

University of Southern Queensland  
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## **Epoxidised Resins from Natural Renewable Resources**

A dissertation submitted by

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In fulfilment of the requirements of

**Bachelor of Engineering (Mechanical)**

**October 2009**

## Abstract

This research was based on the premise that vegetable oils may present a viable alternative to petrochemical feedstocks for the creation of epoxy resins. Vegetable oils are a natural and renewable product in an age of dwindling fossil oil reserves and growing demand from the energy and materials sectors. Vegetable oils present as likely candidates for conversion into polymeric materials because of their molecular structure. They already contain the long carbon chains that define polymeric materials, as well as carbon to carbon double bonds which can be converted to functional groups through chemical synthesis.

For this research locally sourced vegetable oils high in unsaturated fatty acids such as oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) were epoxidised with peroxyacetic acid formed *in situ* by the reaction of aqueous hydrogen peroxide and acetic acid in the presence of an acidic ion exchange resin as catalyst. The reaction was carried out in a constantly stirred batch reactor, stirred with a low profile ship's anchor stirrer. A number of parameters were examined including: (1) the molar ratios of ethylenic unsaturation to acetic acid to hydrogen peroxide, (2) the amount of catalyst loading, (3) the steady state operating temperature of the reactor, (4) the time required to achieve maximum carbon to carbon double bond consumption, (5) the time required to achieve maximum oxirane group formation. Results of epoxidation were examined using Fourier Transform Infrared Spectroscopy and the titration methods for determining iodine value and oxirane-group oxygen content.

Initial testing was conducted on linseed oil, sunflower oil and mutton tallow, but it was decided that locally sourced hemp oil would become the primary focus of this research. This was because hemp oil is high in saturated fatty acids, and there appeared to be little in the existing literature regarding the epoxidation of hemp oil. It was found that optimum processing conditions for hemp oil existed at:

**Molar ratio:** Hemp oil (1.0 mole of double bonds) : Acetic acid (0.67 moles) : H<sub>2</sub>O<sub>2</sub> (1.0 moles)

**Catalyst loading:** 15 wt% of hemp oil

**Reaction time:** 7 hours

**Reaction temperature:** 75°C

At these conditions an 88% conversion of double bonds to epoxy groups was found to occur. This result was comparable to the results of other authors conducting similar research.

## Acknowledgements

I would like to thank my supervisors Dr Hao Wang and Dr Francisco Cardona for their invaluable support and assistance during this research, the CEEFC for allowing me access to such wonderful resources and equipment and the staff of the CEEFC who made me feel very welcome.

I would also like to extend a special mention to Mr. Kim Larsen from the faculty of sciences who gave his time and knowledge freely to help me with some difficult topics.

Last but not least I would like to thank my wife Bobbi who was understanding and supportive when the demands of an honours thesis seemed all too much.

**University of Southern Queensland**

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**ENG4111 Research Project Part 1 &**

**ENG4112 Research Project Part 2**

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## Nomenclature

AA = Acetic Acid

$A_i$  = Atomic weight of iodine

$A_o$  = Atomic weight of oxygen

DB = carbon to carbon double covalent bond

EHO = Epoxidised hemp oil

ELO = Epoxidised linseed oil

ESFO = Epoxidised sunflower oil

EVO = Epoxidised vegetable oil

FTIR = Fourier Transform Infrared Spectroscopy

$H_2O_2$  = Hydrogen peroxide

HO = Hemp oil

$IV_o$  = Initial iodine value, (g of  $I_2$ / 100 g sample)

$IV_f$  = Final iodine value, (g of  $I_2$ / 100 g sample)

LO = Linseed oil

$OO_e$  = experimentally obtained oxirane oxygen, (g / 100 g sample)

$OO_t$  = theoretically obtainable maximum oxirane oxygen, (g / 100 g sample)

SFO = Sunflower oil

T = Normality

TAG = Triglyceride oil

VO = Vegetable oil

# 1 Introduction

## 1.1 Aims

The aim of the project is to investigate the synthesis of polymer resins from natural renewable resources, namely vegetable oils. Although there are a great many types of polymer resin, this research will focus on the process of epoxidation. Once the method and process parameters have been identified and comprehended, then the optimum conditions will be determined. The majority of the research will concentrate on hemp oil, which is under-represented in the literature. Laboratory experimentation and analysis, backed up by a literature research will constitute the majority of the work.

## 1.2 Objectives

Currently it is foreseeable that the research will be broken up into three categories, these being pre-synthesis, synthesis and post synthesis. Each of these can in turn be broken down into two categories, literature review and laboratory work.

### **Pre-synthesis**

There currently exists a large amount of literature concerning the process of converting vegetable oils into polymer resins, especially epoxy resins. This literature will be reviewed to determine:

- What processes currently exist
- Which process is suitable to this research
- What chemicals are used and at what concentrations
- Why are vegetable oils suitable candidates for this research
- What are the properties of vegetable oils
- Which vegetable oils have been examined

Laboratory work will include:

- Measurement and preparation of the raw materials and chemicals

## Synthesis

From the literature:

- What process parameters are used, including temperature, time and stirring speed
- How does the epoxidation process work

Laboratory work:

- Determine how the reactor and software work

## Post-Synthesis

- Wash and dry the resin and prepare for testing
- Analyse the samples with Fourier Transform Infrared Spectroscopy and the titration methods for determining the iodine value and oxirane oxygen content
- The chemical structure and characteristics of the epoxy resin
- How does the resin compare with resin made using different process parameters

It should be noted that the last point provides information that can lead back to the pre-synthesis stage, indicating that the overall process, by nature, has an iterative element or trial and error approach, while still being guided by the theory.

## 1.3 General background

Petrochemical feedstocks currently dominate the polymeric materials industry. There is growing uncertainty about the long term sustainability of these resources, and mounting concerns over the possible environmental impacts that are attributed to their use. As a result opportunities have arisen to explore the development of more environmentally friendly and sustainable alternatives.

One arena that is currently receiving considerable attention is the synthesis of polymer resins from triglyceride oils (TAG), specifically the type derived from vegetable oils (VO). As of 2002 the manufacture of plastics consumed 7% of all worldwide oil and gas produced. These fossil fuel feedstocks are limited and non-renewable, with claims that we are only decades away from peak global oil production. Indeed, some observers claim that we have already reached peak production.

With the dramatic increase in oil and gas prices over the past two years, and society becoming ever more reliant on energy driven technology, it is conceivable that the competition for and expense of petrochemical feedstocks will pose considerable challenges to the plastics industry. The shake up in



the fossil fuels sector however is not just driven by the fact that supplies are expected to diminish to a point where they are unable to support future demands.

There is also growing concern and mounting proof that the use of fossil fuels is having a negative effect on the planet's climate. As a result of these concerns there are a number of institutes around the world, both industrial and academic, that are taking an active interest in developing natural and renewable alternatives to petrochemical based plastics (Green, A and Catizone I, 2009).

Another problem that faces petrochemically-derived plastics is their disposal. It is reported that the majority of landfill, especially in developed nations like the UK, Australia and North America, consists of polymer based materials such as plastic bottles, bags, food packaging, nappies, and disregarded homewares. In seeking natural renewable alternatives, there is also pressure to make these new polymeric materials recyclable and/or biodegradable. (Williams, CK Hillmyer MA, 2008)

An example that the move towards sustainable and conscientious materials is already underway. The European Union has stipulated to its member countries that 95% of all car parts must be recyclable by 2015 (Olsen et al, 2005).

### **1.3.1 Vegetable oil, the renewed plastics feedstock**

Although there has been a renewed interest in this renewable resource, the ability to convert TAG oils (vegetable oils) into useful polymeric materials has long been recognised. Triglyceride oils have been used in the preparation of polymeric materials such as paint bases since the 19<sup>th</sup> century (Guner et al, 2006), and some laboratories have reported conducted research into the synthesis of polymers from renewable materials for the past 20 years (Gandini A, Belgacem MN, 2002).

One of the prohibiting factors, and the reason there are currently few commercial examples of plant derived plastics is because they haven't been price competitive with plastics derived from fossil fuels (Williams CK, Hillmyer MA, 2008). Strong examples do however exist where the epoxidation of plant oils such as soybean oil is carried out on an industrial scale. These products currently include plasticisers, polymer stabilisers, and additives in lubricants (Dinda et al, 2007). Other commercially available products made from plant derived TAG oils include plastic panels for John Deere machinery and foams for Ford truck seats.

### **1.3.2 Supply of vegetable oil**

Australia is a large producer of the world's oilseeds crops. Annually Australia produces between 2 and 3 million tonnes of oilseeds, with production going as high as 3.7 million tonnes in the 1999 to

2000 harvest. More than 90% of local production is made up of canola and cottonseed. The remaining 10% consists mainly of sunflowers and soybean, and there is some minor production of oilseed crops such as safflower, peanut and linseed. (Australian Oilseeds Federation)

	2007/08	2006/07	2005/06	2004/05	2003/04
Canola	1069	512	1440	1531	1622
Sunflowers	75	20	95	61	39
Soybeans	35	30	56	54	74
Cottonseed	200	350	800	850	420
Other	10	10	20	7	10
Total	1985	922	2411	2503	2165

**Figure 1 Australian oilseed production in 1000 tonnes per growing year.**

Australia's largest oilseeds crop is canola, and as the second largest exporter of canola in the world, over a million tonnes are sent overseas every year. Canola production today in Australia represents a \$2.5 billion industry, and this is expected to swell to \$3.3 billion by the end of the decade. (Australian Oilseeds Federation)

This production of oilseeds translates into over 600,000 tonnes of vegetable oils each year (Australian Oilseeds Federation). Most of this production goes towards edible products such as cooking oils, spreads and shortening, food preparation and livestock meal. The industry recognises that there is also a growing demand from other industries for uses such as cosmetics, lubricants, fuels and plastics. With the ability to produce so many useful products from vegetable oils, it is expected that the demand for oil bearing crops will continue to grow.

This poses an economical and ethical problem for the future of vegetable oil production. On one hand it is beneficial to move away from the production of petrochemical based products towards more renewable and sustainable alternatives. On the other hand, as the demand rises for a product, so does the expense. The more vegetable oil stocks are syphoned off to produce other industrial products, the less remain for food stocks. What remains will probably become more expensive due to competition.

This has been recognised by Goud et al (2007) in their research into the epoxidation of vegetable oils. This group is based in India, and they report that non-edible oil crops such as rice bran, neem, sal and karanja are readily available in India. Current annual production of karanja is only 8000 MT, although there exists a capacity to produce up to 135,000 MT annually. They suggest that this is because of a lack of viable uses for the crop.

The advantage of growing non-edible oil crops is that certain varieties are high yielding, grow in less arable lands and under harsher conditions. Therefore they pose little competition to existing food crops.

### 1.3.3 Industrial hemp

A crop that presents considerable potential for the production of sustainable materials is *Cannabis sativa* L, commonly referred to as industrial hemp, or just hemp. The plant is widely accepted to have originated from China and has long been used as a source of fibre for rope, clothing and other materials (AGov. Hemp). In the early 19<sup>th</sup> century hemp was the world's largest fibre crop (O'Donnell A, 2004), but its production since has dwindled due to the advent of synthetic fibres. The classification of the plant as a drug throughout most of the western world since the 1920's has also had a negative impact on the plant's commercial production.

As well as fibre, oil is also produced from the plant. Oilseed production in the European Union in 1999 was reported at 6200 tonnes, and as such did not represent a considerable contribution to overall production (Karus *et al.* 2000, cited Small and Marcus 2002). Canada currently sees a future in hemp oilseeds, working on breeding new varieties and associated technologies for its growing, harvesting and processing. The by-product of producing oil from hemp oil-seed is also a useful product as it can be used as a nutrient rich stockfeed.

The use of hemp oil for food is restricted in Australia, although it is extensively used as such in other parts of the world. With the laws governing the production of hemp oil in Australia being relaxed under the Industrial Hemp Scheme, it is possible that it may represent a good feedstock for the polymers industry, without competing with food crops. Should it eventually be accepted as a food source, then the industry would already have been established. Currently oilseed crops yield between 0.9 to 1.5 tonnes per hectare.

Hempseed oil is high in unsaturated fatty acids, which makes it a strong candidate for the conversion to polymeric materials. Properties of hemp oil are: oleic acid (C18:1, 10% - 16), linoleic acid (C18:2, 50%–60%), alpha-linolenic acid (C18:3, 20%–25%), and gamma-linolenic acid (C18:3, 2%–5%) (Small and Marcus). Hemp oil for this project was supplied by Eco-fibre, who report properties of: oleic acid (12%), linoleic acid (57%), and alpha-linolenic acid (19%), gamma-linolenic acid (1.7%), palmitic acid (6%) and stearic acid (2%).

## 1.4 Technical background

### 1.4.1 Triglycerides

Vegetable oils have such functional properties because they are comprised of a structural unit called a triglyceride. Triglycerides are made up of a carbon backbone in the form of a glycerol molecule which is attached to three fatty acid chains. The glycerol molecule has the following chemical structure.

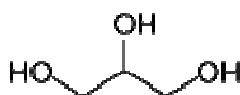


Figure 2 Glycerol molecule

It is common practice in the field of organic chemistry to represent organic molecules in this fashion. At each of the line intersections, where an element or functional group doesn't appear, is a carbon atom. Then, from the illustration it is clear that the glycerol molecule has a chain of three carbon atoms connecting three hydroxyl groups. Through the process of esterification, a fatty acid group is bonded to each of the hydroxyl groups. With few exceptions these fatty acid chains range from 14 to 22 carbon atoms in length. The formation of a triglyceride is shown in the following structural model, where  $R_1$ ,  $R_2$  and  $R_3$  represent functional groups which in this case are fatty acid chains.

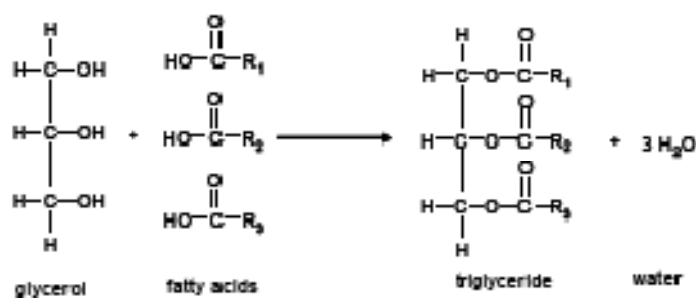


Figure 3 Formation of a triglyceride molecule from the bonding of one glycerol molecule and three fatty acid chains

Triglycerides comprise both saturated and unsaturated fatty acids. Unsaturated means that the fatty acid contains a number of double or triple carbon to carbon bonds. The designation for this is typically  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$ , respectively. Saturated means that all of the carbon to carbon bonds are single bonds, indicated by  $\text{C}-\text{C}$ . Although saturated fatty acids such as palmitic acid and stearic acid

are common constituents in triglycerides, vegetable oils are predominately comprised of the unsaturated fatty acids oleic acid, linoleic acid and linolenic acid. The structure of some common fatty acids are given in Figure 4

Name	Formula	Structure
Myristic acid	$C_{14}H_{28}O_2$	$CH_3(CH_2)_{12}COOH$
Palmitic acid	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$
Palmitoleic acid	$C_{16}H_{30}O_2$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic acid	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$
Oleic acid	$C_{18}H_{34}O_2$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic acid	$C_{18}H_{32}O_2$	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7COOH$
Linolenic acid	$C_{18}H_{30}O_2$	$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH(CH_2)_7COOH$
$\alpha$ -Eleostearic acid	$C_{18}H_{30}O_2$	$CH_3-(CH_2)_3-CH=CH-CH=CH-CH=CH(CH_2)_7COOH$
Ricinoleic acid	$C_{18}H_{33}O_3$	$CH_3(CH_2)_4CH-CH-CH_2-CH=CH(CH_2)_7COOH$ $\begin{array}{c}   \\ OH \end{array}$
Vernolic acid	$C_{18}H_{32}O_3$	$CH_3(CH_2)_4CH-CH-CH_2-CH=CH(CH_2)_7COOH$ $\begin{array}{c} \diagup \\ O \end{array}$
Licanic acid	$C_{18}H_{28}O_3$	$CH_3(CH_2)_3CH=CH-CH=CH-CH=CH-CH(CH_2)_4C(=O)(CH_2)_2COOH$ $\begin{array}{c}    \\ O \end{array}$

Figure 4 The structure of some common fatty acids

### 1.4.2 Desirable properties

If polymers derived from triglyceride oils are to gain widespread acceptance, they need to possess the same or better properties as their currently available petrochemical counterparts. Classes of naturally derived plastics should be able to display varying combinations of the following attributes, depending on the plastic's designation.

- Thermal stability
- Mechanical strength
- Resistance to chemicals
- Biocompatibility
- Biodegradability
- Adhesion to metallic substances
- Gas permeability
- Electrical conductivity or resistivity
- Fire resistance

Güner et al gives examples of characteristics typically associated with classes of polymers. Aromatic (structures consisting of cyclic hydrocarbon groups such as benzene) polymers are typically resistant to high temperatures. Polymers containing high levels of halogen, such as chlorine, are inherently non-flammable. The inclusion of fluorine (also a halogen) helps to improve a polymers resistance to both water and solvents.

## 1.5 References

1. Williams. C.K., 2008, Polymers from Renewable Resources: A perspective for a Special Issue of Polymer Review, Polymer Reviews
2. Kaup M, Karus M, and Ortmann S, 2003. Evaluation of a market survey 2002: The use of natural fibres in composite materials in the German and Austrian automotive industry. Status 2002, analysis and trends. Nova-Institut GmbH, Goldenbergstrasse 2, 50354 Hürth, Germany.
3. Small E, and Marcus D, 2002, 'Hemp: A new crop with new uses for North America', In J. Janick and A. Whipkey (eds) pp. 284-326. *Trends in new crops and new uses*. ASHS Press, Alexandria, VA. <http://www.hort.purdue.edu/newcrop/ncnu02/v5-284.html> (accessed 20 January 2004)
4. Green, A Catizone, I 2009, 'Helping wean the chemicals industry off crude oil' CSIRO media releases, viewed 26/10/09. <http://www.csiro.au/news/OilsForChemicalIndustry.html>
5. Mustafa AF, McKinnon JJ, and Christensen DA, 1999. The nutritive value of hemp meal for ruminants. *Canadian Journal of Animal Science* **79**: 91-95.
6. Kozlowski R, and Mackiewicz-Talarczyk M, 2004. Statistical data on industrial hemp. Euroflax Newsletter No. 20 p.35. (accessed March 2004)
7. Okada, M. "Chemical synthesis of biodegradable polymers", *Prog. Polym. Sci.* **2002**, 27, 87-133
8. Olsen, J Kelly, S and Underhill, B, 2005 'Industrial hemp scheme', *Department of Agriculture and Food*, Australian Government, Special Information Paper.
9. O'Donnell, A Dweib, MA Wool, RP 2004, 'Natural fibre composites with plant oil-based resin', *Composites Science and Technology*, vol. 64, issue. 9, pp. 1135 - 1145

## 2 Literature review

### 2.1 Introduction

This chapter serves to present an overview of the relevant literature concerning the epoxidation of VO. Specifically it will examine the techniques and methods that have been applied by other researchers, and the results they achieved. The aim of the literature review is to identify a method that can be applied in this research, and to develop an understanding of the underlying principles and terminology associated with the process. Considerations taken by the author while conducting the literature review were; which method or methods

- achieved the best results
- were achievable within the allocated timeframe
- were achievable with the available resources, and
- were within the realms of the authors technical abilities.

### 2.2 Epoxidation technologies

The method for converting vegetable oils into epoxidised polymer resins is well documented in the literature. Currently there are four generally accepted methods of producing epoxides from olefinic molecules (unsaturated chemical compounds containing at least one carbon to carbon double bond) (Goud et al, 2006). These are:

- i. Epoxidation *in situ* with peroxyacetic or peroxyformic acid, with peroxyacetic acid showing a higher conversion to oxirane (Dinda et al, 2008). This method is common practice in both industry and laboratory research, and represents the majority of the literature published on the topic. These can be catalysed by acids such as  $H_2SO_4$  and  $H_3SO_4$ , and enzymes, though the most common catalyst is an acidic ion exchange resin (AIER) (Mungroo et al, 2008).
- ii. Epoxidation with organic and inorganic peroxides catalysed by a transition metal catalyst. The most common of these is nitrile hydrogen peroxide, which is an inorganic chemical (Goud, 2006).
- iii. Epoxidation with halohydrines, using hypohalous acids (HOX) and their salts as reagents for the epoxidation of olefins with electron deficient double bonds. Epoxidation using halohydrines is highly environmentally unfriendly.



