity = 1 - \frac{height\ OH\ peak\ soybean\ oil}{height\ OH\ peak\ reference} \tag{4.1}$$

Where the height OH peak of soybean oil is 0.023 as seen from the figure 4.3, instead the peak OH reference is 0,9689 as seen from the figure 4.4
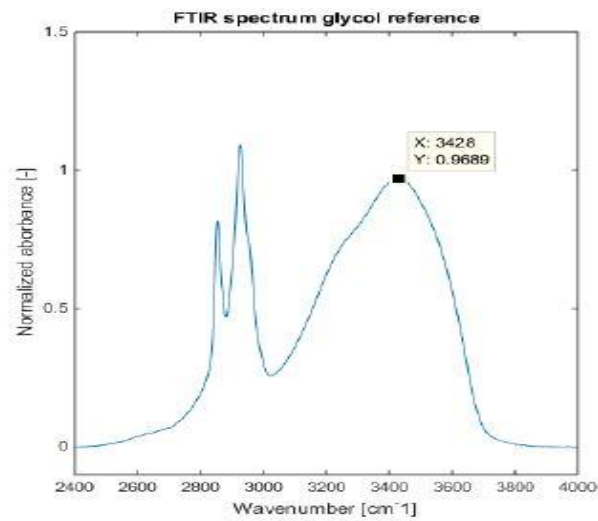
Figure 4.4 *Height OH peak reference*

then the selectivity it is equal to 97.63%. Now the results of the FTIR analysis related to soybean oil but with the mixing program have been reported.
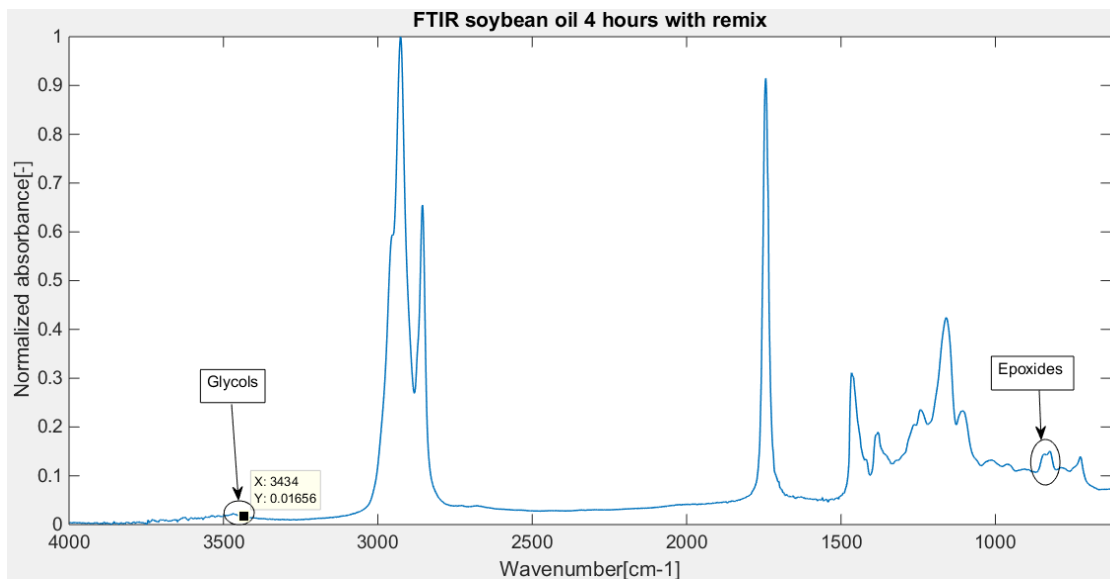

Figure 4.5 *FTIR spectrum of soybean oil. Process carried for 4 hours with a mixing program*

It is possible to see that the peak of epoxides is present, that the peak of double bond is absent, and that the peak of glycols it is smaller than previous case. The conversion is nearly total(100%) and the products are nearly totally epoxides. As the conversion is total and it is possible to calculate the selectivity with the formula (4.1), where the eight of OH peak ofsoybean oil is 0.01658, and the eight OH peak reference is like before 0.9689.The selectivity is 98.29%. It is possible to note that the amount of glycols is less than case without remix.

4.1.2 Epoxidation for 5 hours: thermal profile and effect of mixing program ,FTIR analysis
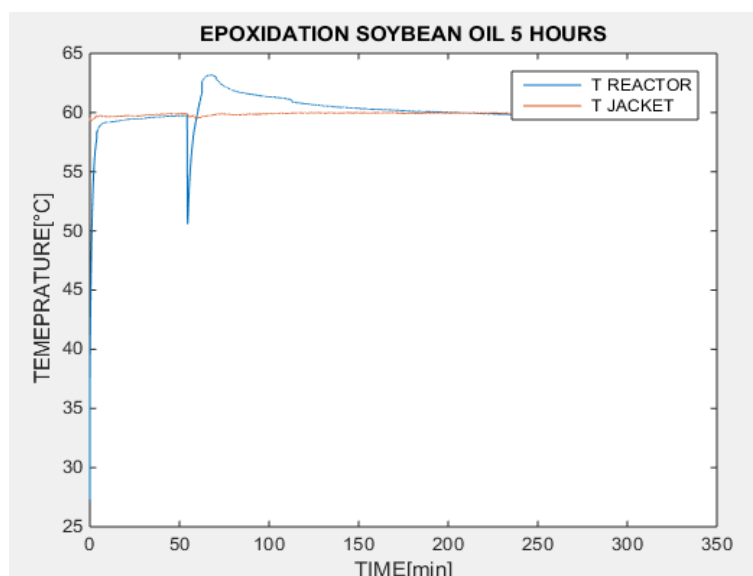

Figure 4.6 *Thermal profile (temperature vs time) soybean oil for a reaction of epoxidation conducted for 5hours, with a velocity of the impeller of 600 rpm*

In figure 4.6 the thermal profile soybean oil with a reaction of epoxidations carried out for 5 hours without remixing program has been represented. It is possible to note that the epoxidation reaction has occurred, there is an overshoot at about 63°C that confirm the exothermic character of the reaction, and that the conversion is almost 100%. In figure 4.7 it has been reported the thermal profile for the soybean oil obtained with a mixing program
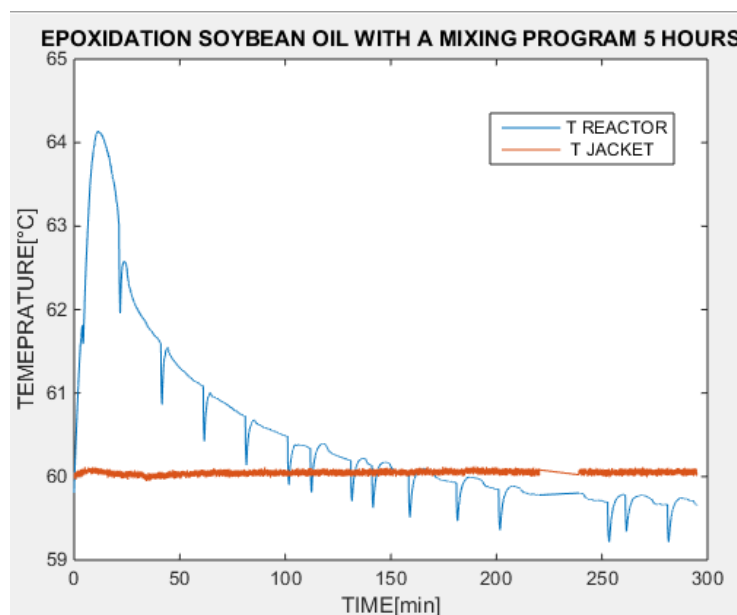

Figure 4.7 *Thermal profile (temperature vs time) soybean oil for reaction of epoxidation with a mixing program for 5 hours*