- iv. Epoxidation with molecular oxygen. Silver is the recommended catalyst for heterogeneous epoxidation, but it produces very low rates of double bond conversion. It is also only effective on very simple ethylenic substances. A cheap and green oxidiser is O<sub>2</sub>, but when used in the epoxidation of vegetable oil it leads to the degradation of the oil to smaller volatile compounds such as aldehydes and ketones as well as short chain dicarboxylic acids. Therefore it is not an efficient method for epoxidation of vegetable oils (Goud 2006).

From the above four technologies, it is evident that for clean and efficient epoxidation of vegetable oils, only the first two mentioned above are worth exploring. These technologies can be rendered cleaner by using heterogeneous catalysts (AIER) replacing traditional homogeneous ones.

### 2.3 Selected method

The method for epoxidising vegetable oils that has received the most attention in the literature is by the reaction with percarboxylic acid formed *in situ* in the presence of an acidic ion exchange resin (AIER) as catalyst (Goud et al, 2006., Goud et al, 2007A., Goud et al, 2007B., Mungroo et al, 2008., Petrovic et al, 2002., Sinadinovic-Fiser, 2001., Campanella A., Baltanas M.A., 2006., Perez et al, 2008.).The constituents used in this process are a carboxylic acid (formic acid or acetic acid), hydrogen peroxide and an AIER.

As detailed earlier, vegetable oils are comprised of triglycerides made up of fatty acid chains containing double bonds. When a triglyceride is epoxidised, an oxygen atom is added to this double bond creating a highly reactive three membered C-O-C ring called an oxirane. The oxygen atom in this ring is donated by the hydrogen peroxide. It is possible to use organic or inorganic peroxides (Mungroo et al, 2008), but the use of the inorganic hydrogen peroxide is most common.

The generation of percarboxylic acid *in situ* is by the reaction of carboxylic acid and hydrogen peroxide. While it is possible to use either formic acid or acetic acid as the carboxylic acid (Goud et al, 2006, Petrovic et al, 2002), it was found that while the rate of formation of oxirane was higher with formic acid (Dinda et al, 2008) using acetic acid resulted in a 10% higher conversion of double bonds to oxirane (Mungroo, 2008) and a lower amount of undesirable products formed. An explanation for this is that due to the very high activity of the formic acid, the hydrogen peroxide is rapidly decomposed leaving the batch oxygen depleted (Petrovic et al, 2002). Another advantage of acetic acid is that it is highly available, relatively cheap, has a high epoxidation efficiency and is

reasonably stable at moderate temperatures (Goud et al, 2007). The key role of the acetic acid is as the oxygen carrier, transporting the oxygen from the aqueous phase to the oil phase (Campanella. A., Baltanas. M.A., 2006). It also functions as a catalyst in the formation of the oxirane ring (Goud et al 2007). The acetic acid and the hydrogen peroxide react to create peroxyacetic acid, which then diffuses into the pores of the catalyst (Goud et al 2007).

The catalyst is a gel type acidic ion exchange resin (AIER). An AIER is an insoluble (high degree of crosslinking) solid material with a framework held together by chemical bond or lattice energy. This structure carries a surplus negative or positive electrical charge. So that the structure is electrically neutral, it carries what are called counter-ions. These counter ions are of opposite charge to that of the structure, and are free to move about within the structure. It is possible for these counter ions to leave the structure, as long as they are replaced by other ions of the same sign.

A useful analogy is to imagine a sponge, where the structure of the sponge is the structure of the ion exchange resin, which has an electrical charge being either positive or negative. The pores of the sponge are filled with an adequate number of ions having the opposite charge so as to achieve electro-neutrality. When submerged in solution these counter ions can float free of the sponge as long as they are replaced from the solution (Helfferich. F, 1995)

In the case of the reaction under consideration, once the AIER is installed into the mix the peroxyacetic acid is allowed to enter the pores of the resin. The resin is hydrophilic meaning that the oil phase, due to its large molecular structure, can't enter the AIER's polymer network (Campanella. A., Baltanas. M.A., 2006). As a result, the degradation reaction can only occur at the surface of the AIER.

The reaction for epoxidising triglyceride oils by the use of acetic acid (AA), hydrogen peroxide ( $H_2O_2$ ) and an AIER is well established. However the amounts of these constituents used in the synthesis process has the potential to vary from VO to VO, depending on the nature and percentages of the unsaturated fatty acids present in the triglyceride molecules. Much work has been done already by researchers on common vegetable oils with known fatty acid distributions. Examples include:

- Soybean oil (Campanella. A., Baltanas. M.A., 2006, Petrovic et al, 2002, Sinadinovic-Fiser et al, 2001)
- Jatropha oil (Goud et al, 2007)
- Canola oil (Perez et al, 2008, Mungroo et al, 2008)
- Mahua oil (Goud et al, 2007)
- Cottonseed oil (Srikanta et al, 2007)

- Karanja oil (Goud et al, 2007)

There also exist references to the polymerisation of vegetable oils such as corn oil, linseed oil, tung oil, rapeseed oil, sunflower oil and castor oil (Guner et al, 2006, Mauldin et al, 2008, both citing other references) by other methods in an attempt to create other varieties of polymer resins. This research however intends to stick exclusively to epoxy resins. Hemp oil seems to be under-represented in this group, and no reference to its use for the creation of epoxy resins has been located to date. This is surprising given its high percentage of linoleic acid.

### 2.3.1 Effect of VO unsaturation to AA to H<sub>2</sub>O<sub>2</sub> molar ratio

In research to date, researchers have studied the effects of varying the molar ratios of acetic acid and hydrogen peroxide to the ethylenic unsaturation molar ratio (moles of DB / 100 g oil) of the triglyceride oil. This ratio is generally given as:

$$\text{vegetable oil} : \text{acetic acid} : \text{H}_2\text{O}_2 \quad (\text{Ratio 1})$$

where vegetable oil is equal to 1 mole of DB per 100 g of VO.

In experiments on karanja oil, jatropha oil and canola oil, it was found that optimum results were achieved when the values in ratio 1 are 1.0 : 0.5 : 1.5 (Goud et al, 2006, Goud et al, 2007, Mungroo et al, 2008). It was noted that an excess of acetic acid had the potential of decreasing the final epoxide yield, as the acid promoted the hydrolysis of the oxirane ring. Another group, while working on canola oil, found that a slightly different ratio produced the highest conversion of double bonds to epoxy groups, listing 1.0 : 0.5 : 2.0 (Perez et al, 2008). In other experiments on mahua oil and soybean oil the ideal molar ratio was found to be 1.0 : 0.5 : 1.1 (Goud et al 2007, Sinadinoviv-Fiser et al, 2001)

### 2.3.2 Catalyst loading

As noted earlier, the effect of the catalyst is directly proportional to the surface area of the AIER particle (Campanella, A Baltanas, M.A, 2006). Therefore, the higher the concentration of catalyst, the more surface area exists at which double bonds are converted to epoxides. The following table gives some values for the optimum catalyst load by wt % of VO, as found by researchers.

**Table 1 Optimum catalyst loading for different VO as found by other researchers**

Triglyceride oil	Optimal catalyst loading wt %	Researcher
Soybean oil	5%	Sinadinovic_Fiser et al 2001
Jatropha oil	16%	Goud et al 2006
Mahua oil	16%	Goud et al 2007
Karanja oil	16%	Goud et al 2007
Canola oil	25%	Perez et al 2008
Canola oil	22%	Mungroo et al 2008

### 2.3.3 Temperature

Temperature is an important consideration in this reaction process. Increasing the temperature of the batch aids in the formation of peroxyacetic acid, which is an exothermic reaction (Mungroo et al, 2008). Increasing the temperature also increases the rate of reaction, the relative conversion to oxirane, and the ethylenic unsaturation consumption (Goud et al, 2006).

Disadvantages of raising the reaction temperature are that the oxirane ring becomes more unstable. This leads to hydrolysis of the oxirane ring, raising the glycol content and lowering the oxirane content. Also, since the AA-H<sub>2</sub>O<sub>2</sub> reaction is exothermic, high reaction temperatures could lead to excessive temperatures and the possibility of an explosion (Mungroo et al, 2008). The following table summarises some of the temperatures over time that the researchers found optimised their results.

**Table 2 Optimum temperature and time for epoxidising VO as found by other researchers**

Triglyceride oil	Temperature (degrees C)	Time (h)	Researcher
Soybean oil	75	7	Sinadinovic_Fiser et al 2001
Jatropha oil	70	4	Goud et al 2006
Mahua oil	70	3.5	Goud et al 2007
Karanja oil	70	4	Goud et al 2007
Canola oil	NA	NA	Perez et al 2008
Canola oil	65	5	Mungroo et al 2008

It can be thus seen that in general the best results are found to exist around 70°C over a period of 3.5 to 7 hours.

### 2.3.4 Effect of stirring speed

In experimental work published by Goud et al (2006, 2007), the effect of the stirring speed on the percentage conversion to oxirane was examined. They reported these results while examining the epoxidation of; Mahua oil by a H<sub>2</sub>O<sub>2</sub>-AA combination (Dinda, 2008), Karanja oil and Jatropha oil by a H<sub>2</sub>O<sub>2</sub>-AA-AIER combination (Goud et al, 2006), and Cottonseed oil by a H<sub>2</sub>O<sub>2</sub> and liquid inorganic mixture (Goud et al, 2007). In all instances the stirrer used was a six-bladed glass disk turbine impeller, and the combination of oil and acids were stirred in the reactor vessel for 30 min prior to the addition of the oxygen source (commonly hydrogen peroxide). The completed addition of the oxygen source was taken in each experiment as time zero.

Experiments were carried out on functionalised cottonseed oil at a varying speeds ranging from 600 rpm to 2400 rpm, each conducted over a 4 hour period. The relative percentage conversion to oxirane that was observed at each speed was 69.3% at 600 rpm, 72.2% at 1200 rpm, 77.3% at 1800 rpm and 77% at 2400. These figures indicate that at stirring speeds over 1800 rpm, there was limited additional affect on the formation of oxirane. It was assumed by the authors that this occurred because there was negligible resistance to mass transfer mechanisms beyond this speed.

In a similar study on mahua oil, speeds ranged from 1000 to 2500 rpm. The group found that at speeds above 1500 rpm the formation of oxirane was not substantially affected. They offer the following table of information summing up their results.

	Stirring speed, rev/min							
	1000		1500		2000		2500	
<i>t</i> (h)	5	10	5	10	5	10	5	10
Oxirane oxygen (%) <sup>a</sup>	1.45	1.81	1.65	1.92	1.68	1.92	1.55	1.81
Iodine value (IV) <sup>b</sup>	44.21	31.01	42.21	35.17	48.52	39.21	63.45	44.41
Conversion of IV( <i>x</i> ) <sup>c</sup>	0.50	0.65	0.52	0.60	0.49	0.55	0.28	0.50
Relative conversion to oxirane (RCO)	0.27	0.35	0.31	0.36	0.32	0.36	0.31	0.35

IV<sub>0</sub> = Initial iodine value = 88.

<sup>a</sup> Experimentally determined oxirane oxygen content (OO<sub>e</sub>).

<sup>b</sup> Experimentally determined iodine value.

<sup>c</sup> Conversion of IV(*x*), conversion of double bonds as related to IV<sub>0</sub>, calculated as  $x = [(IV_0 - IV)/IV_0]$ .

**Figure 5 Relative conversion to oxirane at different stirring speeds. Source: (Goud et al, 'Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide', 2006**

These results were confirmed in further experiments conducted on karanja oil and jatropha oil, with each showing that stirring speeds in excess of 1500 rpm had little added affect on the percentage conversion to oxirane. To ensure that the reaction was kinetically controlled the group performed all subsequent experiments at a stirring speed of 2500 rpm.

### 2.3.5 Analytical techniques

In the literature there are four commonly used methods for determining the success of the epoxidation reaction and the overall quality and properties of the epoxidised vegetable oil. These include three quantitative titration techniques and one qualitative spectroscopic technique (Güner et al, 2006). They characterise the sample by providing information on:

- Oxirane oxygen content. This is done by the direct titration method using hydrobromic acid solution in glacial acetic acid (Dinda et al, 2008; Mungroo et al, 2008; Goud et al, 2007; and as detailed by Paquot, C, 1979).
- Iodine Value. This is done using the Wij's method. (Dinda et al, 2008; Mungroo et al, 2008, Goud et al, 2007, and as detailed by Paquot, C, 1979).
- The alpha-glycol content. This is a titration method, the details of which are laid out by Stenmark (1958)
- The percentage consumption of the DB present in the (=C-H) group. This is achieved through Fourier Transform Infrared Spectroscopy (FTIR). (Mungroo et al, 2008; Espinoza Perez et al, 2008)

The following presents a brief overview of each of the above characteristics and methods.

#### Oxirane oxygen content

An oxirane ring is created when an oxygen atom is added to the double bonds present in long chain fatty acids such as oleic acid, linoleic acid and linolenic acid. This cyclic ether has the general structure:



Figure 6 Oxirane ring, otherwise known as an epoxy group. The oxirane oxygen content refers to the content of the oxygen atom present in the group.

The bond angles are about 60°, making the ring highly strained and highly reactive (Mungroo et al, 2008). The presence of these high strain energy rings on the fatty acid chains allows crosslinking to occur when the epoxy resin is cured. The higher the conversion of double bonds to epoxides

(oxiranes), the more crosslinking can occur, and the higher the quality of the resulting plastic (Goud et al, 2006).

The oxirane oxygen content refers to the content of the oxygen atom in this group, and is a measure of the amount of DB which has converted via the epoxidation process into epoxides. Therefore the higher the oxirane oxygen content, the higher the conversion to epoxides.

### Iodine value

The degree of unsaturation, or degree of double bonds present, in the triglyceride oil is measured by the iodine value. Iodine is mixed with a sample of vegetable oil, and the degree of unsaturation is calculated from the amount of iodine that reacts with the double bonds in the triglyceride oil under specific conditions. The iodine values of oleic acid, linoleic acid and linolenic acid are 89.9, 181 and 273.5, respectively. (Güner et al, 2006).

### Glycol content

Glycol is a by-product of the epoxidisation reaction, and is considered an impurity. Glycol is formed through the hydrolysis of the oxirane ring which tends to be highly unstable (Goud et al, 2007). This instability can lead to degradation of the epoxides which lower the quality of the resin. As the amount of epoxides are decreased through hydrolysis, the glycol content increases (Mungroo et al, 2008).

### Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is one of the most widely used methods for analysing the structure of triglyceride oils and their polymer derivatives (Güner et al, 2006). In general terms FTIR measures the vibrational frequency present in molecules as a result of the varying strengths of bonds between atoms and the mass of those atoms. This can be imagined as a spring connecting balls with mass, Figure 7. The stiffness of the spring represents the strength of the bond, and the mass of the ball represents the mass of the atoms.

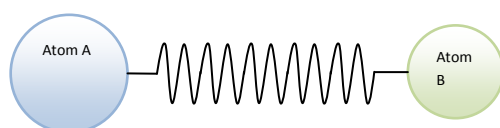


Figure 7 Ball and spring model of a covalent bond

Different molecules vibrate with varying frequencies depending upon their composition. When a beam of infrared light (electromagnetic waves in a set range of frequencies) is shone through a sample an amount of infrared radiation is absorbed by the vibrating molecules. The frequency of the radiation absorbed equals the frequencies of the nuclear vibrations present (Ebbing and Gammon, 2005). It is quite unlikely that two different compounds would absorb the same frequency of infrared radiation. This makes it possible to accurately identify which compounds are present in a sample.



## 2.4 References

1. Dinda S, Goud VV, Patwardhan AV, Pradhan NC (2008) Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic acids. *Bioresour Technol*.
2. Espinoza Perez, JD Wiesenborn, DP Haagenson, DM, Ulven, CA 2008, 'Study of the Process Parameters of the Canola Oil Epoxidation', *ASABE*, PN. 084617
3. Goud VV, Patwardhan AV, Pradhan NC (2006) Studies on the epoxidation of mahua oil (*Madhumica Indica*) by hydrogen peroxide. *Bioresour Technol* 97(12):1365–1371
4. Goud VV, Patwardhan AV, Pradhan NC (2006) Epoxidation of karanja (*Pongamia Glabra*) oil by H<sub>2</sub>O<sub>2</sub>. *J Am Oil Chem Soc* 83(7):635–640
5. Goud VV, Patwardhan AV, Dinda S, Pradhan NC (2007) Epoxidation of karanja (*Pongamia glabra*) oil catalyzed by acidic ion exchange resin. *Eur J Lipid Sci Technol* 109(6):575–584
6. Goud VV, Patwardhan AV, Dinda S, Pradhan NC (2007) Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chem Eng Sci* 62(15):4065–4076
7. Helfferich. F., 1995, *Ion Exchange*, Courier Dover Publications
8. May CA (1973) *Epoxy resins: chemistry and technology*. Marcel Dekker, New York, pp 672–673
9. Mungroo R, Pradhan NC, Goud VV, Dalai AK, (2008) Epoxidation of Canola Oil with Hydrogen Peroxide Catalyzed by Acidic Ion Exchange Resin. *J Am Chem Soc* 85:887-896
10. Paquot C (1979) *Standard methods for the analysis of oils, fats and derivatives part I*, 6th edn. Pergamon, Oxford, pp 66–70
11. Petrovic AS, Zlatanovic A, Lava CC, Sinadinovic-Fiser S (2002) Epoxidation of soybean oil in toluene with peroxyacetic acid and peroxyformic acids—kinetics and side reactions. *Eur J Lipid Sci Technol* 04:293–299
12. Sinadinovic-Fiser S, Jankovic M, Petrovic ZS (2001) Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. *J Am Oil Chem Soc* 78(7):725–731
13. Stenmark, GA 1958, 'Determination of the alpha-Glycol content of epoxy resins', *Analytical chemistry*, vol. 30, pp. 381 – 383
14. Vleck T, Petrovic ZS, 2006, *Optimisation of the chemoenzymatic epoxidation of soybean oil*, *J Am Chem Soc* 83:247-252

## 3 Experimental methods

### 3.1 Introduction

This research project will use the method of epoxidising vegetable oils that is commonly used in research and industry. Peroxyacetic acid will be formed *in situ* by the reaction of aqueous hydrogen peroxide and acetic acid in the presence of an acidic ion exchange resin as catalyst.

Throughout the course of this research project a considerable amount of time was spent in the laboratory preparing and testing the samples. Initially sunflower oil and linseed oil, purchased from the local supermarket and hardware store respectively, were used. One batch of epoxidised linseed oil (ELO) and four batches of epoxidised sunflower oil (ESFO) were made, each with varying molar ratios of: **vegetable oil : acetic acid : hydrogen peroxide**. Each batch was then tested by both qualitative and quantitative methods. This initial testing would pave the way for more thorough testing later.

After the process became familiar, then testing began on locally grown hemp oil, sourced from Eco-Fibre, and supplied in a 20 litre drum. The following discussion outlines the synthesis process and subsequent testing procedures carried out to date on the original linseed and sunflower oils and subsequent hemp oil, with the specific details being relevant to the hemp oil. Mutton tallow was also considered as a possible candidate.

The procedure of the experiments can be broken up into the following steps. A detailed discussion of each of the four steps will then be presented.

#### I. **Vegetable Oil Characterisation**

Characterisation of the vegetable oil to be used for epoxidation according to its fatty acid composition is important for determining the concentration of oil in the reaction. It also allows the iodine value of the oil and the theoretical maximum oxirane oxygen content of its epoxidised derivative to be calculated, along with predictions about the quality of the cured resin.

#### II. **Process parameters**

The reaction process relies on many parameters in its execution, namely:

- Molar ratios of: **vegetable oil : acetic acid: hydrogen peroxide**.
- Catalyst loading

- Reaction time
- Reaction temperature
- Stirring speed

This research mainly focused on the molar ratios of chemicals, and the optimum reaction time. The optimum parameters of other researchers were used to establish the reaction temperature, and the stirring speed was determined by observing at what speed homogenous mixing appeared to occur.