Also in this case   the temperature decreases with time, at each remixing the temperature decreases because increase the heat exchange coefficient. The thermal transient is exhausted before the case without remixing because the speed of reaction is greater. The same considerations that have been done for the cast at 4 hours ,it can be done for the case at 5 hours. The graphs related to the FTIR analysis both in the case without remixing and with remixing have been reported below.
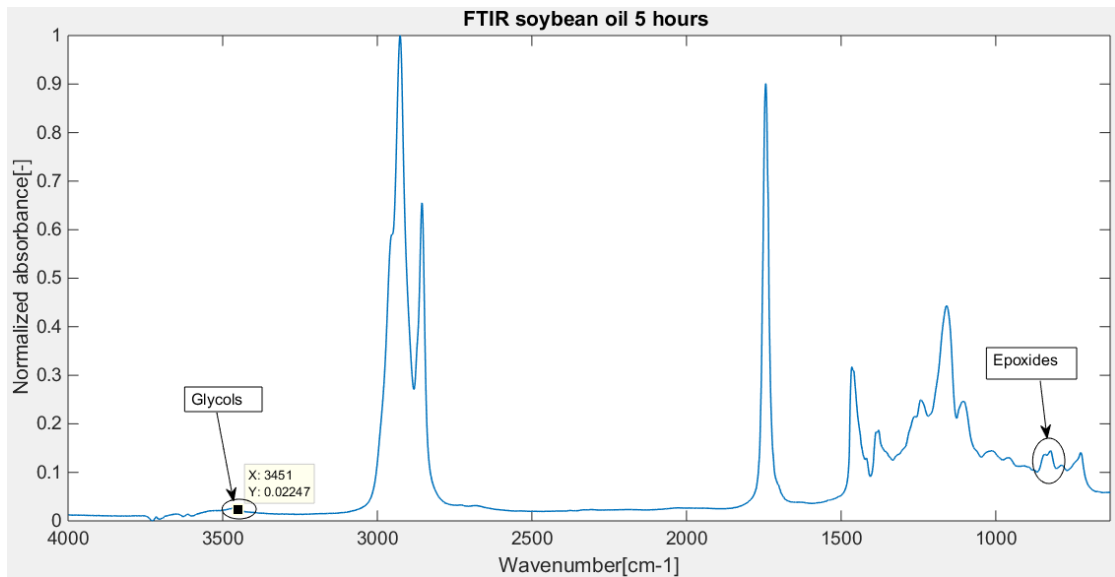

Figure 4.8 *FTIR spectrum of soybean oil. Process carried out for 5 hours at 600 rpm*
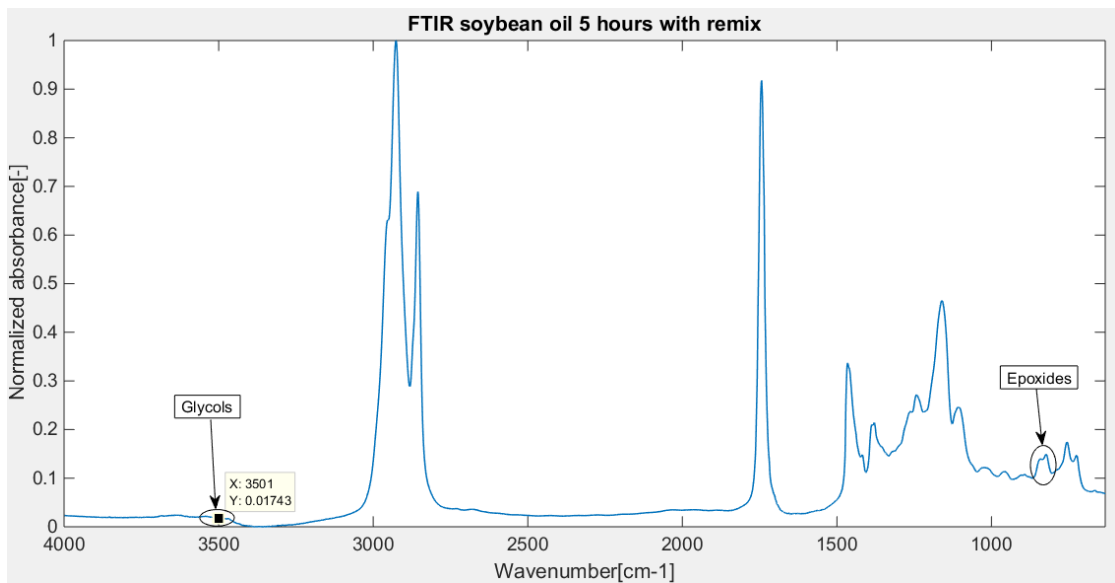

Figure 4.9 *FTIR spectrum of soybean oil. Process carried out for 5 hours with a mixing program*

In the both case the reaction of epoxidation has occurred, and this because there is the epoxides peak. There aren't double bonds C = C and that we have only traces of glycols. The conversion is almost 100% and we have mainly epoxides as products of the reaction. Being therefore the conversion close to 100% it is possible to calculate selectivity with the formula (4.1) in both case. In the first case that is, the epoxidation without remix : the high of OH peak of soybean oil is 0.02241, and the high OH peak reference is like before 0.9689, so the selectivity is 97,69%. In the second case instead the high of OH peak equal to 0.01743, and the high OH peak reference the same as before or rather 0.9689. The selectivity is 98.21%.

Also in this case the peak of the epoxides in the epoxidation with remix is higher than epoxidation without remix, and this because the remix increase the velocity of the reaction and so there is a greater quantity of epoxides.

Table 4.1 *Values of conversion, selectivity and amount of glycols for the epoxidation of the soybean oil both with remixing and without remixing at 4 and 5 hours*

	Soybean oil reaction for 4 hours without remixing	Soybean oil reaction for 4 hours with remixing	Soybean oil reaction for 5 hours without remixing	Soybean oil reaction for 5 hours with remixing
Conversion	$\approx 100\%$	$\approx 100\%$	$\approx 100\%$	$\approx 100\%$
Selectivity	97.63%	98.29%	97.69%	98.21%
Amount of glycols	2.37%	1.71%	2.31%	1.79%

From the table it is possible to see that for both cases the conversion is almost total, that is the majority of C=C reacted. It is possible to note that in the case of the epoxidation with remix there is a less amount of glycols and a greater selectivity and so there is a greater quantity of epoxized oil than glycols, this because as it has been said previously, the remix increase the rate of reaction and so increase the amount of reactants that are converted in desideratum product. Moreover it is possible to note the reaction with the highest selectivity is that carried out for 4 hours with a remix, so it means that it takes 4 hours for the reaction to complete, after this time the epoxy ring starts to break and unwanted products start to form. Considering instead the reaction without remix, it is possible to note that that an increase in time could favour the complete reaction, this does not apply in the case of remixes as seen in advance because the remix allows to take unreacted oil and to introduce it in the aqueous phase to make it reacts, and therefore 4 hours are enough. Anyway it is important to say that the value obtained are very similar among them.

4.2 Epoxidation with sunflower oil

As previously done with soybean oil, also in this case the following proportions and quantities have been used: acetic acid: double bonds molar ratio is equal to 0.5:1 and hydrogen peroxide: double bonds is equal to 1.5:1, 100 gr of sunflower oil, 16.74 gr of acetic acid, 88.82 gr of hydrogen peroxide and 3 gr of acid sulfuric , for a total of solution of 205, 6 gr.

4.2.1 Epoxidation for 4 hours: thermal profile and effect of mixing program ,FTIR analysis

In figure 4.10 e 4.11 the thermal profile of sunflower oil without remixing for a reaction conducted for 4 hours, and thermal profile with a remixing for a reaction conducted for 4 hours, have been represented:
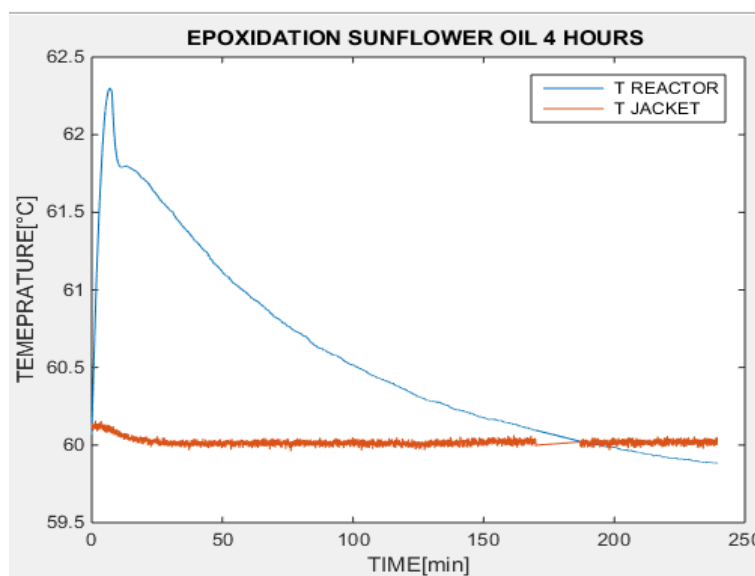

Figure 4.10 *Thermal profile (temperature vs time) sunflower oil for a reaction of epoxidation conducted for 4*

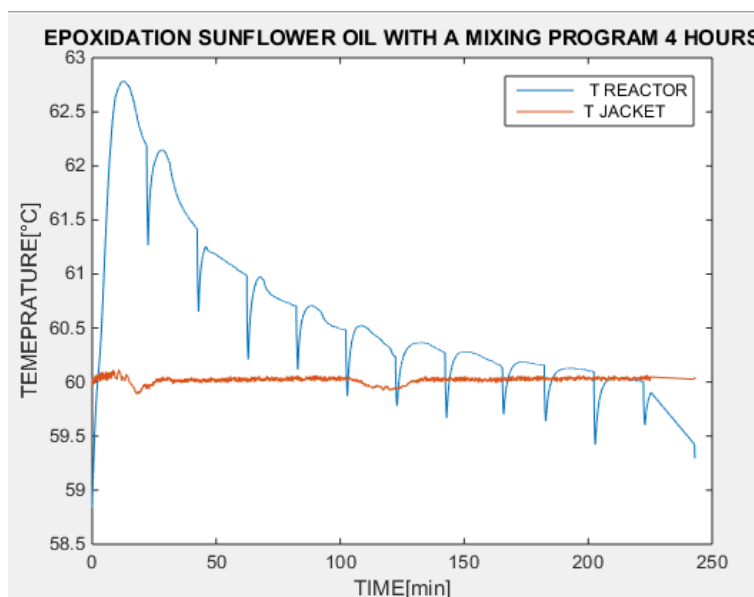*hours with a velocity of the impeller of 600 rpm*

Figure 4.11 *Thermal profile (temperature vs time) sunflower oil for reaction of epoxidation with a mixing program for 4 hour*

From figure 4.10 it is possible to notice the exothermic behaviour of the reactions, because there is a temperature peak of about 62.5 ° C which confirms what has been said. The overshoot represented in figure 4.10 is lower than in figure 4.11. In figure 4.11 it is possible to see that at each remixing the temperature decrease, for the same considerations done previously for the soybean oil. The temperature decrease over the time. Now in figure 4.12 e 4.13 respectively the results of FTIR analysis have been reported:4.13 respectively the results
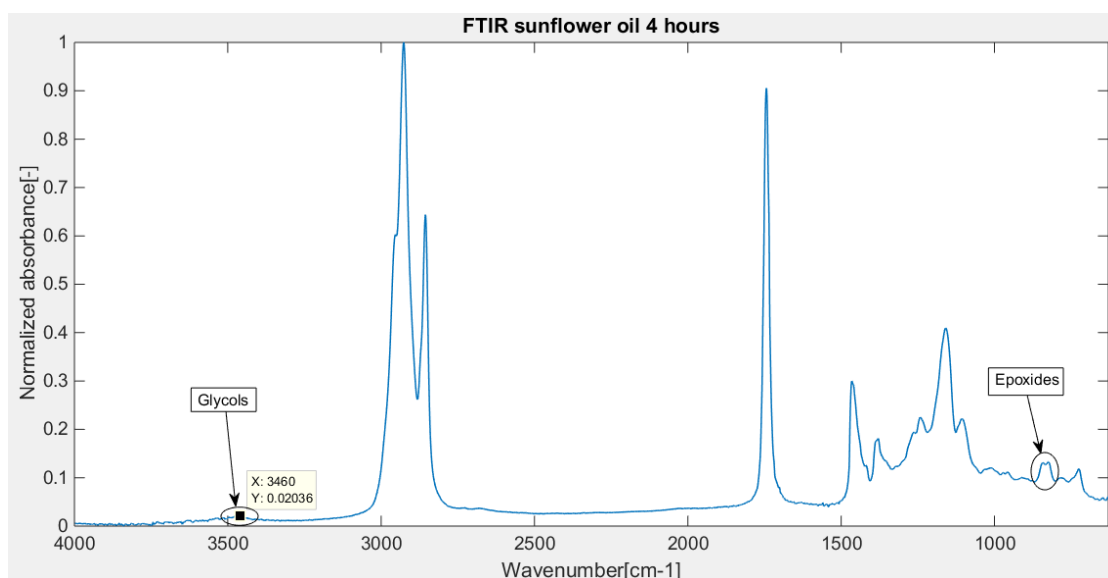

Figure 4.12 *FTIR spectrum of sunflower oil. Process carried for 4 hours at 600 rpm*
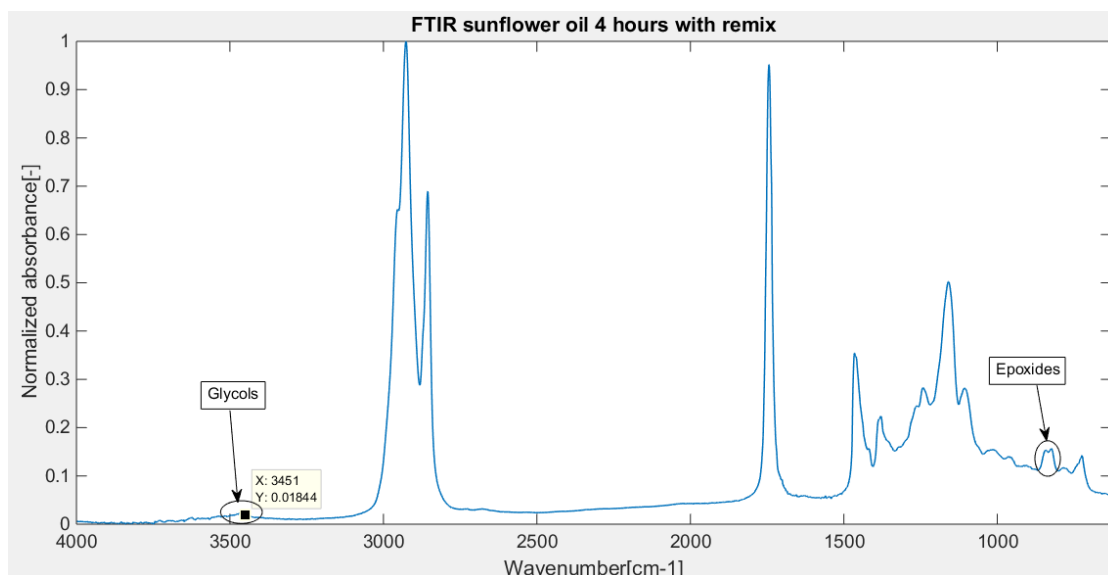
Figure 4.13 *FTIR spectrum of sunflower oil. Process carried for 4 hours with a mixing program*

In both the graphs there are not the double bonds C = C, that means that almost all the double carbon-carbon bonds have reacted. In both cases there is a peak related to epoxides, this means that the products obtained are almost all epoxides. The conversion is almost 100% in both case. Moreover it is possible to note that in both cases there is a very few amount of glycols, in the case of remixing there is a slightly lower quantity because as previously mentioned the remixing accelerates the epoxidation reaction.

Since the conversion is close to 100%, the selectivity through the formula(4.1) it is possible to calculate.

For a epoxidation without remixing : high of OH peak of sunflower oil is 0.020 and the high OH peak reference is like before 0.9689 and so the selectivity is equal to 97.9%.

For a epoxidation with remixing instead : high of OH peak of sunflower oil is 0.0184, high OH peak reference is like before 0.9689 and so the selectivity is equal to 98.11%.

4.2.2 Epoxidation for 5 hours: thermal profile and effect of mixing program ,FTIR analysis

In figure 4.14 and 4.15 the thermal profiles for what concerns epoxidation of sunflower oil at 5 hours with and without remix have been reported.
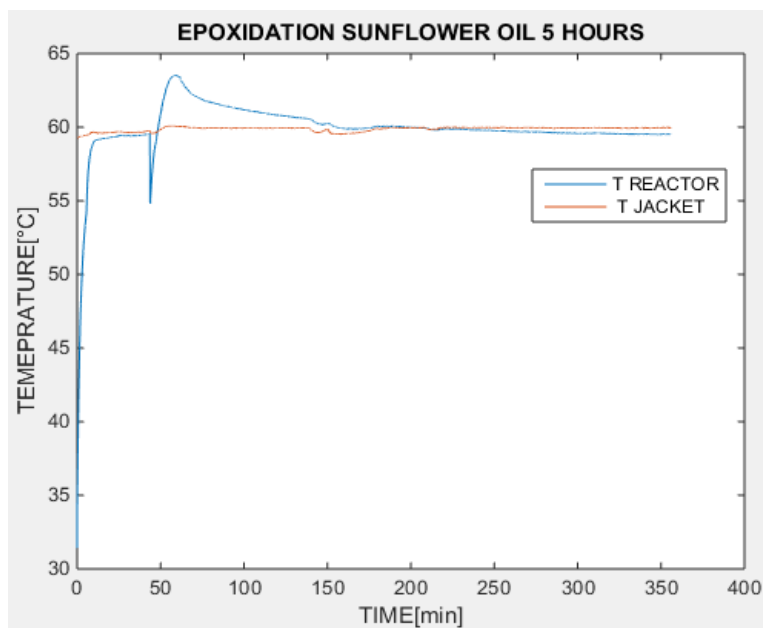
Figure 4.14 *Thermal profile (temperature vs time) sunflower oil for a reaction of epoxidation conducted for 5 hours, with a velocity of the impeller of 600 rpm*
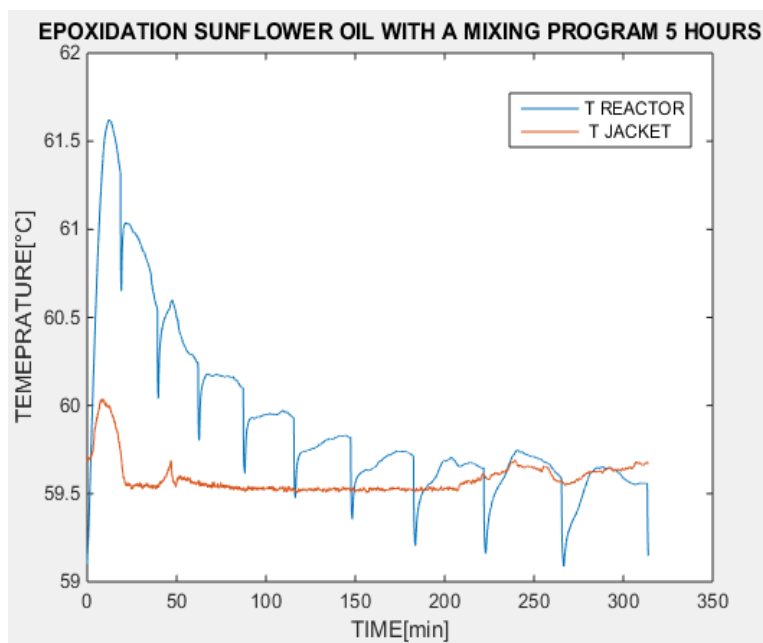
Figure 4.15 *Thermal profile (temperature vs time) sunflower oil for reaction of epoxidation with a mixing program for 5 hours*