### III. **Synthesis**

A constantly stirred batch reactor with a low profile ships anchor stirrer and a diaphragm dosing pump was used to epoxidise the VO. Parameters such as reactor temperature, stirring speed, duration of concentration of H<sub>2</sub>O<sub>2</sub> dosing and effective reaction time were computer controlled.

### IV. **Post treatment**

After completion of the reaction, or at allotted time intervals, the epoxidised sample was removed from the reactor. Once removed the sample required preparation before testing could commence. This consisted of washing the resin with clean water in a separation funnel until the peroxyacetic acid and catalyst was removed. This commonly took three washes, the first with cool water to assist in neutralising the reaction, the second with hot to boiling water, and the third with cool water once again.

Once the sample was washed it was centrifuged, aerated and dried with anhydrous sodium sulphate.

### V. **Epoxidation measurement**

Once the batch has been cleaned, its properties are tested using Fourier Transform Infrared (FT-IR) and titration methods.

## 3.2 **Vegetable oil characterisation**

The epoxidation reaction is dependent upon the fatty acid composition of the oil's triglycerides. Vegetable oils high in unsaturated fatty acids are most suitable for epoxidation because of the presence of double carbon to carbon bonds in the tail of the fatty acid (FA) chain. It is at these

double bonds (DB) that epoxy groups form, which in turn provide sites for crosslinking to occur during curing.

Vegetable oils are commonly comprised of varying percentages of the fatty acids oleic acid (C18:1), linoleic acid (C18:2), alpha-linolenic acid (C18:3) and gamma-linolenic acid (C18:3), along with some small amounts of saturated fatty acids. Establishing the percentage composition of each FA in a measure of VO allows the experimenter to determine some important properties of the oil.

Firstly, it is important to know the moles of DB present in 100 g of VO. This allows the experimenter to determine the concentration (in grams) of VO required in the reaction so that 1 mole of DB is correctly met with the corresponding molar ratios of AA and  $H_2O_2$  to be used in the reaction. An example of how to calculate this quantity if VO is given below in the section on process parameters. A VO high in linolenic acid (Figure 8b, with three DB per FA chain) will have more moles of double bonds per 100 g of VO than one high in oleic acid (Figure 8a, with one DB per FA chain). Secondly, the percentage FA composition of a VO is used to theoretically determine the oil's iodine value and the maximum oxirane oxygen content of the oil's epoxidised derivative.

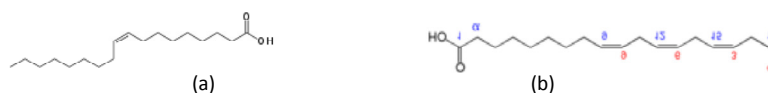


Figure 8 Structure (a) Oleic acid and (b) alpha-linolenic acid

Finally, a prediction of the quality of the cured epoxy resin can be made based on the location of the DB in the prominent fatty acids. For instance, alpha-linolenic acid has a DB located three carbons from the end of its FA chain; compared to oleic acid whose DB is 9 carbons from the end. Theoretically, crosslinking of the epoxidised oleic acid will produce a less ridged polymer matrix because more of the FA tail is left to 'waggle' about and not contribute to the overall structure.

It is common for suppliers of vegetable oils (VO) to supply data on the oil's fatty acid composition. The accuracy of this information depends on the regularity of testing, and the variability in the oil's fatty acid composition due to factors such as the impact of weather conditions, breeding and genetic manipulation of the oilseed crop. This research uses the manufacturer's specifications for determining the above mentioned characteristics. It would be more appropriate to experimentally determine the fatty acid composition for each individual sample of oil used for testing by a technique such as liquid-gas chromatography. This however is a considerable process for the novice and the manufacturer's classification will be used keeping in mind that it is only a guide.

The following outlines the methods and equations for determining characteristics such as:

- Moles of DB per 100 g of VO
- Theoretical Iodine Value of VO
- Theoretical Maximum Oxirane Oxygen Content of Epoxidised VO Derivative

These are relevant considerations in both determining the parameters of the experiment and analysing the results. Since hemp oil (supplied by Eco-Fibre) comprises the majority of this research it will be used in demonstrating the calculations.

### 3.2.1 Moles of double bonds in 100g hemp oil

It is first necessary to determine the number of moles of double bonds (DB) and the molar mass (MM) of the triglyceride (TAG). These will be statistically averaged values because TAG molecules can vary in fatty acid (FA) composition throughout the oil. The composition of the hemp oil used and the properties of the fatty acids present are given in Table 3.

The moles of DB per mole of TAG are calculated from Equation 1:

Equation 1

$$\text{Moles of DB per mole of TAG} = \sum \left( \frac{\text{mol DB}}{100 \text{ g oil}} \right) \times \sum \left( \frac{1}{100 \text{ g oil}} \right) \times \left( \frac{\text{mol FA}}{\text{mol TAG}} \right)$$

where the first two terms on the right of Equation 1 come from the following. Each unsaturated FA contributes a number of moles of DB for each 100 g of VO. This contribution is determined for each type of FA by; the product of the number of DB in the FA and what percentage of the VO is comprised of this FA, divided by the molar mass of the FA. This is summarized by Equation 2, the sum of which gives the total moles of DB in 100 g of VO

Equation 2

$$\frac{\text{mol DB}}{100 \text{ g oil}} = \frac{(\text{Number of DB per FA}) \times (\% \text{ FA})}{\text{molar mass of FA}}$$

The moles of FA in 100 g of VO is determined from Equation 3

Equation 3

$$\frac{\text{mol FA}}{100 \text{ g oil}} = \frac{(\% \text{ FA})}{\text{molar mass of FA}}$$

The value of the third term on the right of Equation 1 is simply 3, as each triglyceride has three FA chains.

**Table 3** Some basic properties of fatty acids, and their composition in a VO allows some important properties to be determined.

Fatty Acid (FA)	% FA	Molar Mass (g/mol)	Number of double bonds (DB)	Moles of DB per 100 g oil	Moles of FA per 100g oil
Oleic acid (C18:1)	12	282.4614	1	0.042	0.042
Linoleic (C18:2)	57	280.4500	2	0.406	0.203
alpha-Linolenic (C18:3)	19	278.4300	3	0.205	0.068
gamma-Linolenic (C18:3)	1.7	278.4300	3	0.018	0.006
Palmitic	6	256.4200	0	0.000	0.023
Stearic	2	284.4800	0	0.000	0.007
other	2.3	292.0000	0	0.000	0.008
<b>TOTAL</b>	<b>100</b>			<b>0.672</b>	<b>0.358</b>

#### Example 1 - Moles of double bonds per moles of triglyceride for hemp oil

The following example uses the values in Table 3 and Equation 1 to determine the moles of DB per moles of TAG for hemp oil.

$$\text{Moles of DB per moles of TAG} = \frac{0.672 \text{ mol DB}}{100 \text{ g oil}} \times \frac{100 \text{ g oil}}{0.358 \text{ mol FA}} \times \frac{3 \text{ mol FA}}{1 \text{ mol TAG}} = 5.63 \frac{\text{mol DB}}{\text{mol TAG}}$$

Next we will look at the molar mass for each triglyceride of hemp oil. A triglyceride is formed by the bonding of one glycerol molecule and three FA chains. As a result of this reaction three water molecules are also produced. The structural formula is shown in Figure 9, where  $R_n$  represents the FA chain. The equation for determining the molar mass of free fatty acids in 100 g of VO is:

Equation 4

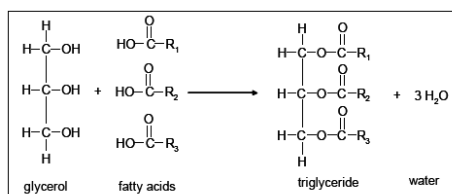
$$MM_{FFA} = \left( \frac{100 \text{ g oil}}{\sum(\text{mol FA per 100 g oil})} \right)$$

The equation for determining the molar mass (MM) of the TAG is as follows:

Equation 5

$$MM_{TAG} = 3 \times MM_{FFA} + MM_{glycerol} - 3 \times MM_{water}$$

Where the molar masses are; glycerol (92.09 g/mol), water (18 g/mol), and for each unsaturated FA in Equation 5 the molar mass can be found in Table 3.



**Figure 9** In the formation of a triglyceride molecule three fatty acids bond to glycerol to give one triglyceride and three water molecules.

### Example 2 – Molar mass per triglyceride of hemp oil

The molar mass of free fatty acids in hemp oil is:

$$MM_{FFA} = \frac{100 \text{ g hemp oil}}{0.358 \left( \frac{\text{mol FA}}{100 \text{ g hemp oil}} \right)} = 279.33 \left( \frac{\text{g}}{\text{mol}} \right)$$

The molar mass per triglyceride of hemp oil is:

$$MM_{TAG} = 3 \times 279.33 \left( \frac{\text{g}}{\text{mol}} \right) + 92.06 \left( \frac{\text{g}}{\text{mol}} \right) - 3 \times 18 \left( \frac{\text{g}}{\text{mol}} \right) = 876.05 \left( \frac{\text{g}}{\text{mol}} \right)$$

The quantity of interest is the moles of DB for a specific amount of hemp oil. For 100 g of hemp oil there are 0.64 moles of double bonds.

$$\frac{5.63 \text{ mol BD}}{\text{mol TAG}} \times \frac{\text{mol TAG}}{876.05 \text{ g}} \times (100 \text{ g hemp oil}) = 0.64 \text{ mole DB}$$

This result will later become useful when determining the ratios of reacting chemicals required in performing the synthesis of the resin.

### 3.2.2 Iodine value

The degree of unsaturation present in a vegetable oil's FA chain is an important consideration, as it is at these carbon to carbon DB that the reactive epoxy group forms. A highly suitable vegetable oil will start out with many double bonds, and a successful reaction will see a high percentage of those double bonds consumed to form epoxides.

The iodine value gives an indication of the degree of unsaturation present in a sample of VO or epoxidised resin. The carbon-carbon double bonds have the ability to react with the halogen iodine, and it is this reaction that is utilized in the test. The iodine added to the test sample is absorbed until all of the fatty acid chains become saturated, at which point no more iodine can be added. The

iodine value is defined as the number of grams of iodine absorbed by 100 grams of oil, and refers not to the amount of iodine in the oil, but refers to the amount of iodine required to saturate the oil. There are two methods for determining the iodine value of a VO. The first uses a calculation dependent on the FA composition of the VO, the details of which are highlighted below. The next uses a titration method which relies on the principles outlined above. Figure 10 shows the degradation of the double bonds by the addition of iodine. It can be seen that iodine atoms act to saturate the FA chain. Details of the titration methods will be given in a later section.

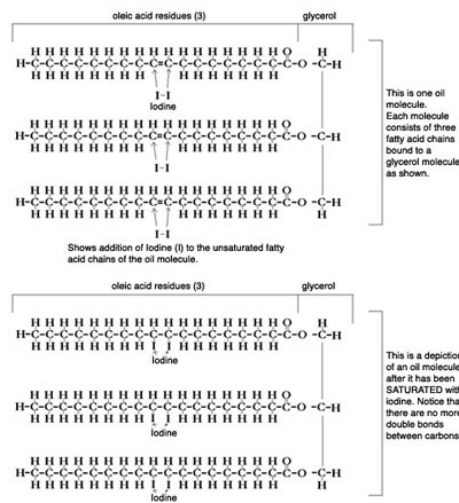


Figure 10 A depiction of how the halogen iodine saturates the unsaturated fatty acid. The picture was sourced from: [http://journeytoforever.org/biodiesel\\_yield.html#iodine](http://journeytoforever.org/biodiesel_yield.html#iodine)

### Calculating the iodine value of a VO from FA composition

It is possible to predict the iodine value ( $IV_o$ ) of hemp oil if the FA composition is known. The following are used to calculate the iodine value of the free fatty acids and the triglycerides respectively. The coefficients in Equation 6 and Equation 7 are calculated by Equation 8

#### Free fatty acids:

Equation 6

$$IV_{FFA} = (\% \text{ palmitoleic acid} \times C_{FFA}) + (\% \text{ oleic acid} \times C_{FFA}) + (\% \text{ linoleic acid} \times C_{FFA}) + (\% \text{ linolenic acid} \times C_{FFA}) + (\% \text{ gadoleic acid} \times C_{FFA}) + (\% \text{ erucic acid} \times C_{FFA})$$



**Triglycerides:**

Equation 7

$$IV_{TAG} = (\% \text{ palmitoleic acid} \times C_{TAG}) + (\% \text{ oleic acid} \times C_{TAG}) + (\% \text{ linoleic acid} \times C_{TAG}) + (\% \text{ linolenic acid} \times C_{TAG}) \\ + (\% \text{ gadoleic acid} \times C_{TAG}) + (\% \text{ erucic acid} \times C_{TAG})$$

Equation 8

$$C_{FFA} = \frac{253.81 \times \text{number of DB}}{\text{molar mass of fatty acid}} \quad C_{TAG} = \frac{253.81 \times \text{number of DB}}{\text{molar mass of fatty acid} + 12.68}$$

The iodine values of the free fatty acids and the triglycerides are given in Table 4 for hemp oil, along with the coefficients for each fatty acid.

**Table 4 Determination of the iodine value for hemp oil based on its fatty acid composition**

Fatty Acid (FA)	Percentage	Molar Mass (g/mol)	Number of double bonds (DB)	Coefficient FFA	Coefficient TAG	Iodine Value (Free fatty acid)	Iodine Value (Triglyceride)
Oleic acid (C18:1)	12	282.4614	1	0.899	0.860	10.783	10.320
Linoleic (C18:2)	57	280.4500	2	1.810	1.732	103.171	98.708
alpha-Linolenic (C18:3)	19	278.4300	3	2.735	2.616	51.960	49.697
gamma-Linolenic (C18:3)	1.7	278.4300	3	2.735	2.616	4.649	4.447
Palmitic	6	256.4200	0	0.000	0.000	0.000	0.000
Stearic	2	284.4800	0	0.000	0.000	0.000	0.000
other	2.3	292.0000	0	0.000	0.000	0.000	0.000
<b>TOTAL</b>	<b>100</b>					<b>170.563</b>	<b>163.171</b>

For hemp oil the iodine value  $IV_o$  is determined to be 163.171 (g /100 g hemp oil). When later the iodine value of the epoxidised VO is determined using titration methods, the percent conversion can be calculated using Equation 9, where  $IV_f$  refers to the iodine value of the epoxidised sample, and  $IV_o$  is the iodine value of the original VO.

Equation 9

$$\% \text{ Conversion}_{\text{relative to IV}} = 100 \times \frac{IV_o - IV_f}{IV_o}$$

### 3.2.3 Theoretical maximum oxirane oxygen content

Oxirane oxygen content measures the degree of epoxidation by quantifying the oxygen of the epoxy ring. The theoretical oxirane oxygen content can be estimated from Equation 10, where  $IV_o$  is the triglyceride iodine value of the VO,  $A_i$  (126.9) is the atomic mass of iodine and  $A_o$  (16.0) is the atomic mass of oxygen.

## Equation 10

$$OO_t = \left[ \frac{\left( \frac{IV_o}{2 \cdot A_i} \right)}{100 + \left( \frac{IV_o}{2 \cdot A_i} \right) \cdot A_o} \right] \times A_o \times 100$$

### Example 3 – Theoretical oxirane oxygen content of hemp oil

In the case of hemp oil the theoretical maximum oxirane oxygen content is:

$$OO_t = \left[ \frac{\left( \frac{163.171}{2 \times 126.9} \right)}{100 + \left( \frac{163.171}{2 \times 126.9} \right) \times 16} \right] \times 16 \times 100 = 9.327$$

Once the epoxy group oxygen titration has determined the oxirane oxygen content the percent conversion can be calculated from Equation 11

## Equation 11

$$\% \text{ Conversion}_{\text{relative to } OO} = 100 \times \frac{OO_e}{OO_t}$$

### 3.3 Process parameters

#### 3.3.1 Ratio of unsaturation to acetic acid to hydrogen peroxide

The procedure for practical experimentation to date has used the research of others as a guideline. It was decided to commence with a molar ratio of: ethylenic unsaturation to acetic acid to hydrogen peroxide that produced optimum results for other varieties of triglyceride oils. This molar ratio is predominately found to be **1.0 : 0.5 : 1.5**. From here it is possible to vary the molar ratio of either acetic acid or hydrogen peroxide for each batch.

It was previously established that the moles of double bonds in 100g of Hemp Oil is 0.64, and in research by Petrovic et al the moles of double bonds in 100 g of soybean oil was reported as 0.49 (Petrovic et al, 2002). Since the Petrovic paper was the first paper used for the basis of practical experimentation, and the method of determining the moles of double bonds was unknown to me at the time, 0.49 mole of double bonds was applied to all vegetables oils. The following example shows how to calculate the mass of VO required to achieve a certain molar percentage, normally one.

#### Example 4 – Determining the amount of VO for 1 mole of DB

Hemp Oil

As was previously calculated, 100 g of hemp oil contains 0.64 mole of DB. So, to achieve 1 mole of DB the experimenter would require 156.25 g of hemp oil.

$$\frac{0.64 (M)}{100 (g)} = \frac{1.00 (M)}{m (g)}$$

$$m_{hemp\ oil} = \frac{1.00 (M) \times 100 (g)}{0.64 (M)} = 156.25 (g)$$

Soybean Oil

$$m_{soybean\ oil} = \frac{1.00 (M) \times 100 (g)}{0.49 (M)} = 204.08 (g)$$

As can be noted from this, the amount of vegetable oil required to achieve 1 mole of DB varies considerable from one VO to another.

The molar mass of acetic acid (AA) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are: acetic acid (60.06 g/mol), and H<sub>2</sub>O<sub>2</sub> (34.015 g/mol). Applying the following formula, the mass (in grams) of chemical for a particular ratio can be determined.

Equation 12

$$\frac{\text{molar mass} \times \text{ratio}}{\text{percentage concentration}}$$

The percentage concentration for AA is 1, and for H<sub>2</sub>O<sub>2</sub> concentrations of 30% and 35% have been used. The following table shows masses for AA and H<sub>2</sub>O<sub>2</sub> for molar ratios of 0.5, 1.0 and 1.5.

**Table 5 Masses of key epoxidation chemicals for varying moles of chemical**

Moles of Chemical	Acetic Acid (g)	Hydrogen Peroxide 30% (g)	Hydrogen Peroxide 35% (g)
0.5	30.03	56.7	48.6
1	60.06	113.4	97.2
1.5	90.09	170.1	145.8

For each batch, between 400 g and 1000 g of VO was used. The following works on the basis that one mole of DB equates to about 200 g of a particular vegetable oil.

#### Example 5 – Determining quantities of VO and reactants

For a batch using 600 g of vegetable oil (1 mole DB per 200 g of VO) and a molar ratio of 1:0.5:1.5 then the following applies:

Vegetable oil (1 mol):  $600g (3 mol) = 3 \times 200g (1 mol)$

Acetic Acid (0.5):  $90g (1.5 mol) = 3 \times 30g (0.5 mol)$

Hydrogen Peroxide 30% (1.5):  $510.3g (4.5 mol) = 3 \times 170.1g (1.5 mol)$

The required amounts of VO and AA are measured out using digital scales, taking care while handling the AA. The dosing pumps will apply the required amounts of H<sub>2</sub>O<sub>2</sub> in a dropwise fashion, so it is only necessary to ensure there are adequate supplies in the dosing pump tank. The H<sub>2</sub>O<sub>2</sub> tank is situated on scales (Figure 11) so that after the reaction has run, it can be seen that the correct amounts of chemical have been dosed.



**Figure 11** As the hydrogen peroxide is dosed the scales register a negative value. It is worth checking this value after the dosing stage is complete to ensure the correct amount has been administered.

### 3.3.2 Acidic ion exchange resin (catalyst)

The acidic ion exchange resin (AIER) comes in the form of small solid bead-like particles. A product called Amberlite and designated IR-120, sourced from Fluka chemicals, has been used as the AIER. Amberlite is a cation exchange resin with a styrene-divinylbenzene matrix displaying 8% crosslinking, and has a maximum usage temperature of 121°C.



Figure 12 Acidic ion exchange resin (AIER) in bead form

It is measured out as a wt % of the vegetable oil used in the reaction. In chapter 2 it was reported that optimum results have been achieved using wt % of between 5% and 25%. For all of the initial experiments in this research project, it has been decided to use a measure of 10 wt % of vegetable oil i.e. for 600 g of vegetable oil, 60 g of Amberlite IR-120 is used.

## 3.4 Synthesis

The measured quantities of VO, acetic acid and Amberlite IR-120 are added to the reaction vessel, and the stirrer is activated. It is important at this stage to also turn on the water. The reactor has an insulating layer of silicone oil that surrounds the vessel, which is used to control the vessel's temperature. The running water plays a role in this operation and is sensed by the reactor's computer. If the water is not running then the temperature may not be correctly controlled, and the reactor will shut off, potentially wasting a batch of resin.

Once the constituents have been added to the reactor and stirring set to 80 rpm, then the reaction sequence is activated. Initially the temperature of the reactor is raised so that the mixture has a uniform temperature of 40°C. Originally 50°C was being used, but it was discovered that due to the combination of the raising reactor temperature and the exothermic reaction between the H<sub>2</sub>O<sub>2</sub> and the acetic acid, the temperature tended to peak to around 130°C. This resulted in dangerously high reactor vessel pressures and a cooking of the AIER, so it was lowered to 40°C.

The total required quantity of H<sub>2</sub>O<sub>2</sub> is then dosed in dropwise fashion over a period of 1 hour. Once this has been completed then the stirring speed is increased to 100 rpm and the temperature is

raised to 75°C over a period of 45 minutes. These conditions are then maintained for 8 hours, after which the stirring continues, but the temperature is allowed to settle to ambient room temperature.

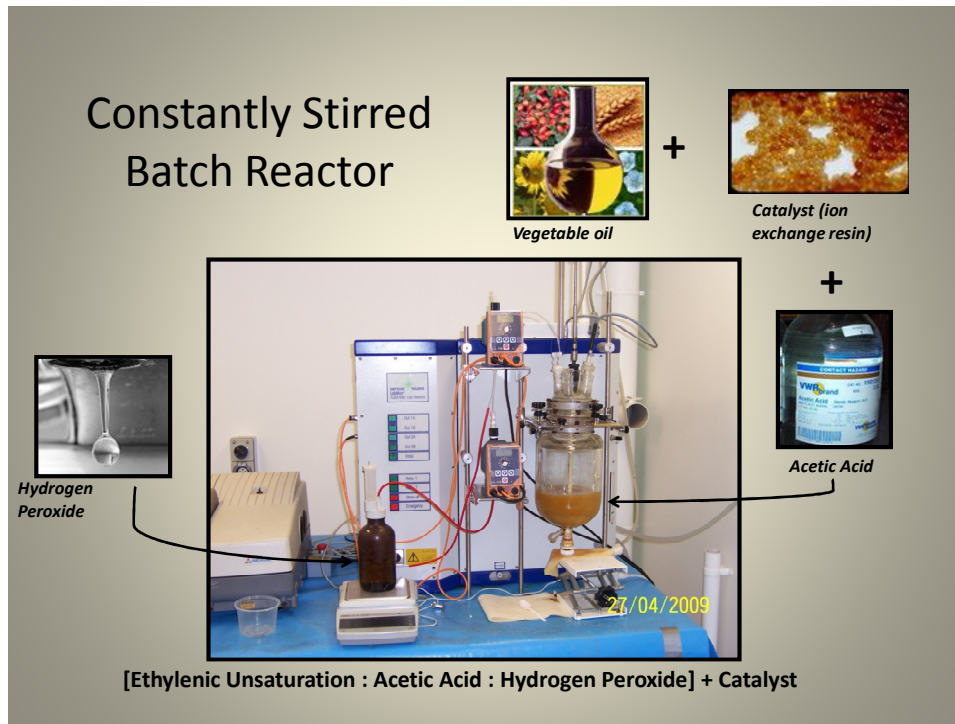


Figure 13 A constantly stirred batch reactor was used for this research

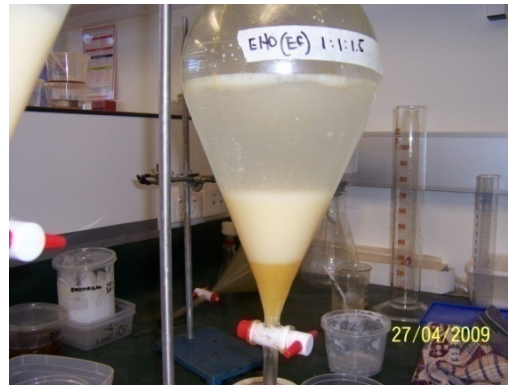
### 3.5 Post treatment

Once the reaction process is completed, the batch needs to be cleaned to remove the peroxyacetic acid and catalyst. This is done by pouring the batch into a separating funnel, adding water, and agitating the mixture vigorously by manual shaking, for around 3 minutes. The funnel is then allowed to sit in its upright position so that the contents can settle. Mungroo et al report washing first with cold water (presumably to halt any reaction that may still be occurring), and then successively with slightly hot and cold water to remove any free acid (Mungroo et al, 2008). It was found in this research that three washes was normally adequate, with the first and last washes using cool clean water, and the second wash using boiling water. The batch was normally considered to be washed when no more AIER settled to the bottom of the separation funnel.

It is expected that the AIER will fall to the bottom of the funnel, and the remaining liquid will separate into an aqueous phase and a more viscous resin phase. The resin phase is generally less dense than the aqueous phase and will settle on top. This has not always occurred, with the resin phase occasionally falling below the aqueous phase. This presumably happens when an emulsion occurs in the resin phase.



**Figure 14** A washed batch of resin usually looks like that in the picture, with a resin phase on the top, a relatively clear aqueous phase in the middle and the AIER on the bottom.



**Figure 15** In this case the resin emulsified. The general top layer is the aqueous phase, the middle phase is the emulsion and the bottom phase is the AIER. The very top layer is unidentified.

As can be seen from the above photographs, there is a tap located at the base of the funnel. This allows the AIER and aqueous phase to be drained off, leaving the resin phase. The resin is then transferred into vials especially suited for use in a centrifuge. The centrifuge is operated at 1500 rpm for 10 to 15 minutes.



**Figure 16** The centrifuge, used to separate the aqueous phase from the oil phase after washing

This will force any remaining aqueous phase and AIER to the bottom of the vial, and the resin can be poured off the top. Once the resin has been washed, centrifuged and collected into a beaker, the next step is to aerate it. This involves allowing a steady stream of air to bubble up from the base of the beaker. An unproved analogy for the function of this is air blowing across a wet surface. The water is atomised and carried away by the motion of the air. The process is similar as the air bubbles up through the resin.





Figure 17 The sample is dried by bubbling air up through the resin.

As a final step the resin is dried with anhydrous sodium sulphate in the proportion of 1 to 2 g per 10 g of resin. Once the anhydrous sodium sulphate is added to the resin it is then placed in an oven at 50 °C. The mixture is stirred vigorously and then filtered using a small funnel and filter paper. The filtrate constitutes the test sample.

### 3.6 Epoxidation measurement

Determining the characteristics of the resin is done by Fourier Transform Infrared Spectroscopy (FTIR) and titration methods. The FTIR is used to determine the relative difference between the amount of double bonds present in the original triglyceride oil, and the amount remaining after epoxidation. It also gives an indication of the formation of epoxides.

#### 3.6.1 Analyses using Fourier Transform Infrared Spectroscopy (FTIR)

Once the cleaned and dried resin has been collected, it is possible to collect its spectrum. The first step is to make a potassium bromide tablet. Potassium bromide (PB) is a salt and needs to be ground into a fine powder before being placed into the central hole of a small metal disc. It is then pressed in a small manual press to form a tablet. The tablet and associated equipment are shown in the following photographs.



Figure 18 Equipment for making a FTIR sample plate



Figure 19 FTIR sample plate

The second step is to use the PB tablet to create a background spectrum with the FTIR. The tablet is placed in the FTIR and its spectrum is collected, resulting in a background such as that in Figure 20. The point of the background spectrum is that the sample has to be somehow held in position so the beam of infrared radiation can be shone through. The sample is placed on the PB plate, which when pressed resembles a small window. Since we don't want the PB background spectrum mixed with the VO or resin spectrum, the background spectrum is subtracted from the sample spectrum, leaving only the spectrum of the VO or resin sample.

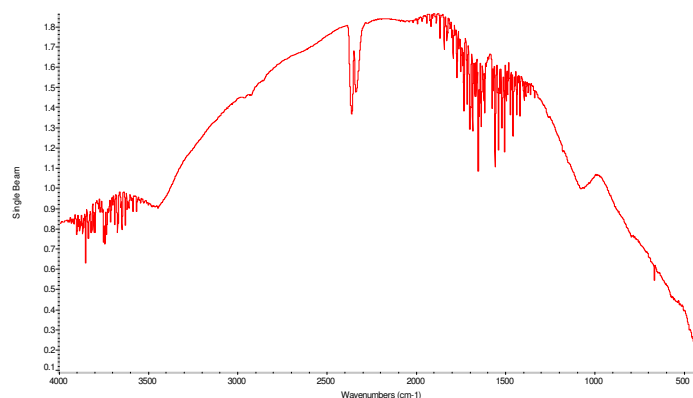


Figure 20 A background spectrum taken from a potassium bromide plate

Fourier Transform Infrared Spectroscopy (FT-IR) is a qualitative method for investigating sample structure. Samples such as vegetable oil and epoxidised resin both have characteristic spectrums. When a molecule present in the sample's structure absorbs radiation of a given wavenumber ( $frequency/c$ ) it is presented in the spectrum as a peak at that wavenumber (Ebbing and Gammon, 2005). Depending on the atom and bond type composition of a molecule, that molecule will always appear at the same wavenumber on a spectrum. This assumes of course that such thermodynamic properties such as pressure and temperature are also consistent for each sample spectrum.

The spectrum presented in Figure 21 is taken from a sample of hemp oil (Eco-Fibre) at room temperature. Although triglyceride oils of varying fatty acid composition would produce differing spectrums, Figure 21 provides a fairly good representation of the type of spectrum one could expect.

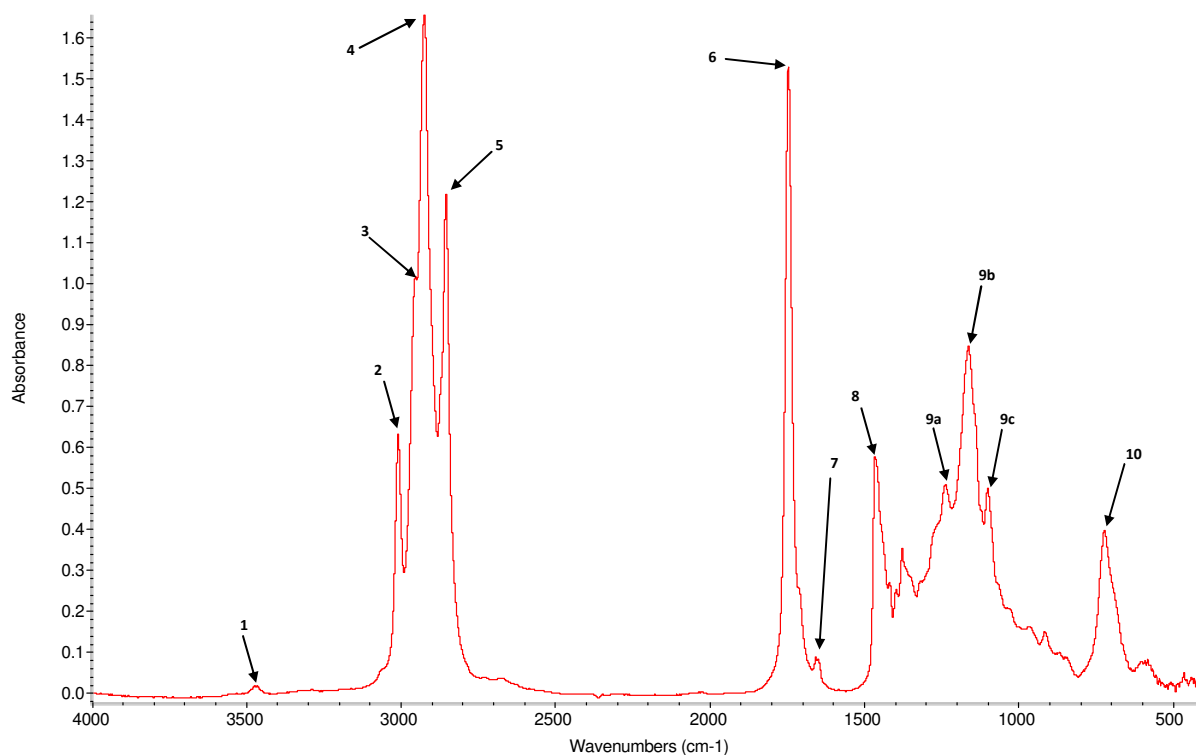
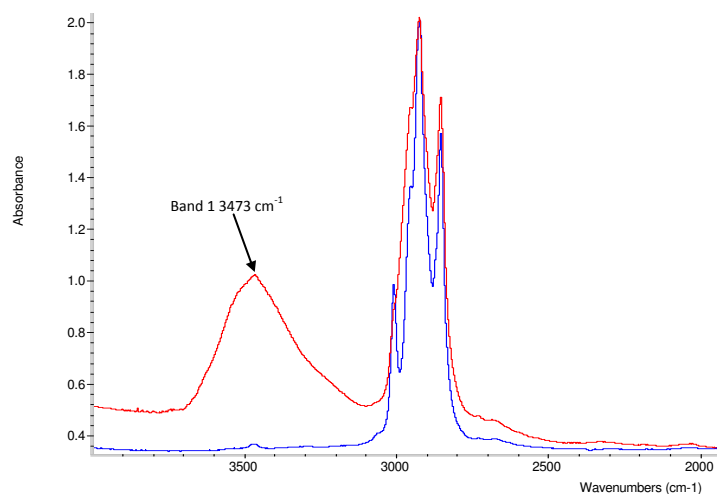


Figure 21 FT-IR spectrum of hemp oil. Wavenumbers of significant peaks occur at: (1)  $3473\text{ cm}^{-1}$ ; (2)  $3010\text{ cm}^{-1}$ ; (3)  $2955\text{ cm}^{-1}$ ; (4)  $2926\text{ cm}^{-1}$ ; (5)  $2854\text{ cm}^{-1}$ ; (6)  $1745\text{ cm}^{-1}$ ; (7)  $1656\text{ cm}^{-1}$ ; (8)  $1465\text{ cm}^{-1}$ ; (9a)  $1238\text{ cm}^{-1}$ ; (9b)  $1163\text{ cm}^{-1}$ ; (9c)  $1100\text{ cm}^{-1}$ ; (10)  $723\text{ cm}^{-1}$ ;

The peaks of molecules with significant structural importance to the triglyceride molecule are designated band numbers. Band 1 represents the stretching vibration of an OH group. Although OH groups are present in fatty acid chains this group is lost via the ester reaction when a fatty acid chain bonds to a glycerol molecule. It is likely that the OH group appearing at band 1 is due to the presence of a percentage of  $\text{H}_2\text{O}$  in the sample. This assumption is supported by the fact that a sample of epoxidised hemp oil that emulsified while being washed with water produced a spectrum (Figure 22) with a prominent peak at wavenumber  $3473\text{ cm}^{-1}$ .



**Figure 22 Comparison of normalised hemp oil and epoxidised hemp oil spectrums, with the red curve representing the epoxidised sample. The high peak at band 1 is most likely due to the presence of H<sub>2</sub>O as this sample experienced a degree of emulsification.**

It is commonly accepted (Albuquerque et al, 2003) that the vibration at  $3010\text{ cm}^{-1}$  (band 2) is the same for most vegetable oils and is due to the CH stretching related to =C-H bonding. This band is an important consideration in this research as it is this double bond that is consumed to produce an epoxy group. A successful epoxidation reaction is considered to be one that consumes all of peak 2, suggesting that the maximum number of epoxy groups may have formed.

Band 3, band 4 and band 5 are assigned to the C-H stretching of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) groups. Asymmetric stretching of a CH<sub>3</sub> group is responsible for the vibration at  $2955\text{ cm}^{-1}$  (band 3), though it produces only a minor peak. Two highly pronounced bands follow at vibrations  $2926\text{ cm}^{-1}$  (band 4) and  $2854\text{ cm}^{-1}$  (band 5) and are common to most triglyceride oil spectrums. They are the result of CH<sub>2</sub> asymmetric and symmetric stretching vibrations, respectively.

A strong band appears at vibration  $1745\text{ cm}^{-1}$  (band 6) and corresponds to the C=O stretching vibration of the carboxylic groups. This group is present in all fatty acid chains and occurs adjacent to where the fatty acid chain joins to the glycerol molecule. The epoxidation process has little effect on the absorbance of the carboxylic groups, and band 6 will remain virtually unchanged for the vegetable oil and its epoxidised counterpart. This is an advantage as it allows the spectrum of the epoxidised vegetable oil to be normalised against the spectrum of the original vegetable oil. Figure 23 shows a number of epoxidised hemp oil C=O peaks that have been normalised by scaling up or down to match a hemp oil C=O peak.

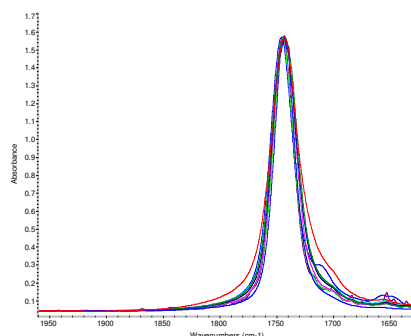


Figure 23 Normalised peaks rely of the stability of the carboxylic groups at  $1745\text{ cm}^{-1}$ .

To the right of band 6 in figure 1 appears a very weak band 7 at vibration  $1656\text{ cm}^{-1}$ . This band is assigned to a C=C stretching vibration. Researchers verify this as being correct as this band doesn't appear on spectrum of saturated vegetable oils, in which the C=C bond doesn't occur (Albuquerque et al, 2003). If while examining the spectrum of epoxidised vegetable oil it is observed that band 7 has diminished or disappeared, there's a distinct possibility that the epoxidation reaction was successful. However while some of the C=C bonds may have become epoxies, others could have formed into other groups such as  $\alpha$ -glycols. As is discussed below, bands which appear in epoxidised vegetable oil spectrums offer a stronger indication that epoxy groups have formed.

Band 8 at  $1465\text{ cm}^{-1}$  is assigned to the  $\text{CH}_2$  scissors deformation vibration. The  $\text{CH}_2$  group is common in the triglyceride molecule, though no information was found relating to whether it is specific to the occurrence of this group in the glycerol or fatty acid segments of the triglyceride molecule, or both. Band 8 should stay relatively unaffected by the epoxidation reaction.

A prominent band occurs at vibration  $1163\text{ cm}^{-1}$  and is designated band 9b. On either side are two weaker bands at vibrations  $1238\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  which carry designations of band 9a and band 9c, respectively. This profile of bands is assigned to the C=C-C-O stretching vibration. They should appear weaker in the spectrum of epoxidised samples compared to the spectrum of the base vegetable oil, due to the consumption of the double bond.

Band 10 in Figure 21 and appearing at vibration  $723\text{ cm}^{-1}$  is assigned to the  $\text{CH}_2$  rocking mode. Another band of great importance which doesn't appear in Figure 21 occurs at wavenumber  $823\text{ cm}^{-1}$ . This band is assigned to the C-O-C epoxy group and is unlikely to appear in the spectrum of vegetable oils, though its occurrence is evident in the spectrum of epoxidised samples, as will be shown below.

Table 6 Summary of significant bands appearing in Figure 21.