Even in this case here there is a large overshoot it is possible to see in figure 4.14. The thermal profile confirms the exothermic character of the reaction and in both case there is a peak about 62- 63°C. With the remix even here it is possible to note that the temperature decrease suddenly because the heat exchange coefficient increase. Now below the results of the FTIR analysis have been reported.
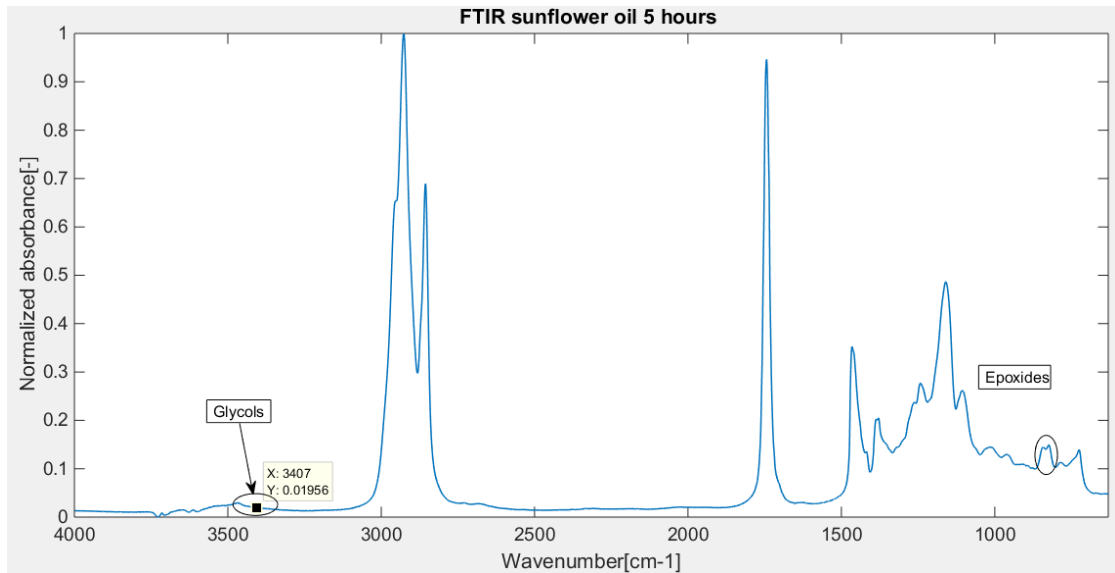
Figure 4.16 *FTIR spectrum of sunflower oil. Process carried for 5 hours at 600 rpm*

Figure 4.17 *FTIR spectrum of sunflower oil. Process carried for 5 hours with a mixing program*

From both figures we see that the conversion is close to 100%.

The reaction of epoxidation occurred because we have a peak of epoxides. The quantity of glycols is really low, it is lower in the epoxidation with remix than epoxidation without remix. There are no presence of double bonds C=C, and so means that the double bonds have reacted all. Since the conversion is near 100% like it has been seen also from the thermal profile, the selectivity through the formula (4.1) in both case it is possible to calculate.
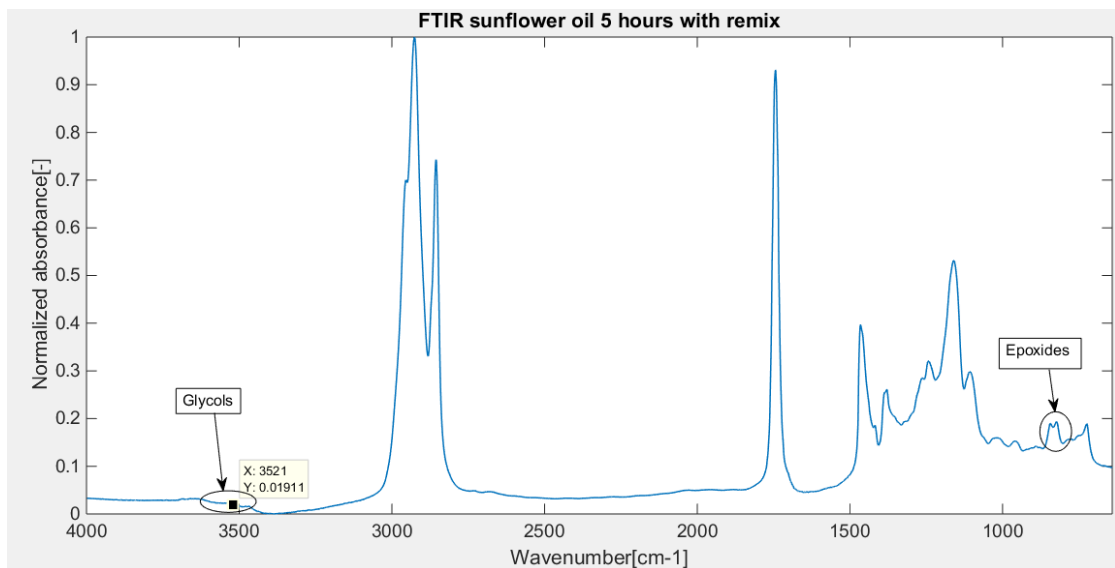
For the epoxidation without remix : high of OH peak is 0.0195, high OH peak reference is like before 0.9689 and so the selectivity is equal to 97.89%. For the epoxidation with remix instead: high of OH peak is 0.0191, , high OH peak reference is 0.9689, and the selectivity is 98.03%.

Table 4.2 *Values of conversion, selectivity and amount of glycols for the epoxidation of the sunflower oil both with remixing and without remixing at 4 and 5 hours*

	Sunflower oil reaction for 4 hours without remixing	**Sunflower oil reaction for 4 hours with remixing**	**Sunflower oil reaction for 5 hours without remixing**	**Sunflower oil reaction for 5 hours with remixing**
Conversion	≈ 100%	≈ 100%	≈ 100%	≈ 100%
Selectivity	97.89%	98.11%	97.99%	98.03%
Amount of glycols	2.11%	1.89%	2.01%	1.97%

From the table it is possible to note that even in this case, remix gives advantages than reaction without remix, this because in the case with remix both for 4 hours as well as 5 hours there is less amount of glycols and a greater value of selectivity. Anyway it is possible to note the reaction with the highest selectivity is that carried out for 4 hours with a remix, so it means that it takes 4 hours for the reaction to complete, after this time the epoxy ring starts to break and unwanted products start to form. The same result has been obtained even with the soybean oil. Considering instead the reaction without remix, it is possible to note that that an increase in time could favour the complete reaction, this does not apply in the case of remixes as seen in advance because the remix allows to take unreacted oil and to introduce it in the aqueous phase to make it regiare, and therefore 4 hours are enough. Anyway it is important to say that the value obtained of the selectivity are very similar among them.

4.3 Epoxidation with rapeseed oil

Also in this case, as was done with sunflower and colza previously, the following portions and quantities have been used: acetic acid: double bonds molar ratio is equal to 0.5:1 and hydrogen peroxide: double bonds is equal to 1.5:1. 100 gr of sunflower oil, 16.74 gr of acetic acid, 88.82 gr of hydrogen peroxide and at the same time 3 gr of acid sulphuric have been added.