<b>Band Number</b>	<b>Wavenumber (cm-1)</b>	<b>Bond</b>	<b>Type</b>
1	3473	<b>OH</b>	Stretching
2	3010	<b>=C-H</b>	Stretching
3	2955	<b>CH<sub>3</sub></b>	Asymmetric Stretching
4	2926	<b>CH<sub>2</sub></b>	Asymmetric Stretching
5	2854	<b>CH<sub>2</sub></b>	Symmetric Stretching
6	1745	<b>C=O</b>	Stretching
7	1656	<b>C=C</b>	Stretching
8	1465	<b>CH<sub>2</sub></b>	Scissors
9	1238(a), 1163(b), 1100(c)	<b>C=C-C-O</b>	Stretching
10	723	<b>CH<sub>2</sub></b>	Rocking

### Interpreting an epoxidised sample

The following two figures compare the spectrums of linseed oil and epoxidised linseed oil. Figure 24 shows region  $3650\text{ cm}^{-1}$  to  $2200\text{ cm}^{-1}$ , and Figure 25 shows region  $2200\text{ cm}^{-1}$  to  $650\text{ cm}^{-1}$ . The spectrum has been split in two simply to promote clarity. The green curve represents the epoxidised sample and the red curve represents the oil sample.

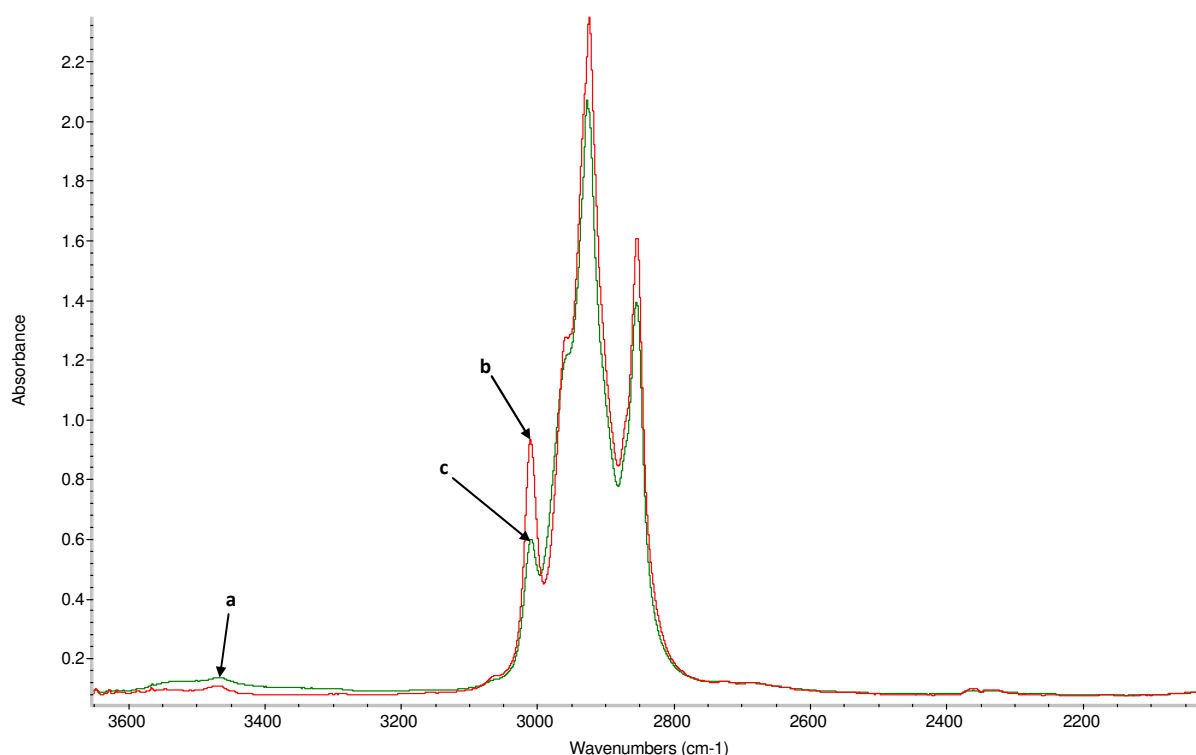


Figure 24 FTIR spectrum of linseed oil and epoxidised linseed oil, from  $3650\text{ cm}^{-1}$  to  $2200\text{ cm}^{-1}$ .

- (a) This peak corresponds to band 1 at wavenumber  $2473\text{ cm}^{-1}$ . We previously established that this peak is most likely due to the presence of  $\text{H}_2\text{O}$  molecules in the sample. It can be observed that this peak is larger for the epoxidised sample, suggesting that the sample contains some residual water from the cleaning process. This is important because the presence of water will affect the results of the iodine test. Further experimentation is required to determine if more thorough drying with anhydrous sodium sulphate would diminish this band.



- (b) Band 2 is strongly dependent on the presence of double carbon to carbon bonds. This band is quite strong in the oil sample but is diminished due to the consumption of double bonds in the epoxidation process.
- (c) The green curve shows the diminished band 2 in the epoxidised sample. The maximum conversion of double bonds to epoxy groups is possible when the green band 2 is completely diminished.

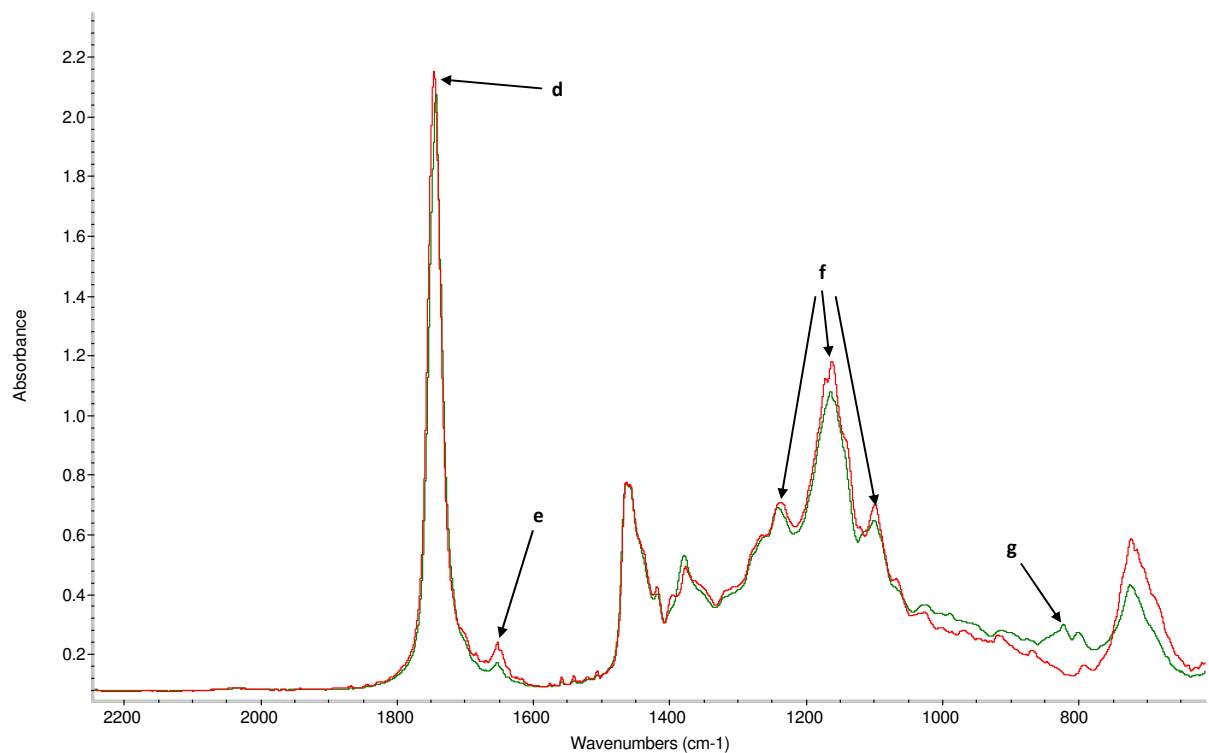


Figure 25 FTIR spectrum of linseed oil and epoxidised linseed oil, from 2200  $\text{cm}^{-1}$  to 650  $\text{cm}^{-1}$ .

- (d) Band 6 at 1745  $\text{cm}^{-1}$  is the same for both the oil sample and the epoxidised sample. The two spectrums are normalised by either scaling the epoxidised band 6 up or down until it matches band 6 of the vegetable oil.

- (e) The weak band 7 is assigned to the C=C stretching vibration. It can be observed that the epoxidation reaction consumes a proportion of the double bonds. Ideally the green band 7 would be completely diminished.
  
- (f) These three peaks belonging to bands 9a, 9b and 9c are also influenced by double carbon to carbon bonds. It can be observed that the bands are diminished by the epoxidation reaction, suggesting that double bonds have been consumed.
  
- (g) This band is not present in the 'red' oil spectrum, but becomes noticeable in the 'green' epoxidised sample. This band at  $823\text{ cm}^{-1}$  is assigned to the epoxy group (C-O-C) and shows that the epoxidation reaction has indeed produced epoxy groups by consuming the double bonds.

### 3.6.2 Titration methods for iodine value and oxirane oxygen content

#### Determining the iodine value (Wij's method)

Determination of the iodine value was in occurrence with the Wijs method (Paquot, 1979), as laid out in: Standard Methods for the Analysis of Oils, Fats and Derivatives, as compiled by the Union of Pure and Applied Chemistry.

#### *Reagents*

- a) Wij's solution
- b) Carbon tetrachloride
- c) Potassium iodide
- d) Starch
- e) Pure water

#### **Wijs solution**

The Wij's solution can be made but is also available as an off-the-shelf product. For this research the Wij's solution used came in this fashion.

#### **Potassium Iodide Aqueous Solution**

The potassium iodide came in a dry granulated form from BHD chemicals. It is necessary to make it into an aqueous solution of concentration: 100 g ( $K^+I^-$ )/ 1000 ml ( $H_2O$ )

1. Into a 500 ml bottle measure accurately 50 g of potassium iodide ( $K^+I^-$ ).
2. Add 500 ml of pure water and dissolve potassium iodide by shaking.

Each titration requires 20 ml of potassium iodide solution.

#### **Sodium Thiosulphate Aqueous Solution**

This constitutes the titrating solution in the iodine test. A 0.1N solution is required. The formulation of sodium thiosulphate used was  $Na_2S_2O_3 \cdot 5H_2O$  which has a molar mass of 248.18 g/mol. To make a 0.1 N aqueous solution of sodium thiosulphate the following method was used.

1. Measure as accurately as possible 25 g of  $Na_2S_2O_3 \cdot 5H_2O$  into a 1000 ml ground neck volumetric flask, keeping an accurate record of exactly how much  $Na_2S_2O_3 \cdot 5H_2O$  was used.
2. Add to the volumetric flask 1 litre of pure water. Store in the dark.

3. It is important to determine the exact normality of the solution for use in the I.V. equation.

This is achieved by applying the equation:

Equation 13

$$T = \frac{n}{V} = \frac{\left( \frac{\text{grams of } Na_2S_2O_3 \cdot 5H_2O}{\text{molar mass of } Na_2S_2O_3 \cdot 5H_2O} \right)}{\text{Volume of Water (litres)}}$$

For instance, say 31.87 g of  $Na_2S_2O_3 \cdot 5H_2O$  was used instead of 25 g. The normality would then be:

$$T = \frac{\left( \frac{31.87 \text{ g}}{248.18 \text{ g/mol}} \right)}{1 \text{ l}} = 0.1284 \text{ N}$$

### Starch Solution

The starch solution is the indicator in this titration. Only about 1.5 ml of starch solution is required per titration, and it is advisable to make a new solution for each day of testing as stored starch can encourage the growth of bacteria. The required concentration is 10 g (starch)/ 1 litre (pure water), which can be scaled up or down.

1. Into a small bottle add 1 g of starch.
2. Add in 100 ml of pure water, place the lid and shake well.

Some starches may settle out of the solution over time so it is may be necessary to shake regularly.

### Procedure

The following table gives an indication of how much sample should be used per titration.

Table 7 Recommended amount of sample depending on the sample's iodine value

Expected iodine value (g I <sub>2</sub> /100 g oil)	Amount of sample (g)
<5	3.00
5 to 20	1.00
21 to 50	0.40
51 to 100	0.20
101 to 150	0.13
151 to 200	0.10

For hemp oil it is expected that the iodine value will fall between about 80 and 130 (g I<sub>2</sub>/100 g oil), and decrease as the epoxidation reaction progresses. It was decided to use 0.3 g of sample per titration.

- 1) Weigh 0.3 g (accurately, and record exact amount) of oil into a ground neck Erlenmeyer flask. Record exact amount used.
- 2) Measure in 15ml (accurately) of Carbon Tetrachloride using a measuring cylinder
- 3) Add exactly 25 ml of Wijs solution using a 25 ml pipette and pipette bulb
- 4) Prepare a blank test sample with the above, but excluding the oil or resin
- 5) Swirl gently, releasing stopper to release gas
- 6) Place test sample and blank in the dark
- 7) For straight oil and blank, leave the sample in the dark for 1 hour. For the polymerised material, leave in the dark for 2 hours
- 8) Add 20 ml of potassium iodide solution, measuring with a measuring cylinder
- 9) Add 150 ml of pure water, measuring with a measuring cylinder
- 10) Add 1.5 ml (approximately) of starch solution as the indicator
- 11) Titrate with sodium thiosulphate solution, stirring constantly with a magnetic stirrer.

The final colour will be white and will occur quickly. Once the titration has been conducted on the sample and the blank, the Iodine value is determined by applying the following equation.

Equation 14

$$I.V. = \frac{12.69 \cdot T \cdot (V_3 - V_4)}{m}$$

T = the exact normality of sodium thiosulphate

V<sub>3</sub> = ml of sodium thiosulphate solution used to titrate the blank

V<sub>4</sub> = ml of sodium thiosulphate solution used to titrate the test sample

m = the mass of the sample material used

### The oxirane oxygen content

A direct titration method is applied to determine the epoxy-group oxygen content. This method uses a hydrobromic acid-acetic acid reagent. The structural formula is given in Figure 26

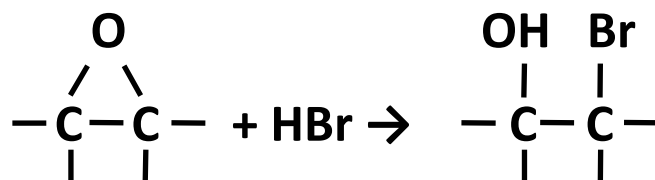


Figure 26 Structural formula of the epoxy group oxygen content titration

Hydrobromic acid is a very strong acid and is ideal for testing as it has a fast rate of reaction with the epoxy oxygen groups.

Determination of the oxirane oxygen content was by the direct method of HBr in AA (Paquot), as laid out in: Standard Methods for the Analysis of Oils, Fats and Derivatives, as compiled by the Union of Pure and Applied Chemistry.

#### *Reagents*

- a) Benzene
- b) Glacial acetic acid
- c) Hydrobromic acid 48% solution
- d) Crystal violet

#### **Hydrobromic Acid - Acetic Acid Solution**

This constitutes the titrating solution in the oxirane-group oxygen test. A 0.1 N solution is required. The molar mass of Hydrobromic acid (*HBr*) is 80.91 *g/mol*. The Hydrobromic acid used came in a 48% solution. To make a 0.1 N solution in 250 *ml* of acetic acid the following method was used.

1. Applying the following equations:

*Mass of HBr*

Equation 15

$$m_{\text{HBr}} = \left( \frac{\text{molar mass of HBr}}{\text{HBr solution concentration}} \times \text{desired normality} \right)$$

$$m_{\text{HBr}} = \frac{80.91(\text{g/mol})}{0.48} \times 0.1 \text{ N} = 16.8563 \left( \frac{\text{g (HBr)}}{\text{litre (acetic acid)}} \right)$$

Note that the above will make 1 litre of Hydrobromic acid in acetic acid solution, which doesn't store well, and it is advisable that it be used in one day. For this reason only a quarter of a litre was made at a time.

2. Measure accurately into a bottle  $4.214 \text{ g} \left( \frac{16.8563}{4} \right)$  of HBr. If it is not possible to measure exactly this amount, accurately record how much is used.
3. Add to the bottle exactly 250 ml of acetic acid
4. Determine the normality using:

Equation 16

$$T = \frac{\left( \frac{0.48(\text{grams of HBr})}{\text{molar mass of HBr}} \right)}{\text{Volume of acetic acid (litres)}}$$

For instance, if 5 g of HBr is used along with 255 ml of acetic acid, then the normality *T* is:

$$T = \frac{\left( \frac{0.48(5)}{80.91} \right)}{0.25} = 0.1187 \text{ N}$$

The value of normality will be required for entry into the oxirane group oxygen equation.

**Crystal Violet Acetic Acid Solution**

This is the indicator solution in the oxirane group oxygen titration. A 1 g/ l acetic acid solution is required. Since only 0.1 ml of indicator is required per titration it is only necessary to make a small quantity.

1. Measure into a bottle 0.1 g of crystal violet
2. Add to bottle 100 ml of acetic acid

Once made it is possible to store the indicator solution for later use.

**Procedure**

- 1) Accurately weigh 0.4 g of sample (oil or resin) into a ground neck Erlenmeyer flask, accurately recording the exact amount.
- 2) Mix in 10 ml of benzene. A 10 ml pipette will make the job easier.
- 3) Add one drop of indicator solution.
- 4) Begin stirring by introducing the magnetic stirring bar.
- 5) Titrate with Hydrobromic acid – acetic acid solution until a bluish-green colour persists for 30 seconds. Record amount of titrating solution has been used.

Once the titration is complete the following formula will yield the percentage (*t*) of oxirane group oxygen in the fat or resin.

Equation 17

$$t = \frac{1.60 \times V \times T}{m}$$

*V* = Amount of HBr – AA solution used in titration in (ml)

*T* = exact normality of the HBr – AA solution

*m* = mass of sample used in (grams)



### 3.7 References

1. Albuquerque, MLS Guedes, I Alcantara Jr, P & Moreira, SGC 2003, 'Infrared absorption spectra of Buriti (*Mauritia flexuosa L.*) oil', *Variational Spectroscopy*, vol. 33, pp. 127-131
2. Dinda S, Goud VV, Patwardhan AV, Pradhan NC (2008) Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic acids. *Bioresour Technol*.
3. Ebbing, DD & Gammon, SD 2005, '*General Chemistry*' 8<sup>th</sup> ed, Houghton Mifflin
4. Goud VV, Patwardhan AV, Pradhan NC (2006) Studies on the epoxidation of mahua oil (*Madhumica Indica*) by hydrogen peroxide. *Bioresour Technol* 97(12):1365–1371
5. Goud VV, Patwardhan AV, Pradhan NC (2006) Epoxidation of karanja (*Pongamia Glabra*) oil by H<sub>2</sub>O<sub>2</sub>. *J Am Oil Chem Soc* 83(7):635–640
6. Goud VV, Patwardhan AV, Dinda S, Pradhan NC (2007) Epoxidation of karanja (*Pongamia glabra*) oil catalyzed by acidic ion exchange resin. *Eur J Lipid Sci Technol* 109(6):575–584
7. Goud VV, Patwardhan AV, Dinda S, Pradhan NC (2007) Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chem Eng Sci* 62(15):4065–4076
8. Mungroo R, Pradhan NC, Goud VV, Dalai AK, (2008) Epoxidation of Canola Oil with Hydrogen Peroxide Catalyzed by Acidic Ion Exchange Resin. *J Am Chem Soc* 85:887-896
9. Paquot C (1979) *Standard methods for the analysis of oils, fats and derivatives part I*, 6th edn. Pergamon, Oxford, pp 66–70
10. May CA (1973) *Epoxy resins: chemistry and technology*. Marcel Dekker, New York, pp 672–673
11. Petrovic AS, Zlatanovic A, Lava CC, Sinadinovic-Fiser S (2002) Epoxidation of soybean oil in toluene with peroxyacetic acid and peroxyformic acids—kinetics and side reactions. *Eur J Lipid Sci Technol* 04:293–299
12. Sinadinovic-Fiser S, Jankovic M, Petrovic ZS (2001) Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. *J Am Oil Chem Soc* 78(7):725–731

## 4 Results and discussion

### 4.1 Introduction

Throughout the duration of this research 12 batches of vegetable oil were epoxidised. Epoxidation has been achieved and the following represents the results garnered for batches that resulted in a useful sample. The effectiveness of the epoxidation reaction has been qualitatively assessed by FTIR for each case. To gain truly insightful information about the success of the reaction the epoxidised sample needs to be tested using titration methods, as these give quantitative results. Titration methods however require considerable laboratory time for the novice researcher, and some time was used sourcing chemicals for and details of the titration methods. As a result it was decided to narrow the field of options by using FTIR to establish the effect of process parameters on VO epoxidation.

Initially experiments were carried out on linseed oil (LO), sunflower oil (SFO), mutton tallow and hemp oil (HO). The results of the epoxidation reaction were inspected using FTIR to determine how much of the band at  $3010\text{ cm}^{-1}$  had been consumed. It should be noted that for most of these batches there was more of a learning process occurring than an experimentation process. Eventually however it was decided to focus the research on HO. It had already been established by FTIR that over 8 hours at  $75\text{ }^{\circ}\text{C}$ , about 99 % consumption of the band at  $3010\text{ cm}^{-1}$  could be achieved with a molar ratio of 1.0:0.4:1.3. No information about the evolution of the reaction had yet been made.

The final part of this research consisted of a closer examination of the epoxidation of hemp oil. Two batches of hemp oil using molar ratios of 1.0:0.34:1.0 and 1.0:0.67:1.0 were epoxidised. These molar ratios more or less fell on either side of that which was shown previously by FTIR to give optimum results for hemp oil. Samples were extracted at 1 hour intervals over an 8 hour period. They were then inspected using FTIR as usual, and these results were supported by titration methods.

### 4.2 Raw linseed oil

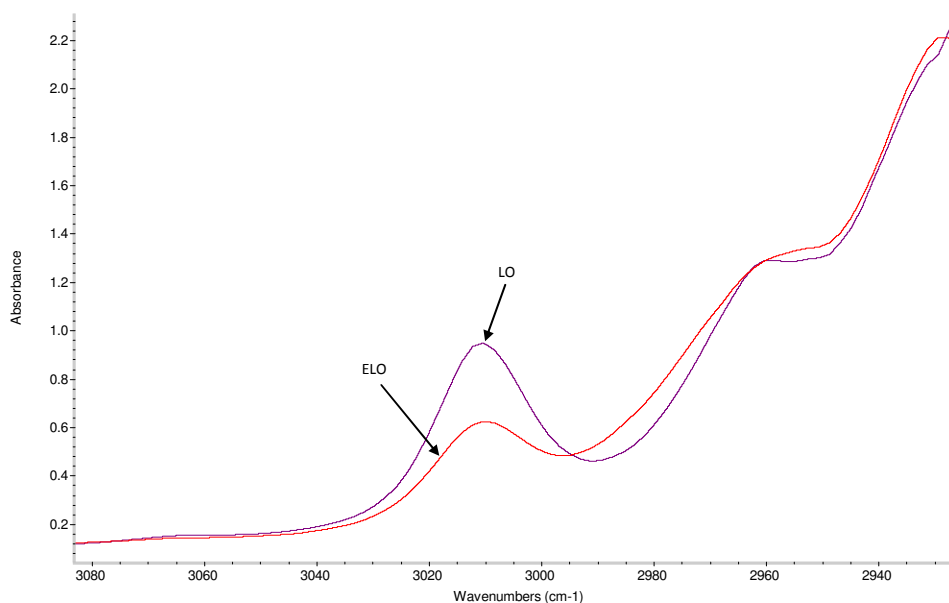
Riggers brand raw linseed oil was purchased from BMS Mitre 10 for the use in this research. This linseed oil is sold as outdoor decking oil, and there is no indication on the label that it contained any additives such as fungicides. This was the first vegetable oil that experiments were conducted on. The parameters of the reaction are presented in Table 8 below. The molar ratio of 1.0:0.5:1.5 was chosen because, as previously established, researchers such as Goud et al (2006, 2007) and Mungroo et al (2008), have often found these to be optimum ratios. The reactor temperature of  $75^{\circ}\text{C}$  was

chosen for similar reasons. The longest reaction time found in the literature to produce optimum results was for soybean oil (Sinadinovic-Fiser et al, 2001) at 7 hours. Eight hours was chosen for this reaction to ensure adequate time for double bond consumption to occur.

**Table 8 Process conditions for the epoxidation of linseed oil**

Linseed Oil								
Batch No:	Molar Ratio			Catalyst Loading (wt% oil)	Stirring Speed (rpm)	Reactor Temperature (°C)	Reaction Time (h)	% Double Bond Consumption
	Linseed Oil	Acetic Acid	Hydrogen Peroxide					
1L	1	0.5	1.5	10	100	75	8	61.2

After the linseed oil was reacted and washed it was analysed using FTIR. The comparisons of the linseed oil and the epoxidised linseed oil are shown in Figure 27 and Figure 28, with the purple line and the red line representing the linseed oil and epoxidised linseed oil respectively. Measurements indicate that the band at  $3010\text{ cm}^{-1}$  in Figure 27 has diminished by 61.20 % as a result of the reaction.



**Figure 27 FTIR of LO against ELO (1.0 : 0.5 : 1.5) showing a 61.2% consumption of band 2 at  $3010\text{ cm}^{-1}$**

Figure 28 shows that a definite band has formed at  $823\text{ cm}^{-1}$  indicating that epoxy groups have formed. It is possible that since the only epoxidised sample was taken at 8 hours, some of the epoxy groups may have degraded into alpha-glycol groups. Since only a 61.20% consumption of double bonds occurred, further refinement of the reaction parameters is required to produce optimum conditions. Higher molar ratios of either acetic acid, hydrogen peroxide or both are most likely required.

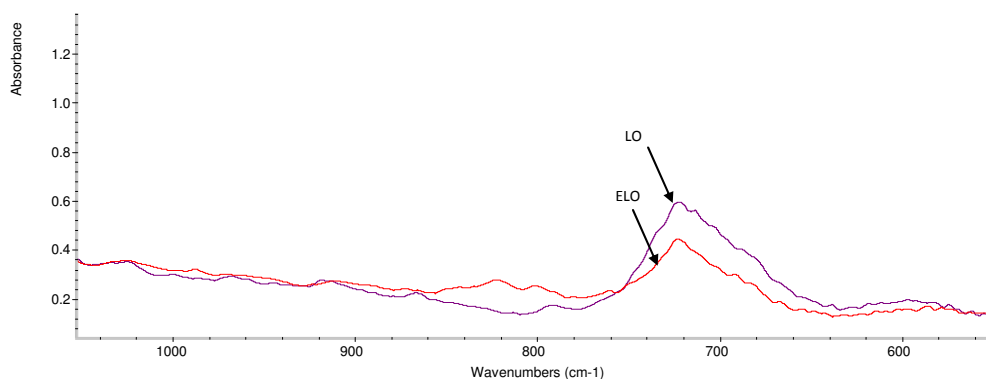


Figure 28 A definite band at  $823\text{ cm}^{-1}$  has formed in the epoxidised linseed oil sample (red line), indicating that the reaction has produced epoxy groups.

### 4.3 Sunflower oil

Commercial food grade sunflower oil was purchased from Coles for this experiment. In total four batches of sunflower oil were epoxidised, though two of these failed due to the formation of an emulsion during cleaning. The following results summarise the affect of processing conditions on the sunflower oil (SFO). The process conditions are summarised in Table 9.

Table 9 Process conditions for epoxidation of sunflower oil

Sunflower Oil								
Batch No:	Molar Ratio			Catalyst Loading (wt% oil)	Stirring Speed (rpm)	Reactor Temperature ( $^{\circ}\text{C}$ )	Reaction Time (h)	% Double Bond Consumption
	Sunflower Oil	Acetic Acid	Hydrogen Peroxide					
1SF	1	0.5	1.5	10	100	75	8	12.5
2SF	1	1	1.5	10	100	75	8	43.6

#### Batch 1 SF

As was the case with the linseed oil it was decided to begin by epoxidising the SFO using the following molar ratio; ethylenic unsaturation (1.0) : Acetic acid (0.5) : Hydrogen peroxide (1.5). The effect of the epoxidation reaction can be observed in Figure 29 and Figure 30, where the spectrum of the SFO sample (blue line) and the ESFO (red line) are compared. After 8 hours only a 12.5%

consumption of double bonds had occurred (Figure 29, band at  $3009\text{ cm}^{-1}$ ) and a very small epoxy group had formed (Figure 30, band at  $823\text{ cm}^{-1}$ ).

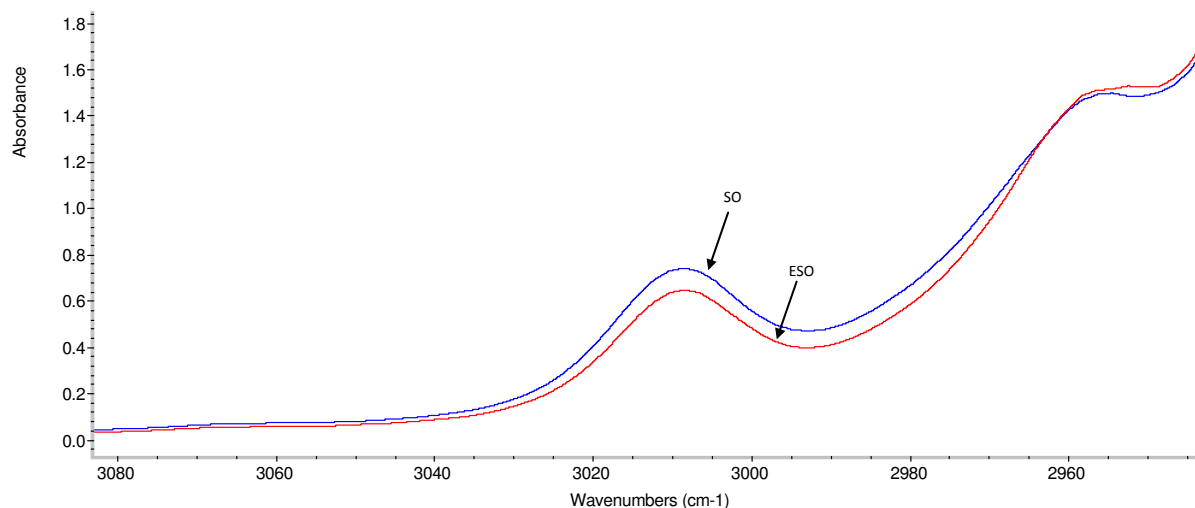


Figure 29 FTIR spectrums for sunflower oil (blue line) and epoxidised sunflower oil (red line). The molar ratios are (1.0:0.5:1.5) ethylenic unsaturation to acetic acid to hydrogen peroxide. The central band at  $3009\text{ cm}^{-1}$  indicates the consumption of double bonds, which in this case is very small.

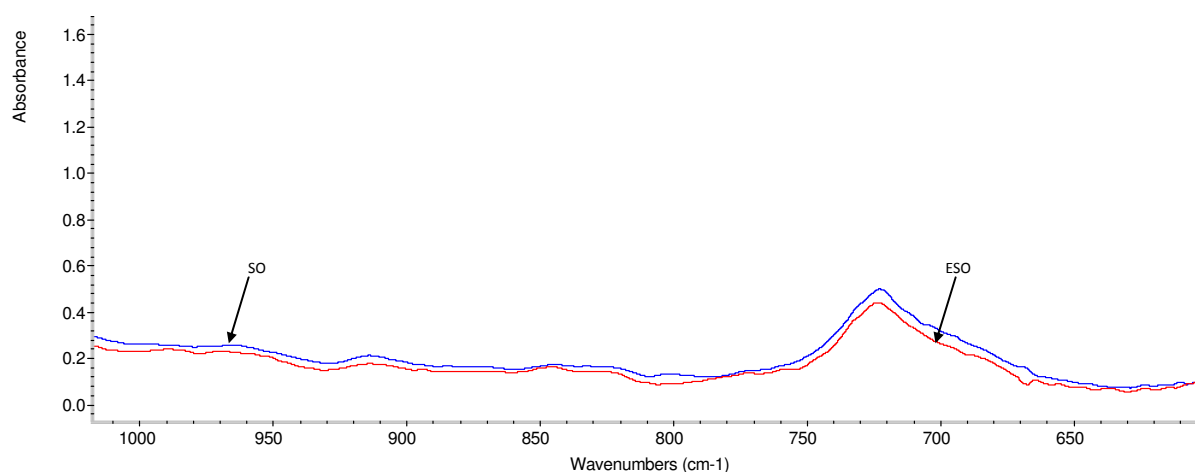


Figure 30 FTIR spectrums for sunflower oil (blue line) and epoxidised sunflower oil (red line). The molar ratios are (1.0:0.5:1.5) ethylenic unsaturation to acetic acid to hydrogen peroxide. The band of interest here lies at  $823\text{ cm}^{-1}$  and indicates the formation of epoxy groups. Very few epoxy groups have formed.

This is quite a poor result since similar reaction parameters have yielded high degrees of epoxidation in other vegetable oils. The molar ratio of acetic acid will be increased to explore the affect this has on the consumption of double bonds.

## Batch 2 SF

The molar ratio of acetic acid was increased from 0.5 to 1.0. The complete set of reaction parameters are given in Table 9. After 8 hours a 43.6% consumption of DB was measured by comparison of the spectrum bands occurring at  $3010\text{ cm}^{-1}$ , see Figure 31. No real peak at the band attributed to epoxy groups ( $823\text{ cm}^{-1}$ ) could be seen, see Figure 32.

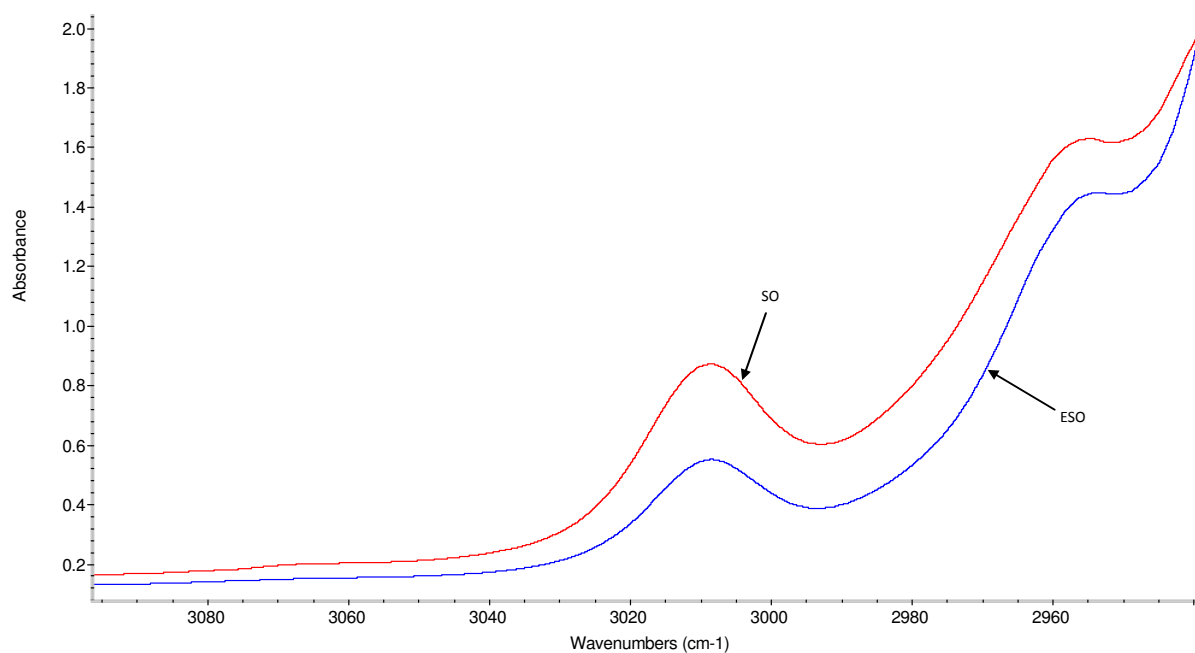


Figure 31 FTIR spectrums for sunflower oil (red line) and epoxidised sunflower oil (blue line). The molar ratios are (1.0:1.0:1.5) ethylenic unsaturation to acetic acid to hydrogen peroxide. The central band at  $3009\text{ cm}^{-1}$  indicates the consumption of double bonds, which is higher at 43.6%, though still not as substantial as expected.

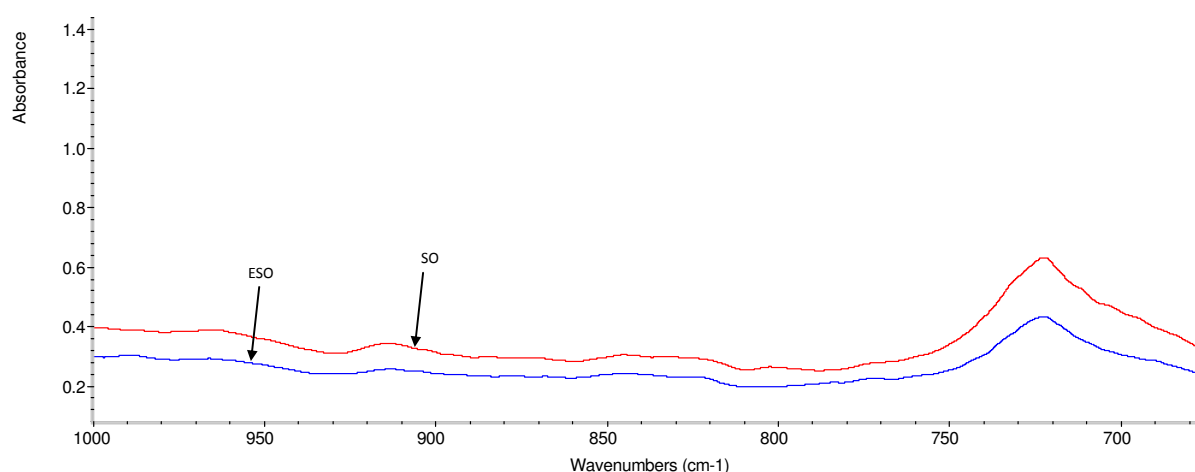


Figure 32 FTIR spectrums for sunflower oil (red line) and epoxidised sunflower oil (blue line). The molar ratios are (1.0:0.5:1.5) ethylenic unsaturation to acetic acid to hydrogen peroxide. The band of interest here lies at  $823\text{ cm}^{-1}$  and indicates the formation of epoxy groups. The indication here is that no epoxy groups have formed.

## 4.4 Mutton tallow

A clean source of mutton tallow became available and its suitability for epoxidation was explored. A spectrograph of the tallow was created by FT-IR, and the baseline was normalised against a spectrograph of hemp oil (as supplied by Eco-Fibre). The tallow was found to only contain 22% of the carbon double bonds present in the hemp oil, indicating that it would be unsuitable for epoxidation.

The lack of carbon double bonds is also indicated by the fact that the tallow is a solid at room temperature. The explanation for this is that the fatty acid chains are saturated and therefore are straighter. The straighter fatty acid chains can pack themselves closer together, resulting in the tallow being solid at room temperature.

A useful analogy is as follows. Imagine a number of strings of similar length, each laid out straight and grouped in a bundle. The strings have the ability to pack closely together. If however the strings have knots tied along their length (where the knots represent carbon double bonds), then this ability to pack closely together is limited. These knotted strings represent the unsaturated structure of vegetable oils and suggest why they are liquid at room temperature.

## 4.5 Hemp oil

Hemp oil (HO) was supplied by Eco-Fibre for use in this research. The process conditions used for this oil were similar to the aforementioned oils. Inspection of the properties in Table 10 shows some peculiar choices of molar ratios. The explanation for this is that the moles of double bonds present in 100 g of HO had been incorrectly calculated when these batches were reacted. The molar ratios shown in Table 10 indicate the corrected molar ratios, based on the presence of 0.64 moles of DB per 100 g of HO, instead of the previously calculated 0.43 moles of DB per 100 g of HO.