4.3.1 Epoxidation for 4 hours: thermal profile and effect of mixing program ,FTIR analysis

In figure 4.18 and 4.19 the graphics of the thermal profile without remix and with remix respectively have been reported;

Figure 4.18 *Thermal profile (temperature vs time) rapeseed oil for a reaction of epoxidation conducted for 4 hours, with a velocity of the impeller of 600 rpm.*

Figure 4.19 *Thermal profile (temperature vs time) rapeseed oil for reaction of epoxidation with a mixing program for 4 hours*

As for the other thermal profiles of rapeseed and sunflower at 4 hours, also here we see a conversion close to 100%. The graph 4.18 without remixes shows has a maximum peak at 64.5 ° C, while the remix has a lower peak at about 62 ° C.

The exothermic behavior of the reactions is represented from the peak of the temperatures.

Also in this case the considerations made previously with the other oils are valid.

Now the results of the FTIR analysis, have been reported in figure 4.20 and 4.21

Figure 4.20 *FTIR spectrum of rapeseed oil. Process carried out for 4 hours at 600 rpm*
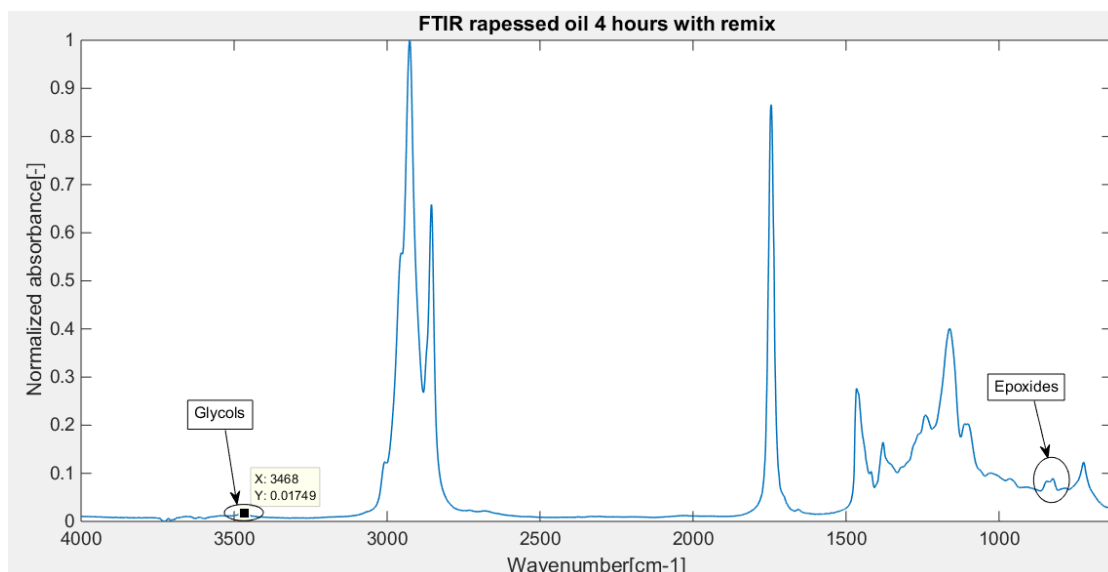
Figure 4.21 *FTIR spectrum of rapeseed oil. Process carried for 4 hours with a mixing program*

How it is possible to see from the graphs above, the reaction of epoxidation occurred.

number of glycols is very low in both case, and the peak of C=C is absent, and this means that a big amount of double bonds C=C has reacted . There are epoxides, and this confirm both the character exothermic of the reaction, and also that the reaction occurred,. The conversion is close of 100% and the selectivity has been calculated with the same formula used before.

For the epoxidation without remix : high of OH peak is 0.025, high OH peak reference is like before 0.9689 and so the selectivity is equal to 97.42%;

For the epoxidation with remix on the contrary : high of OH peak is 0.0174, high OH peak reference is like before 0.9689 and so the selectivity is equal to 98.21%.

4.3.2 Epoxidation for 5 hours: thermal profile and effect of mixing program ,FTIR analysis

In figure 4.22 and 4.23 the thermal profiles for what concerns epoxidation of rapeseed oil at 5 hours and without remix have been reported:
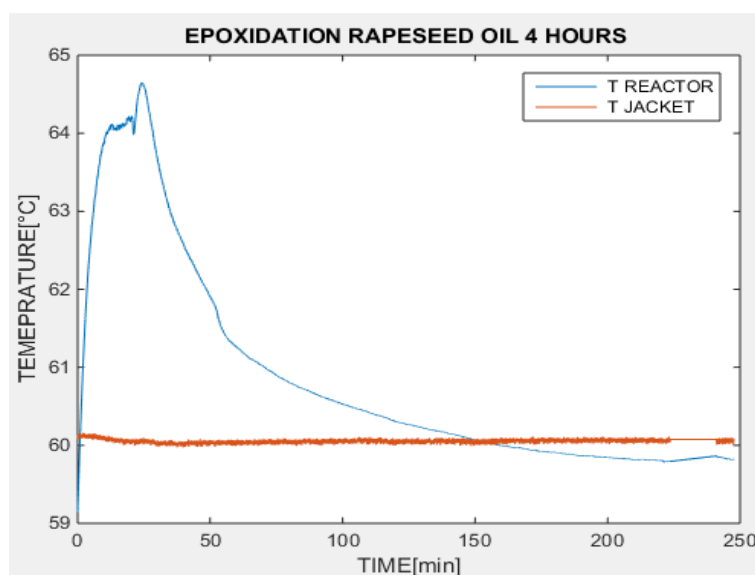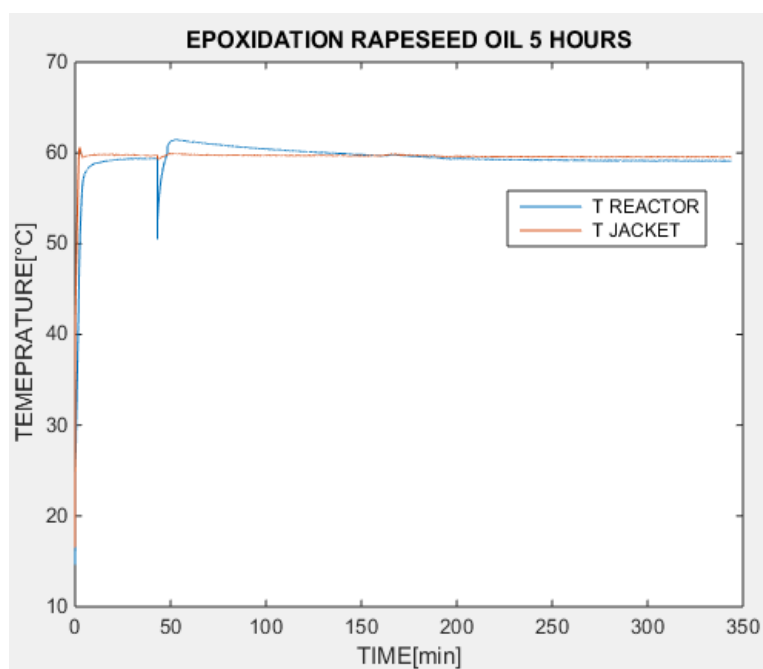
Figure 4.22 *Thermal profile (temperature vs time) rapeseed oil for a reaction of epoxidation conducted for 5 hours, with a velocity of the impeller of 600 rpm*
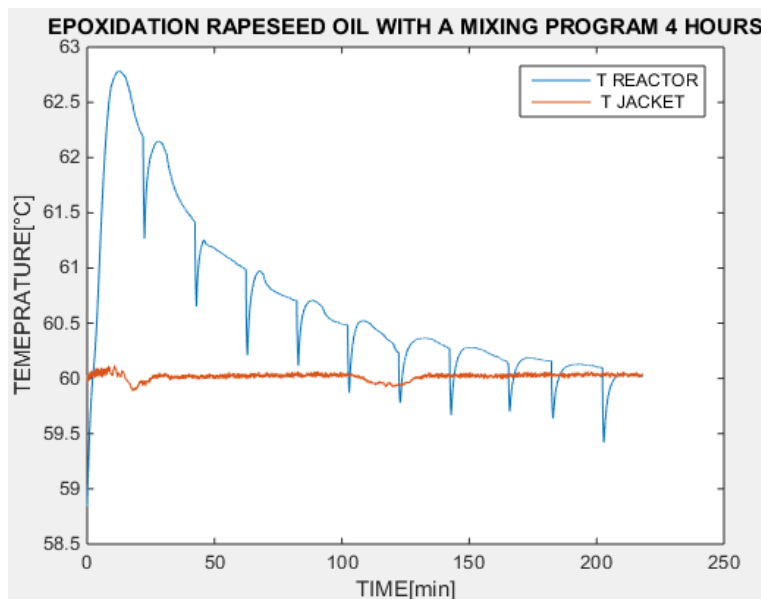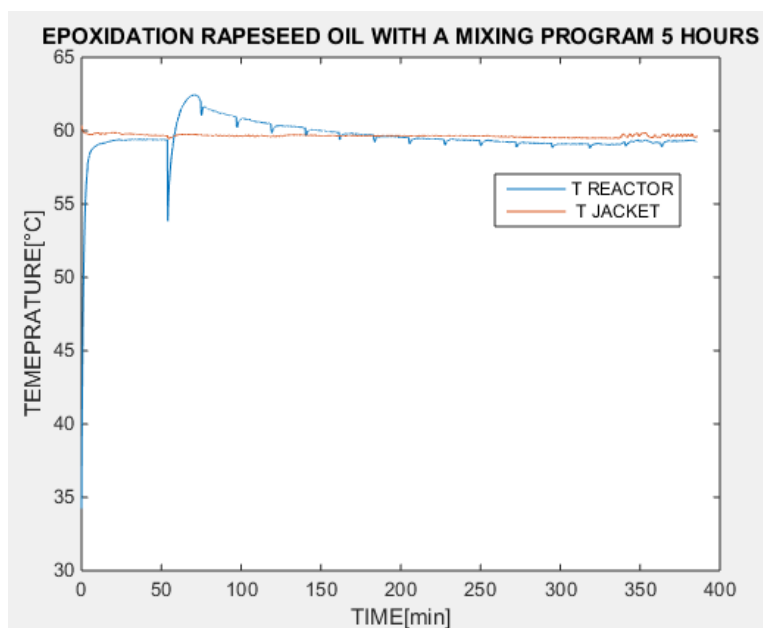

Figure 4.23 *Thermal profile (temperature vs time) rapeseed oil for reaction of epoxidation with a mixing program for 5 hours*

From the thermal profiles it is possible to note that the reaction of epoxidation occurred, and this is confirmed from the presence of the big overshoot that also highlights the character exothermic of the reaction. Also in this case with remix the temperature decrease as time increase, for the same considerations done for the previously oils. The conversion is near 100% in both case. The results of the FTIR analysis both the reaction without remix and the reaction with remix have been reported in figure 4.24 and 4.25 respectively:
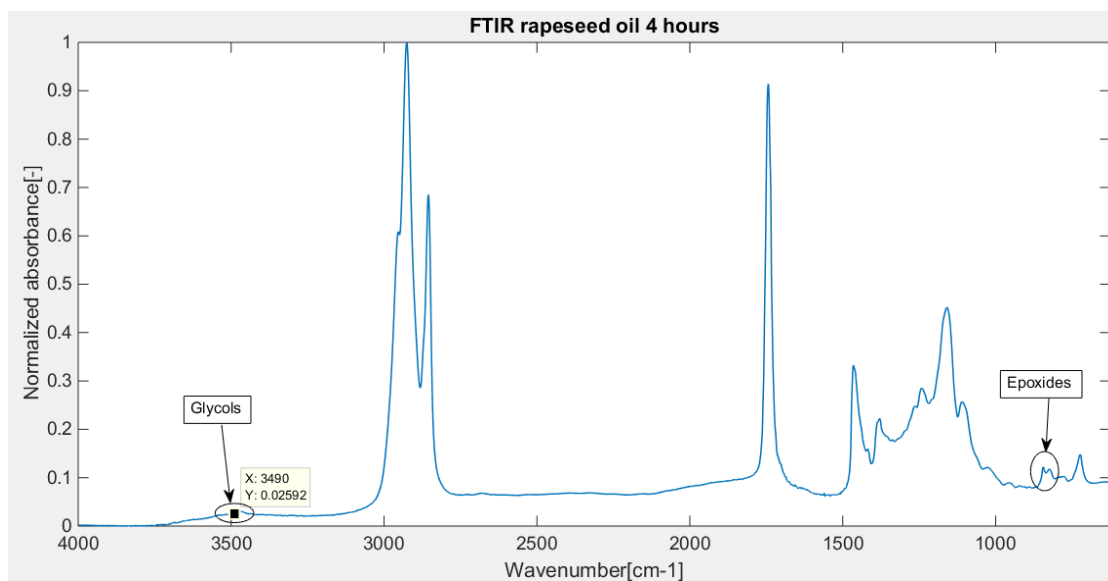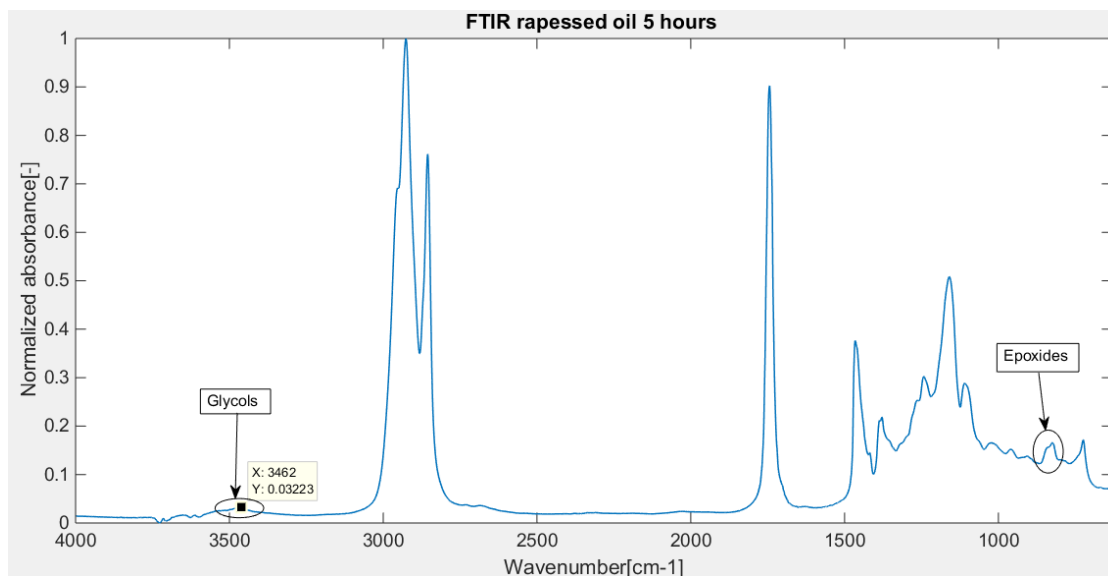

Figure 4.24 *FTIR spectrum of rapeseed oil. Process carried for 5 hours at 600 rpm*
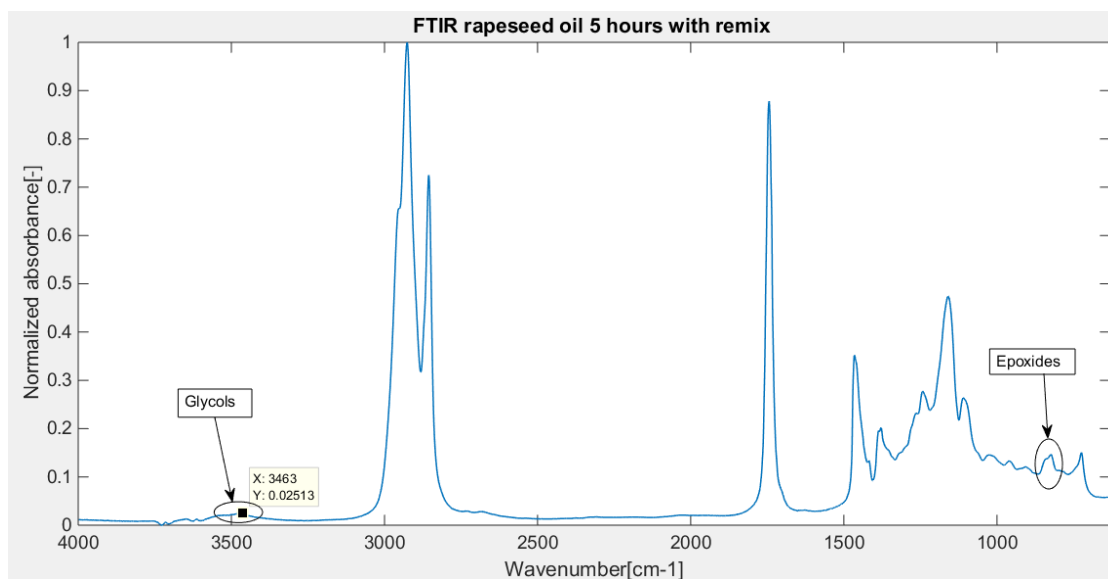
Figure 4.25 *FTIR spectrum of rapeseed oil. Process carried for 5 hours with a mixing program*

Also here like the other case that have been seen previously, the reaction of epoxidation has occurred, and this is confirmed from the presence of the peak of the epoxides. There are no double bonds C=C, and so means that the big amount of double bonds has reacted. The glycols are present in traces, with a peak in the case of without remix higher than case with remix, and this depends on the fact that the remix accelerates the speed of the reaction. Being the conversion near to 100% it is possible to calculate the selectivity.

For the reaction without remix : high of OH peak is 0.032, instead for high OH peak reference we have 0.9689, and so the selectivity is equal to 96.7%.

For the reaction with remix instead : high of OH peak is 0.0251, high of OH peak reference is 0.9689, and the selectivity is 97.49%.