Table 10 Process conditions for epoxidation of hemp oil

Hemp Oil (Eco-Fibre)								
Batch No:	Molar Ratio			Catalyst Loading (wt% oil)	Stirring Speed (rpm)	Reactor Temperature (°C)	Reaction Time (h)	% Double Bond Consumption
	Hemp Oil	Acetic Acid	Hydrogen Peroxide					
1H	1	0.41	1.27	10	100	75	8	99
3H	1	0.81	0.89	10	100	75	8	97.6
4H	1	0.81	1.07	10	100	75	8	96

Batch 1H (1.0 : 0.4 : 1.3)

The first batch of hemp oil used a ratio of 1.0:0.4:1.3 and the reaction was allowed to persist for 8 hours at 75 °C. The sample was examined by FTIR which showed a 99% consumption of band 2 at 3010 cm<sup>-1</sup>, see Figure 33. Examination of the band at 823 cm<sup>-1</sup> in Figure 34 gives an indication that epoxy groups have formed, since a definite peak has formed.

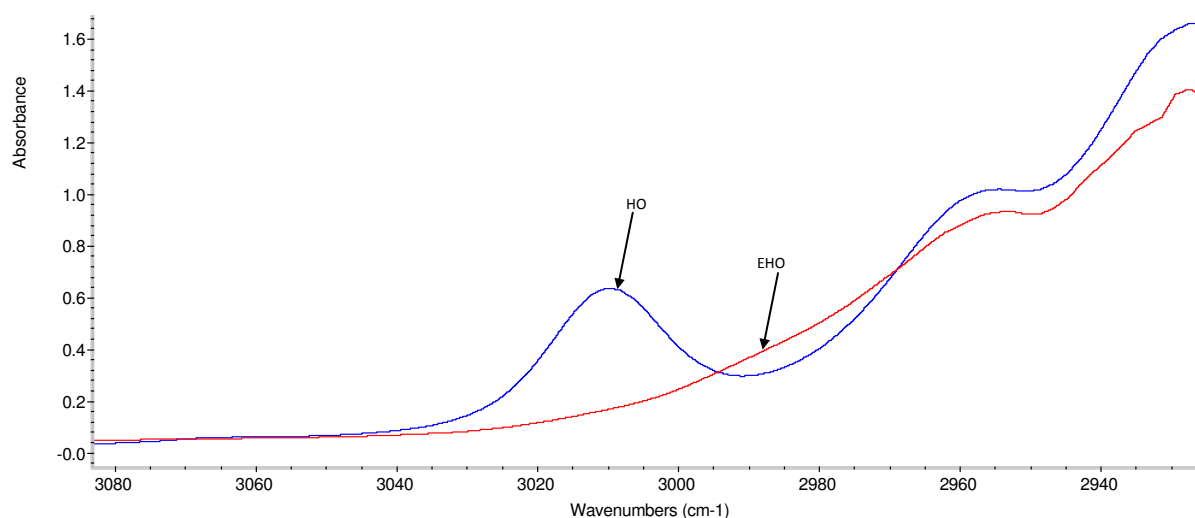


Figure 33 FTIR of HO against EHO (1.0 : 0.4 : 1.3) showing a 99% consumption of band 2 at 3010 cm<sup>-1</sup>



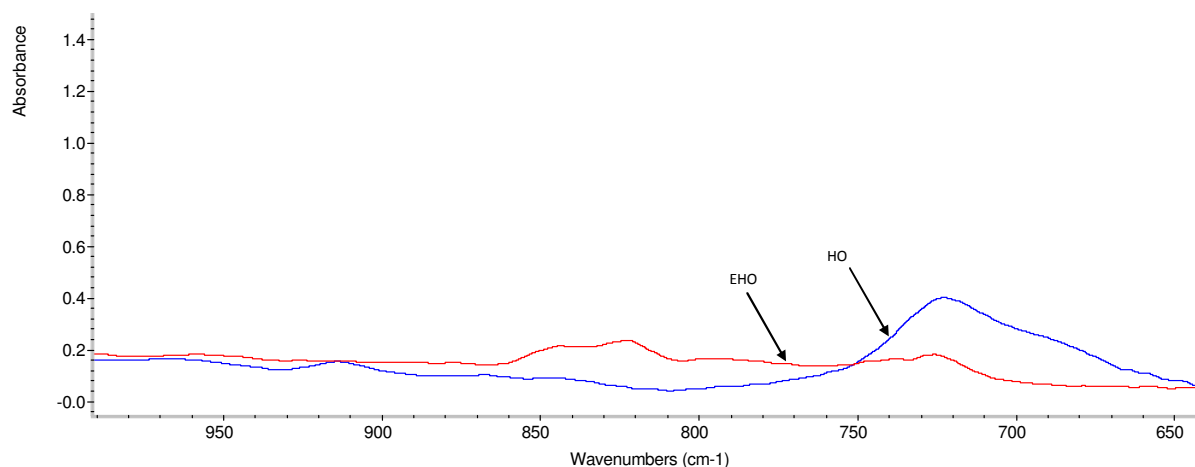


Figure 34 A definite band at  $823\text{ cm}^{-1}$  has formed in the epoxidised hemp oil sample (red line), indicating that the reaction has produced epoxy groups. The molar ration is 1.0 : 0.4 : 1.3.

#### Batch 2H (1.0 : 0.8 : 0.9)

At these molar concentrations a 97.6% consumption of DB was seen to occur. A definite peak can be observed at  $823\text{ cm}^{-1}$  in Figure 36, indicating the formation of epoxy groups. It should be noted that the scale of the plots presented here affects the apparent height of the bands. As a result the band at  $823\text{ cm}^{-1}$  in Figure 36 appears more substantial than that in Figure 34.

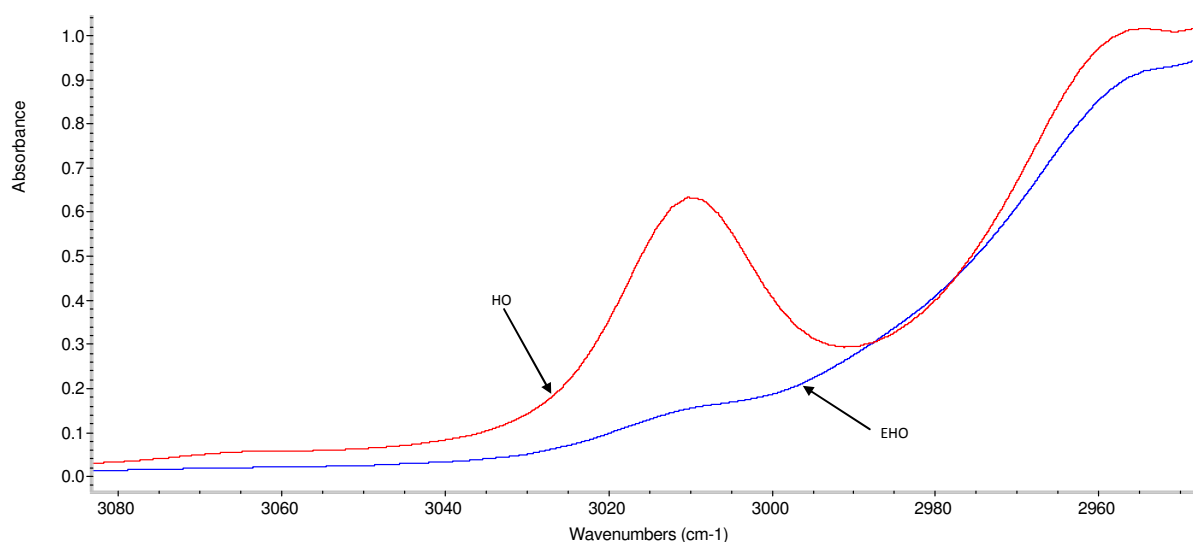


Figure 35 FTIR of HO against EHO (1.0 : 0.8 : 0.9) showing a 97.6% consumption of band 2 at  $3010\text{ cm}^{-1}$

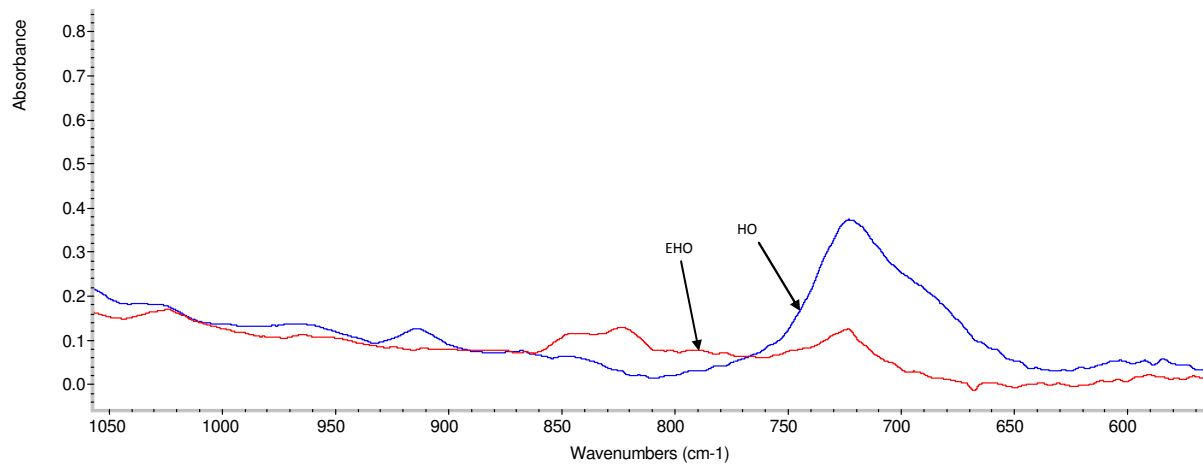


Figure 36 A definite band at  $823\text{ cm}^{-1}$  has formed in the epoxidised hemp oil sample (red line), indicating that the reaction has produced epoxy groups. The molar ratio is 1.0 : 0.8 : 0.9.

Batch 3H (1.0 : 0.8 : 1.1)

At these molar concentrations a 96% consumption of DB was seen to occur. A definite peak can be observed at  $823\text{ cm}^{-1}$  in Figure 38, indicating the formation of epoxy groups.

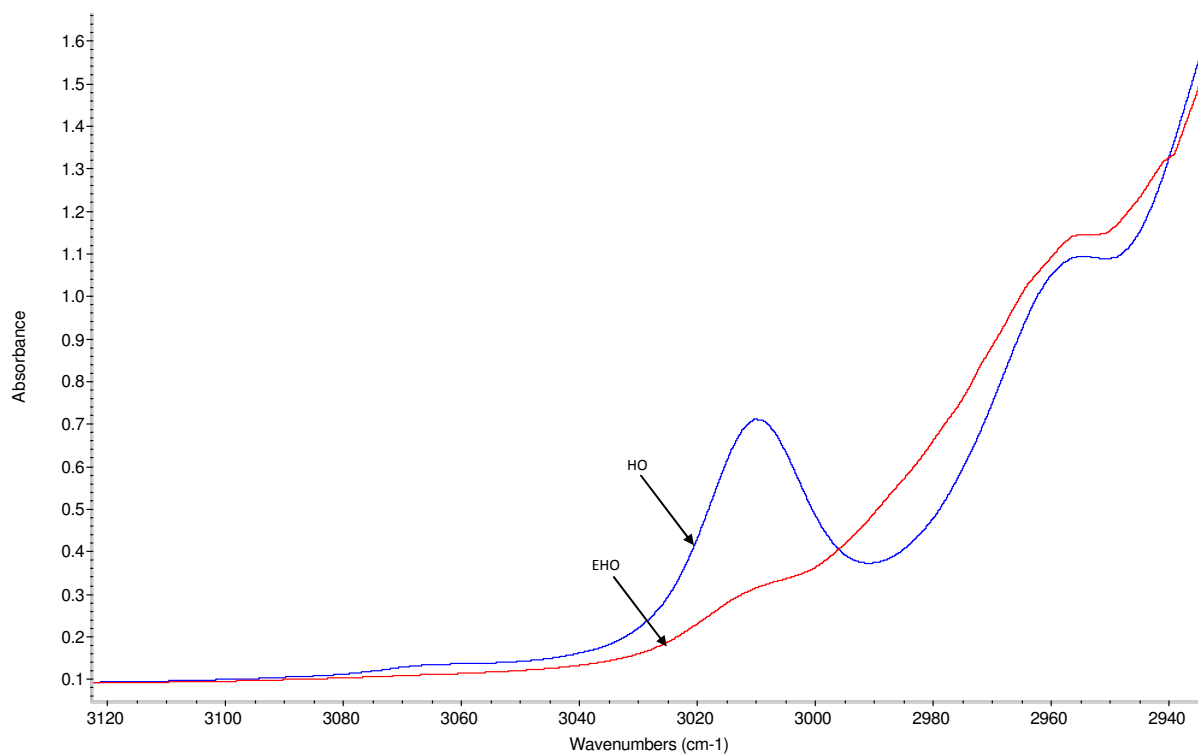


Figure 37 FTIR of HO against EHO (1.0 : 0.8 : 1.1) showing a 96% consumption of band 2 at  $3010\text{ cm}^{-1}$

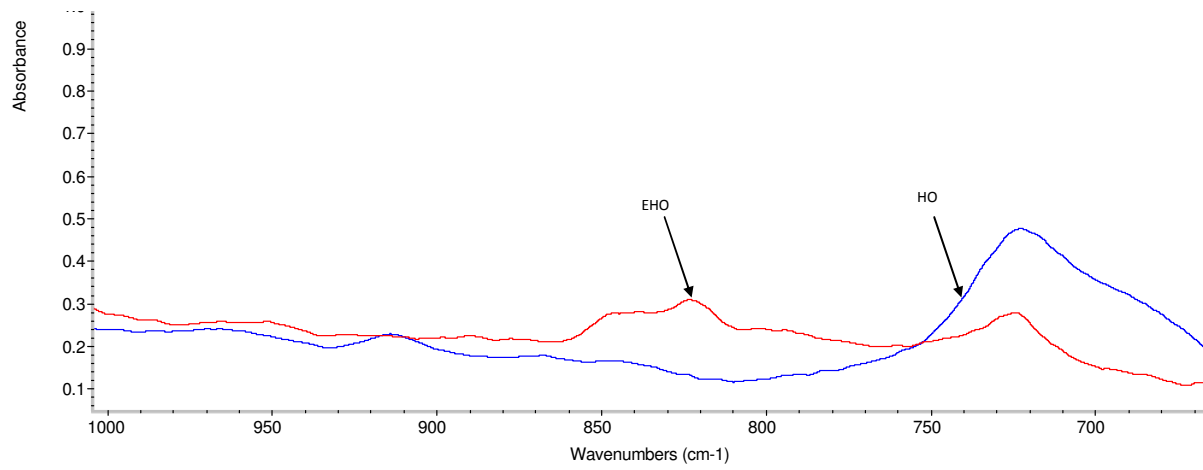


Figure 38 A definite band at  $823\text{ cm}^{-1}$  has formed in the epoxidised hemp oil sample (red line), indicating that the reaction has produced epoxy groups. The molar ratio is 1.0 : 0.8 : 1.1.

## 4.6 Detailed analysis of the epoxidation of hemp oil

Previous analysis of epoxidised HO using FTIR showed that 99% of the DB indicated in the spectrum at  $3010\text{ cm}^{-1}$  were consumed after 8 hours using a molar ratio of 1.0:0.4:1.3 (HO:AA:H<sub>2</sub>O<sub>2</sub>). This suggests that the initial concern of identifying reaction conditions that consumed all of the DB was successful. However there is little supporting evidence that the optimum reaction conditions have been identified. It is possible that lower molar concentrations of AA and H<sub>2</sub>O<sub>2</sub> would also result in a 99% consumption of DB. It is also possible that this occurred sometime before the 8 hour point when the reaction was discontinued. Probably the most important question however is whether the time at which maximum DB consumption occurs corresponds to the time at which the maximum number of epoxy groups has formed. The research of others suggests that at a certain point in the reaction the epoxy groups will begin to degrade into undesirable alpha-glycol groups. To address these concerns it is necessary to collect details of the epoxidation process at each hour of the reaction. This will allow FTIR to be used to create a more thorough overview of the time evolution of the reaction. Quantitative titration methods will also be employed to provide insight into other aspects of the reaction.

The batches of HO were epoxidised using the following process conditions:

**Table 11** Note that the catalyst loading has increased from 10% to 15%, and that the stirring speed has increased from 100 rpm to 130 rpm. The reasoning behind both of these increases was to ensure a more uniform distribution of catalyst through the mixture.

Hemp Oil (Eco-Fibre)								
Batch No:	Molar Ratio			Catalyst Loading (wt% oil)	Stirring Speed (rpm)	Reactor Temperature (°C)	Reaction Time (h)	% Double Bond Consumption
	Hemp Oil	Acetic Acid	Hydrogen Peroxide					
a	1	0.34	1	15	130	75	1 to 8	90.4
b	1	0.67	1	15	130	75	1 to 8	99

Samples were drawn from the two batches of EHO each hour during the reaction. They were washed, dried and examined initially using FTIR so that a general idea of the success of the reaction could be determined. Then titration methods were then used to determine the iodine value of the timed samples along with the percentage conversion to oxirane.

#### 4.6.1 Inspection of epoxidised HO using FTIR

Hemp Oil - 1.0:0.34:1.0 (Timed Samples)

A spectrum of each of the samples, taken every hour for 8 hours, was compiled and normalised against the spectrum of the HO. Attention was paid to bands 2, 7 and 9, (see Table 12) due to the presence of DB in these groups in the HO, and at  $823\text{ cm}^{-1}$  which is attributed to epoxy groups.

Table 12 Summary of significant bands.

<b>Band Number</b>	<b>Wavenumber (cm-1)</b>	<b>Bond</b>	<b>Type</b>
1	3473	<b>OH</b>	Stretching
2	3010	<b>=C-H</b>	Stretching
3	2955	<b>CH<sub>3</sub></b>	Asymmetric Stretching
4	2926	<b>CH<sub>2</sub></b>	Asymmetric Stretching
5	2854	<b>CH<sub>2</sub></b>	Symmetric Stretching
6	1745	<b>C=O</b>	Stretching
7	1656	<b>C=C</b>	Stretching
8	1465	<b>CH<sub>2</sub></b>	Scissors
9	1238(a), 1163(b), 1100(c)	<b>C=C-C-O</b>	Stretching
10	723	<b>CH<sub>2</sub></b>	Rocking

Figure 39 shows how the epoxidation reaction evolved over time by examining the band at  $3010\text{cm}^{-1}$ , which is associated with the group (=C-H). Considerable consumption of this band occurs in the first hour. The rate of consumption steadily decreases from this point, and the maximum consumption is achieved at 7 h at 90.4%. Measurements taken from the FTIR after this point indicate that the consumption decreases to 87.6 %. This is unlikely however to be the case, and it is most probably attributed to variations in the spectrum and operator error. It should be remembered that FTIR is only a qualitative method.

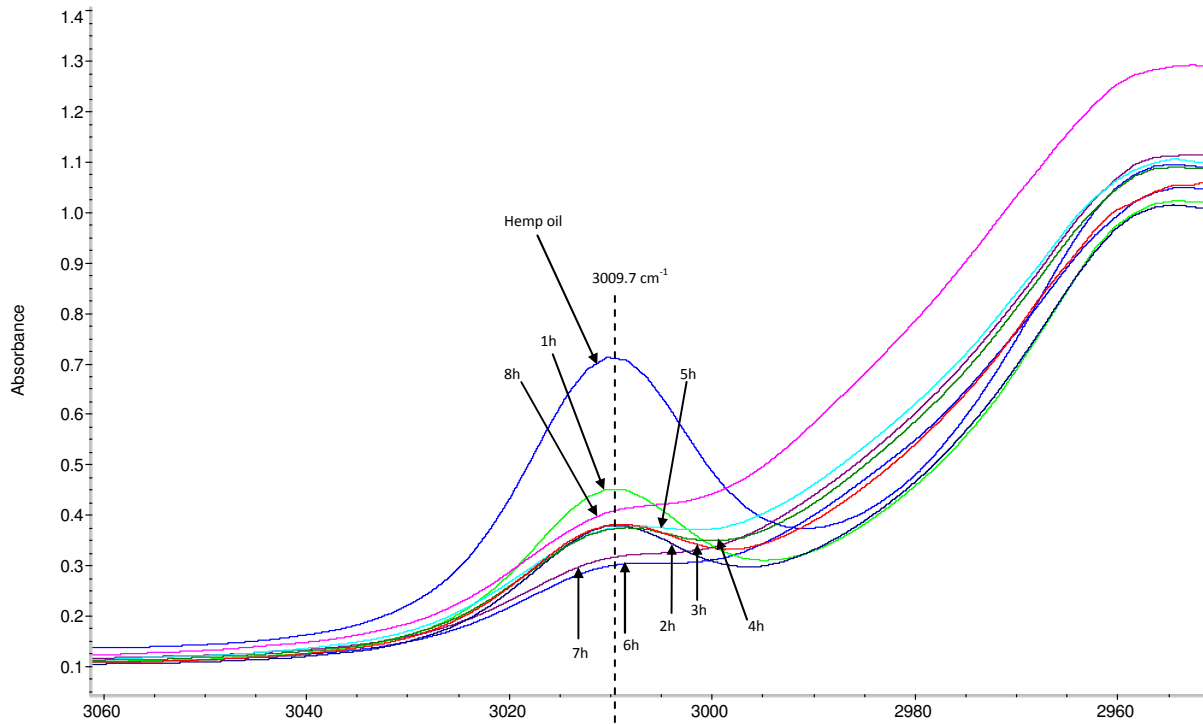


Figure 39 FTIR spectrum of HO compared to epoxidised HO sample spectrums taken at 1 hour intervals over an 8 hour period. The peak at wavenumber  $3010\text{ cm}^{-1}$  relates to double carbon to carbon bonds. After 8 hours there is virtually no peak and a measured DB consumption of 90.4%. The molar ratio was (1.0:0.34:1.0).