Table 4.3 *Values of conversion, selectivity and amount of glycols for the epoxidation of the rapeseed oil both with remixing and without remixing at 4 and 5 hours*

|	Rapeseed oil reaction for 4 hours without remixing	Rapeseed oil reaction for 4 hours with remixing	Rapeseed oil reaction for 5 hours without remixing	Rapeseed oil reaction for 5 hours with remixing
Conversion	$\approx 100\%$	$\approx 100\%$	$\approx 100\%$	$\approx 100\%$
Selectivity	97.42%	98.21%	96.70%	97.49%
Amount of glycols	2.58%	1.79%	3.30%	2.51%

From the table it is possible to note that with remix a little improvements exists, because there is a greater value of selectivity and a less amount of glycols. An important thing that it is possible to evaluate from this analysis is that for what concerns rapeseed oil increasing the time of the reactions it verifies a little worsening (this before it was right only for the reaction carried out with remix), because the selectivity decreases, and amount of glycols increase than reaction carried out at 4 hours. So this means that as far as rapeseed oil is concerned an increase in reaction time could lead to epoxide opening and therefore could create side reactions, for this reason there is a greater quantity of glycols than the reaction carried out at 4 hours. Also in this case the reaction that has the highest selectivity is that with the 4-hour remix, but the difference lies in the fact that before considering the reaction without remixes there was an improvement in selectivity increasing the time(even if little enough), now instead an increase in the time of reaction leads to a change in selectivity both without remixes and with remixes. From the general analysis is possible to see that more or less all oils have the same values of selectivity and amount of glycols. Therefore, going specifically, it is noted that sunflower oil and soybean oil are the oils with higher selectivity value and

consequently the lowest glycol value on average, this it can be explained considering the iodine number(that is the number of double bonds that an oil contains), that is similar both sunflower oil as well as soybean oil. Instead rapeseed oil has the lowest average value of selectivity because its iodium number (111) is low if it is compared with those of the others oils, and therefore it contains a smaller amount of double bonds and therefore a lower possibility of forming epoxides than the other two oils.

4.4 Estimation of heat of reaction for soybean oil , sunflower oil rapeseed oil, without and with remixing, at 4 hours and 5 hours

Since the exchange coefficient has been calculated previously through formula(§3.4),now it is possible to calculate the heat of reaction thorough the follow formula 4.2.

$$Q = \frac{(U*A)*A}{number\ of\ double\ bonds}$$ (4.2)

Where:

U*A= global exchange coefficient [W/°K]
A= area under the curve delimited by the baseline [°K*s];
Number of double bonds has been calculated using the follow formula 4.3

$$number\ of\ double\ bonds = \frac{number\ of\ iodium}{2*moleocular\ weights\ of\ iodium}$$ (4.3)

To calculate the area under the curve, the method of trapezoids in *Matlab* has been used . The temperature profile is integrated once the steady state temperature is subtracted, the integration is performed from the instant 0 to the end of the reaction (4 hours and 5 hours). It is calculated the area under the curve bounded by baseline. The baseline is taken as reference because there are some dispersions the T_{reac} drops slightly below the $T_{jack.}$ Multiplying the latter for the global heat exchange, the heat remixed by the reaction (because exothermic reaction) in KJ has been obtained; finally dividing the heat into kJ by the number of moles of double bonds, the heat released by the reaction according to the number of moles of double bonds of the specific oil has been obtained. In the following table are shown the heat of reaction values for each oil both at 4 hours both without remix and with remix.
Only 4-hour values are considered because the reaction is assumed to have been almost completely after a time equal to 4 hours.

Table 4.4 *Heat of reaction for soybean oil with and without remixing at 4 hours*

	U*A[W/°K]	A [°K*s]	Number of double bonds	Heat of reaction [KJ/mol]
Soybean oil (4 hours without remix)	6.85	18594	0.50	-254.79
Soybean oil (4 hours with remix)	6.85	19449	0.50	-266.45

Table 4.5 *Heat of reaction for sunflower oil with and without remixing at 4 hours*

	U*A[W/°K]	A [°K*s]	Number of double bonds	Heat of reaction [KJ/mol]
Sunflower oil (4 hours without remix)	8.74	11611	0.48	-211.41
Sunflower oil (4 hours with remix)	8.74	12132	0.48	-220.92

Table 4.6 *Heat of reaction for rapeseed oil with and without remixing at 4 hours*

	U*A[W/°K]	A [°K*s]	Number of double bonds	Heat of reaction [KJ/mol]
Rapeseed oil (4 hours without remix)	8.14	14853	0.44	-274.79
Rapeseed oil (4 hours with remix)	8.14	16734	0.44	-309.59

From the results obtained through the 4-hour epoxidation, it is possible deduce that for all three oils the exothermic condition has been respected. Specifically, both for all three oils soybean oil and sunflower oil and rapeseed oil, there is a small increase in heat of reaction due to remix, because with remixing program the turbulence is increase and so the heat exchange improves. The heats of reaction are comparable with the data proposed in the literature, equal to -240KJ -260KJ. As you can see the values between the reaction with the remix and without remixes are very similar, this result is right. The most exothermic reaction has been found to be that conducted with rapeseed oil without remixes, probably this result is due to the structures of the fatty acid molecules that compose it. The least exothermic one is that conducted with the sunflower oil and the reason probably due to the above explanation.

4.5 Estimation of % epoxy oxygen, estimation of theoretical maximum epoxy Oxygen, and yield calculation, for soybean oil, sunflower oil, rapeseed oil, without and with remixing, at 4 hours and 5 hours

Through the titration of epoxidized oil the % of epoxy oxygen has been calculated, that is, the mass fraction of oxygen present in the epoxides than to the total amount of oxygen present in the epoxidized oil. The percentage of epoxidized oil has been calculated using the follow formula:

$$Oepox = \frac{Veq*N*1.60}{m\ epoxidized\ oil} \qquad\qquad (4.4)$$

Where :

1.60= multiplicative factor;

Veq = remaining volume of the bromidric acid in acetic acid solution in the burette;

N= Normality of the bromidric acid solution in acetic acid, that we have calculated using the follow formula:

$$N = \frac{potassium\ acid\ phthalate\ mass}{0.2042*Veq} \qquad\qquad (4.5)$$

So using the formula (4.4) the percentage of oxygen contained in epoxides for all three oils both at 4 hours and at 5 hours , with and without remix has been calculated. The values are reported in the following tables:

Table 4.7 % epoxidized oxygen with regard to soybean oil at 4 hours and 5 hours, both with remixing and without remixing

	Veq(ml)	Normality	Mass oil epoxidized	%Oepox
Soybean oil (4 hours without remixing)	10.60	0.11	0.30	6.53
Soybean oil(4 hours with remixing)	11.50	0.11	0.30	6.85
Soybean oil(5 hours without remixing)	12.55	0.10	0.32	6.54
Soybean oil (5 hours with remixing)	14.20	0.09	0.31	6.56

Table 4.8 *% epoxidized oxygen with regard to sunflower oil at 4 hours and 5 hours, both with remixing and without remixing*

	Veq(ml)	Normality	Mass oil epoxidized	%Oepox
Sunflower oil (4 hours without remixing)	11.10	0.11	0.31	6.39
Sunflower oil(4 hours with remixing)	11.25	0.11	0.31	6.50
Sunflower oil(5 hours without remixing)	12.75	0.10	0.33	6.42
Sunflower oil (5 hours with remixing)	12.00	0.10	0.30	6.47

Table 4.9 *% epoxidized oxygen with regard to Rapeseed oil oil at 4 hours and 5 hours, both with remixing and without remixing*

	Veq(ml)	Normality	Mass oil epoxidized	%Oepox
Rapeseed oil (4 hours without remixing)	11.20	0.11	0.31	6.41
Rapeseed oil(4 hours with remixing)	10.50	0.11	0.32	5.98
Rapeseed oil(5 hours without remixing)	11.75	0.11	0.35	5.97
Rapeseed oil (5 hours with remixing)	9.30	0.12	0.32	5.91

Now knowing the % of epoxy oxygen the theoretical maximum epoxy oxygen% and consequently the yield with can be calculated through the following formula:

$$Yield = \frac{Oepox}{Opeox\ max.theo.} * 100 \tag{4.6}$$

To calculate the theoretical maximum epoxy oxygen the formula 4.7 has been used

$$Oepox\ max.theo. = \left(\frac{\left(\frac{number\ of\ iodium}{2*molecoular\ weights\ iodium}\right)*molecular\ weights\ oxygen}{100+\left(\frac{number\ of\ iodium}{2*molecular\ weights\ iodium}\right)*moleculare\ wights\ oxygen} \right) * 100 \tag{4.7}$$

The following tables are shown below.

Table 4.10 *% O epoxidized maximum theoretical for soybean oil, sunflower oil, rapeseed oil*

	%O epox. Maximum theoretical
Soybean oil	7.40
Sunflower oil	7.13
Rapeseed oil	6.53

Table 4.11 *% Yield for soybean oil at 4 hours and 5 hours with remixing and without remixing*

	Yield %
Soybean oil (4 hours without remixing)	88.24
Soybean oil (4 hours with remixing)	92.56
Soybean oil (5 hours without remixing)	88.37
Soybean oil (5 hours with remixing)	88.64

Table 4.12 *% Yield for sunflower oil at 4 hours and 5 hours with remixing and without remixing*

	Yield
Sunflower oil (4 hours without remixing)	89.62
Sunflower oil (4 hours with remixing)	91.16
Sunflower oil (5 hours without remixing)	90.04
Sunflower oil (5 hours with remixing)	90.74

Table 4.13 *% Yield for rapeseed oil at 4 hours and 5 hours with remixing and without remixing*

	Yield
Rapeseed oil (4 hours without remixing)	98.16
Rapeseed oil (4 hours with remixing)	91.57
Rapeseed oil (5 hours without remixing)	91.42
Rapeseed oil (5 hours with remixing)	90.50

Analyzing the yields obtained for the various oils at both 4 and 5 hours, it is possible to note that both for soybean oil and sunflower oil there is an improvement in yield in the case of reaction carried out with remixes, and this can be noticed both in the case of 4 hours and 5 hours. It is noted that the maximum yield for both oils is in the case of a reaction carried out for 4 hours with remixes. These data confirm the previously calculated selectivity data, this means that a time equal to 4 hours is required for the reaction to be complete, ie after this time the epoxy ring may break and could lead to the formation of undesired products. As far as the rapeseed oil is concerned, it has been obtained that the reaction with the greatest yield is that conducted without remixes for 4 hours; these results disagree with those obtained previously in the calculation of selectivity, moreover the yield decrease increasing the speed impeller both at 4 hours as well as at 5 hours, for this reason the future studies will be aimed at understanding and analyzing the behavior of rapeseed oil.

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Conclusions

In this work the epoxidation reaction was carried out using three different oils: soybean oil, sunflower oil and rapeseed oil. This reaction has been carried out in a jacketed stirred calorimetric reactor, using acetic acid, and sulfuric acid. The process involves the production of peracetic acid as an intermediate that epoxidises the double bonds of the virgin oil. Before getting to study the epoxidation reaction however, other studies have been made. Firstly the composition of the different oils has been studied, which will then affect the exothermic nature of the reactions, then the physical properties have been studied, which were fundamental to understand the meaning of the different value of the global coefficients of exchange, and therefore both the thermal capacity (m * cp) and the cooling time (τ). After that, the epoxidation reaction was studied, and in particular the conventional method used in this thesis. The first tests concerns the calibration. These tests were used to calculate from the cooling transient (τ) ,which represents the necessary time so that the thermal transient is exhausted and the from the stationary state (U * A), which indicates the global heat transfer coefficient. Knowing these two values, it has been possible to calculate the thermal capacity of the mixture inside the reactor, ie the quantity of heat exchanged as a function of the temperature variation. Calibration was performed for all three oils at both 600 rpm and 1500 rpm . The calibration was performed using a solution of acetic acid 98%, 34% hydrogen peroxide and in the first case soybean oil, in the second case sunflower oil and in the third case rapeseed oil. The power was supplied inside the reactor thanks to an automatic power controller designed and built *ad hoc.*

From the study carried out with an impeller speed of 600 rpm, it has been deduced that the oil which has an higher global heat exchange coefficient and therefore a greater thermal capacity is sunflower oil. This can also be deduced by calculating the dimensionless numbers that characterize the global heat exchange coefficient. Sunflower oil according the literature has the largest number of Prandtl therefore is that which gives a better heat exchange by convection, and it is the one that after having calculated the number of Reynolds and the number of Nusselt has the highest value of the global coefficient of heat exchange. In addition at 600 rpm, sunflower oil has the fastest cooling time. At 600 rpm the oil with the worst characteristics is soybean oil which is the less viscous but at the same time it is the heaviest the heaviest oil and so it has the largest number of Reynolds and the lowest Prandtl number, and consequently it has the lowest value of the global exchange coefficient.

By increasing the impeller speed up to 1500 rpm different results have been obtained. For all three oils, an increase of the global exchange coefficient has been noticed, this because increasing the speed of the impeller, the exchange improves. It can be concluded by saying.

that the increase in the impeller speed has brought great benefits to soybean oil, since the difference between the heat exchanged at 600 rpm and 1500 rpm is considerable.

After having calculated the global exchange coefficient and the heat capacity, the epoxidation reaction was performed. The latter has been carried out using acetic acid as carboxylic acid and not formic acid, because acetic acid is less aggressive but at the same time less reactive. Hydrogen peroxide at 34% has been used instead of 60% to prevent runway reactions. First of all, the reaction was carried out by setting the impeller rotation speed to 600 rpm. The thermal profiles were obtained as a function of the time which showed the exothermic behavior of the reaction, as each reaction was accompanied by a temperature peak above 60 ° C. For each oil the FTIR analysis has been carried out , and thanks to this it has been possible to see the reaction status. In other words, thanks to FTIR, it was possible to see the quantity of epoxides, the quantity of C = C and the quantity of glycols. (It must be said that FTIR analysis does not offer a high degree of accuracy). The epoxidation reaction has carried out after with the remix, ie every 20 minutes the impeller speed changed from 600 rpm to 1500 rpm for 30 seconds. The remix was carried out both because this increases the speed of the reaction, and because it reduces the quantity of glycols, since the amount of unreacted oil is taken from the impeller and put into the aqueous solution. Also in this case both FITR analyzes and the selectivity calculation for all three oils were carried out. The results showed that in all three oils the remix brings advantages, as it has been possible to see a decrease in the number of glycols and an increase in selectivity. Both for soybean oil and sunflower oil, the highest value of selectivity there has been obtained in the case of reaction carried out for 4 hours with the remix. This means that the reaction needs a time equal to 4 hours to complete. After 4 hours, the epoxy ring may break and glycol formation may occur. Analyzing the case without remix always for soybean oil and sunflower oil, it is denoted that an increase in reaction time helps the reaction to reach complete conversion (even if the difference between the tests without remix at 4 hours and those without remix at 5-hour are minimal). The tests carried out on rapeseed oil have also shown for this last one greater selectivity in the case of reaction conducted for 4 hours with the remix. In this case, unlike the previous one, an increase in the reaction time even in the case of a reaction carried out without remix leads to a decrease in selectivity, then leads to ring rupture and a greater quantity of glycols. At the end it can be deduced that for all three oils the reaction which has a higher selectivity is that conducted for 4 hours without remixes. Considering the situation without remixes, both for soybeans and sunflowers there is an increase in selectivity increasing the reaction time (even if minimal), for rapeseed oil instead this leads to a decrease in selectivity. After calculating the selectivity, the ΔH of the reaction has been calculated, thanks to the calculation of the

global exchange coefficient calculated by calibration. This calculation was carried out only in the case of a 4-hour, because it was assumed that 4 hours is a time necessary to have a ≈100% conversion. The obtained values confirmed the exothermicity of the reactions. The values obtained both with the remix and without remixes are similar for the different oils, and this result is right, the differences are due to heat loss during the reactions. The most exothermic reaction is that of rapeseed oil at 4 hours with remixing, this result is probably due to the structure of the fatty acids that compose it. The one that is less exothermic is that of sunflower oil both with remix and without remix, and probably the explanation is due to the one mentioned above.

The reaction that most closely approximates the experimental value of ΔH is that conducted with soybean oil. Hence it is deduced that probably the best reaction is that conducted with soybean oil. After calculating the ΔH of the reaction, thanks to the titration of epoxidized oil, % of epoxy oxygen has been calcuted. This would be the % of oxygen contained in the epoxy than the amount of oxygen contained in the epoxidized oil. Titration was performed using bromidric acid in acetic acid, epoxidized oil and (crystal violet). Before making the titration the normality of the solution of bromidric acid has been calculated. Thanks to the % epoxy oxygen, it was calculated after the theoretical maximum % of epoxy oxygen and finally the reaction yield has been calculated. From the calculation of the latter it has been seen that both for soybean oil and sunflower oil there is an improvement in yield in the case of reaction carried out with remixes. It is noticed that the maximum yield values for both soybean oil and sunflower oil occur in the case of reaction with remixing conducted for 4 hours, (this confirms the results obtained from the selectivity calculated previously).Consequently it takes 4 hours for has a greater conversion of the reagents into the desired product, because as the yield increases, the amount of unreacted double bonds decreases and the purity of the epoxidized oil increases. For rapeseed oil, on the other hand, the greatest yield is in the case of a reaction carried out for 4 hours without remixes, and this is in contrast with the previously calculated selectivity data, for these reasons subsequent studies will be carried out to study the behavior of the rapeseed oil.

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