Figure 40 focuses on the band that occurs at  $823\text{ cm}^{-1}$  which occurs as a result of the presence of epoxy groups. In the original oil sample no peaks exists (blue line), and by 8 h a considerable peak exists.

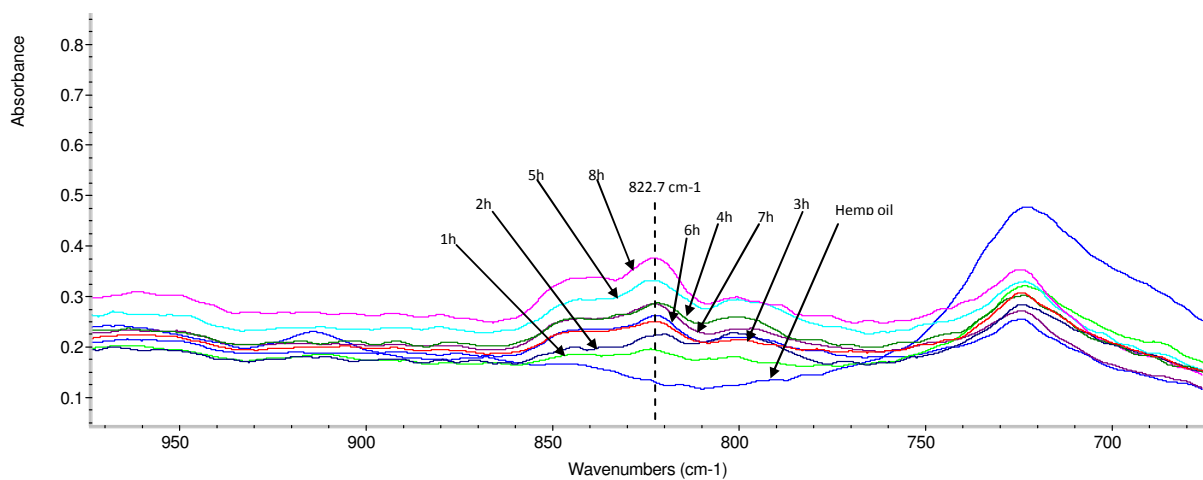


Figure 40 FT-IR of HO and EHO taken at 1 hour intervals over 8 hours. The peak for epoxy groups occur at wavenumber  $823.3\text{ cm}^{-1}$ . The molar ratio was (1.0:0.34:1.0).

Figure 41 shows a band occurring at  $1656\text{ cm}^{-1}$  which also represents the C=C bond. The C=C bond is also present in groups corresponding to bands at  $1238\text{ cm}^{-1}$ ,  $1163\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ . Starting at the band at  $1656\text{ cm}^{-1}$  (C=C, stretching) we see that after 8 hours the peak (red line) is considerably smaller though still clearly present. Bands at  $1238\text{ cm}^{-1}$ ,  $1163\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ , have also been reduced significantly after 8 hours.

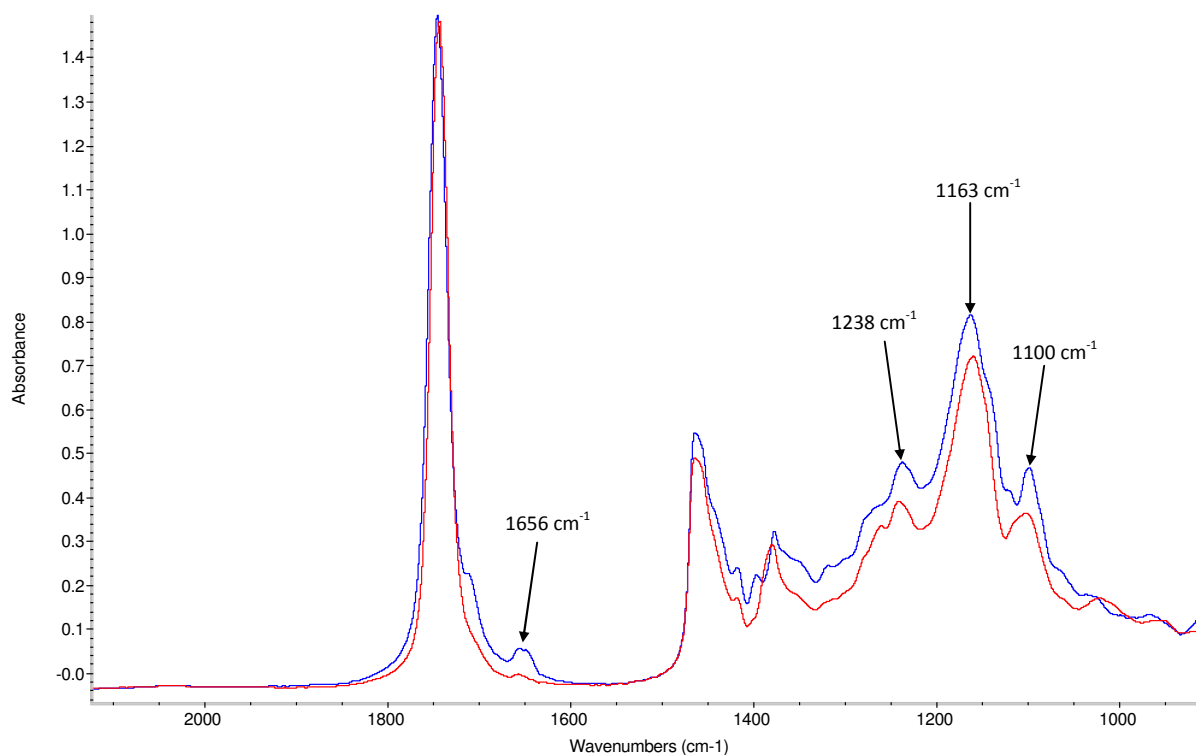


Figure 41 Arrows show bands that are affected by the consumption of double bonds in the epoxidation reaction. Special attention should be paid to the band at  $1656\text{ cm}^{-1}$ , which is attributed to the C=C stretching vibration. After 8 hours it can be seen that a small peak still exists here in the epoxidised sample (red line).

## Hemp Oil – 1.0 : 0.67 : 1.0 (Timed Samples)

A spectrum of each of the samples, taken every hour for 8 hours, was compiled and normalised against the spectrum of the HO. Attention was paid to bands 2, 7 and 9, (see Table 12) due to the presence of DB in these groups in the HO, and at  $823\text{ cm}^{-1}$  which is attributed to epoxy groups.

Figure 42 shows how the epoxidation reaction evolved over time by examining the band at  $3010\text{ cm}^{-1}$ , which is associated with the group  $(=\text{C}-\text{H})$ . Considerable consumption of this band occurs in the first hour. The rate of consumption steadily decreases from this point, and the maximum consumption is achieved at 8 h at 99%.

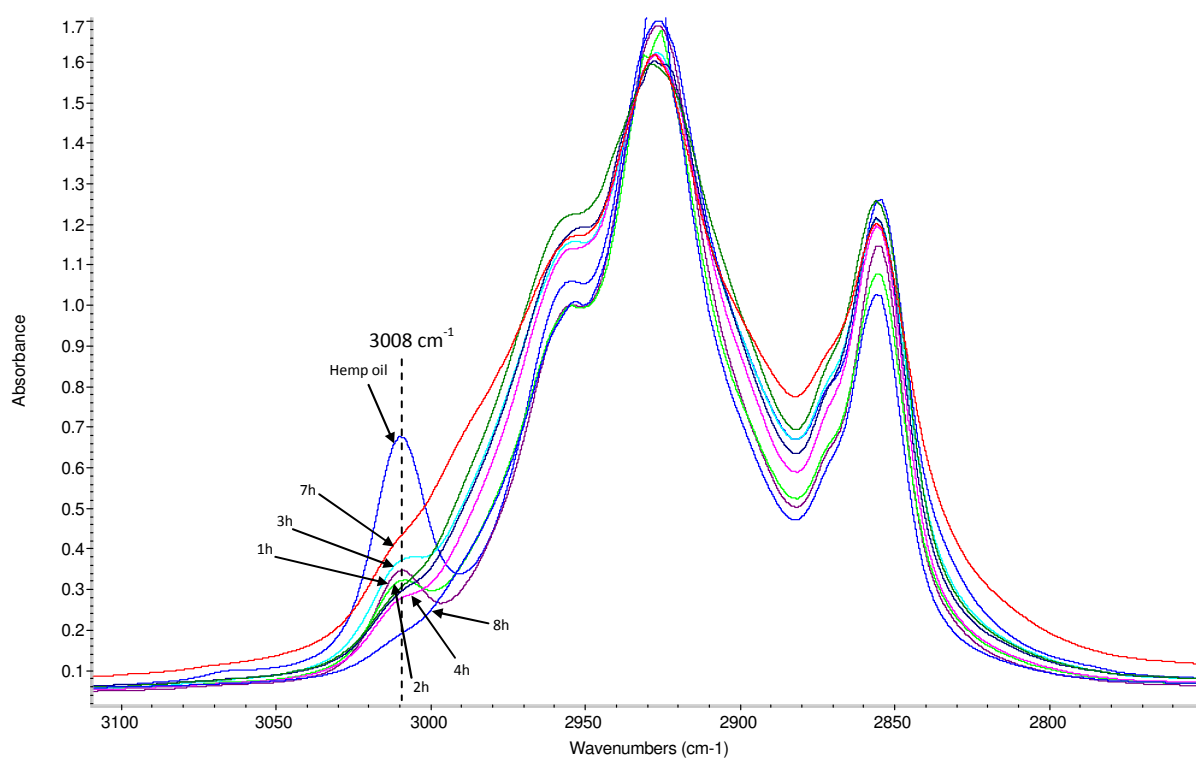
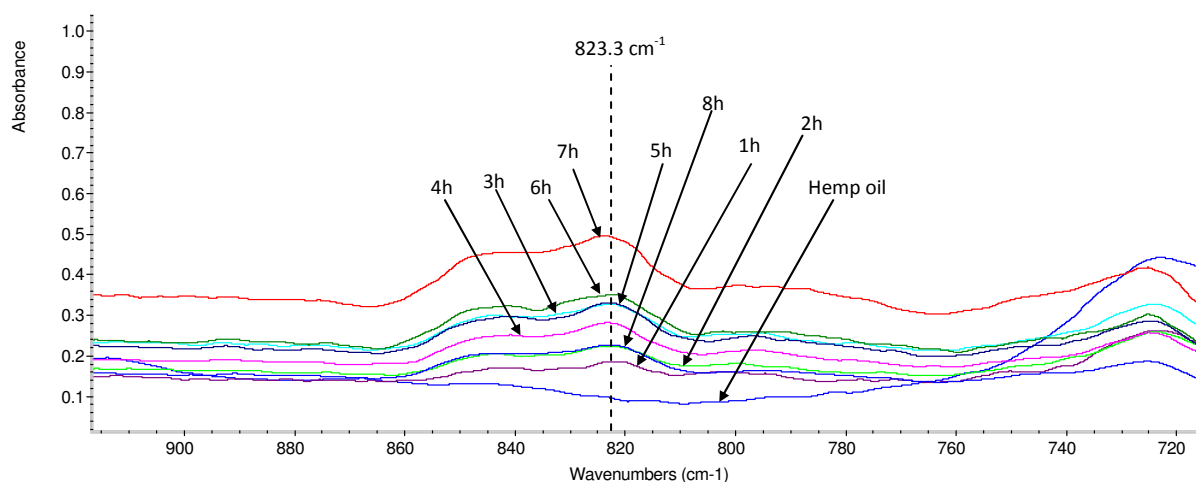


Figure 42 FTIR spectrum of HO compared to epoxidised HO sample spectrums taken at 1 hour intervals over an 8 hour period. The peak at wavenumber  $3010\text{ cm}^{-1}$  relates to double carbon to carbon bonds. After 8 hours there is virtually no peak and a measured DB consumption of 99%. The molar ratio was (1.0:0.67:1.0).

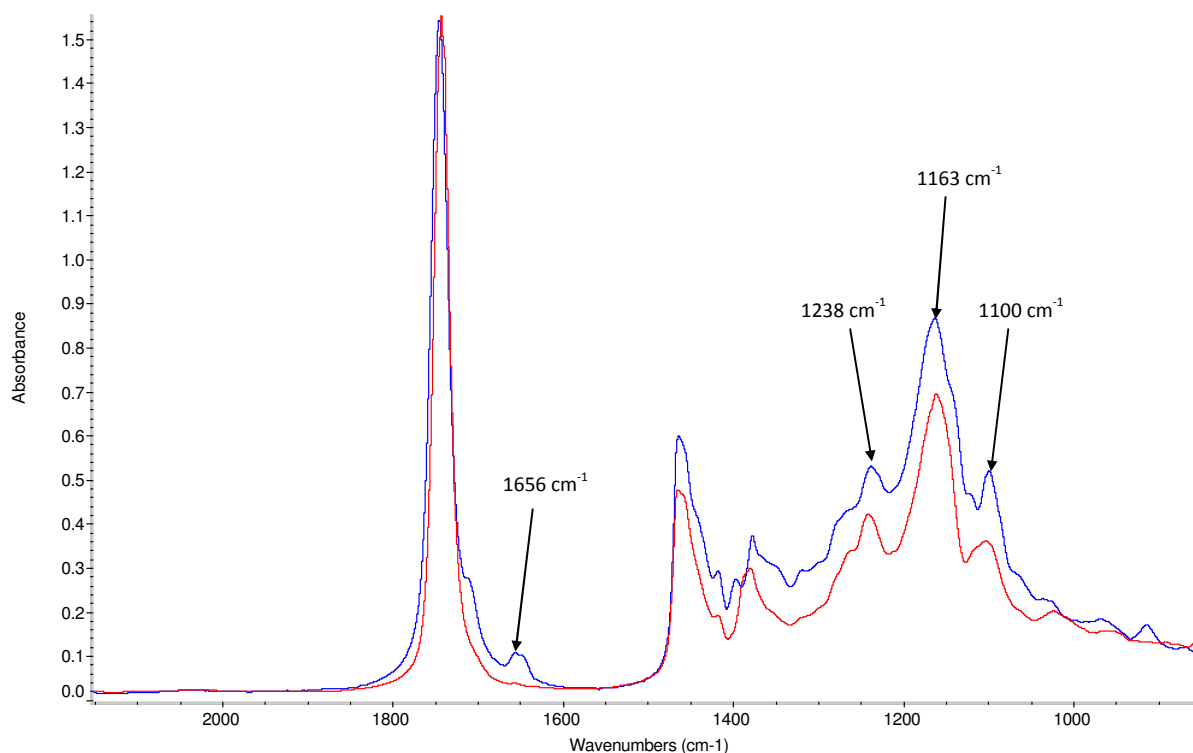


Figure 43 on the band that occurs at  $823\text{ cm}^{-1}$  which occurs as a result of the presence of epoxy groups. Let's start by looking at the spectrum for hemp oil (blue line). We see that at  $823\text{ cm}^{-1}$  no peak is present, then after 1 hour (purple line) a small peak has started to form. From here the curves become a little harder to interpret as it is the area under the curve, and not the height of the peak on the y axis, that indicates epoxy group formation. However some further observations can still be made. By 7 hours (red line) a predominant peak has formed, but by 8 hours (light blue line) the peak has diminished somewhat. It will later be shown by titration methods that the percentage of epoxy groups does begin to degrade after 7 hours.



**Figure 43 FT-IR of HO and EHO taken at 1 hour intervals over 8 hours. The peak for epoxy groups occur at wavenumber  $823.3\text{ cm}^{-1}$ . The molar ratio was (1.0:0.67:1.0).**

Predominantly throughout this research the band at  $3010\text{ cm}^{-1}$  on the spectrum of a VO oil and its epoxidised derivative were compared to give an indication of the consumption of DB. Another band occurring at  $1656\text{ cm}^{-1}$  also represents the C=C bond. The C=C bond is also present in groups corresponding to bands at  $1238\text{ cm}^{-1}$ ,  $1163\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ . Starting at the band at  $1656\text{ cm}^{-1}$  (C=C, stretching) we see that after 8 hours the peak (red line) is almost completely consumed. Bands at  $1238\text{ cm}^{-1}$ ,  $1163\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ , have also been reduced significantly after 8 hours.



**Figure 44** Arrows show bands that are affected by the consumption of double bonds in the epoxidation reaction. Special attention should be paid to the band at  $1656\text{ cm}^{-1}$ , which is attributed to the C=C stretching vibration.

Consumption of DB as determined by the decrease in the strength of the band at  $3010\text{ cm}^{-1}$  in comparison to the original HO sample. Curve (a) represents the lowest molar concentration of acetic acid. The indication is that the maximum DB consumption occurs at 7 hours and is 90.4%. It is unlikely however that by 8 hours a percentage of the double bonds have reformed, as the graph suggests. A more plausible explanation is that the difference between the values at 6, 7 and 8 hours is caused by the accuracy of the measurements taken and the margin of error when measuring the area of normalised curves in a FTIR spectrum. It is then possible to estimate that the maximum consumption of DB occurred sometime shortly after 6 hours from the commencement of the reaction. Curve (b) used the highest molar concentration of acetic acid and slightly less hydrogen peroxide than the other two samples. The highest consumption of double bonds was recorded at 7.5 hours and was 97%. Observation of the curve shows some erratic behaviour between 3 hours and 5.5 hours. Once again it is unlikely that the DB concentration was fluctuating up and down, and that the accuracy of the FTIR spectrum and operator inexperience is to blame. It could also be suspected that the points at 4 and 5 hours are erroneous, as neglecting these would produce a smoother curve. It should also be noted that while running this batch in the reactor there were some less than usual occurrences. The most notable was that in the early stages of the reaction the constituents (HO, AA,  $\text{H}_2\text{O}_2$  and AIER) didn't mix well and this was contributed to the stirring speed being inadequate. This

explains why samples were not taken until 3 hours, at which time the mixture had reached some observable homogeneity. The poorly mixed batch could also go some way in providing an alternative explanation as to why the plot is erratic in nature. If there exists portions of the batch that were being mixed with a differing severity, then different DB concentrations may result. This would also explain why after 6 hours the results became more in accordance with what was expected, as the decreasing volume of reacting materials would invariably be stirred more effectively by a low profile ships anchor stirrer. Curve (c) had a molar concentration somewhere in between the others. At 8 hours when the reaction was halted, a 99% consumption of DB had occurred. The reaction proceeded rapidly for the first hour and began to taper off after that. The difference made by the higher concentration of acetic acid is obvious from the fact that by 1 hour there was a slightly higher consumption of DB than that of curve (a) at 3 hours. By 3.3 hours curve (c) had reached 90%, approximately half of the time it took curve (a) to reach the same point. Curve (c) gave the best results in regards to the percentage consumption of DB, measured by comparing normalised curves for epoxidised HO and HO for the spectrum band at  $3010\text{ cm}^{-1}$ . This was found to occur at eight hours.

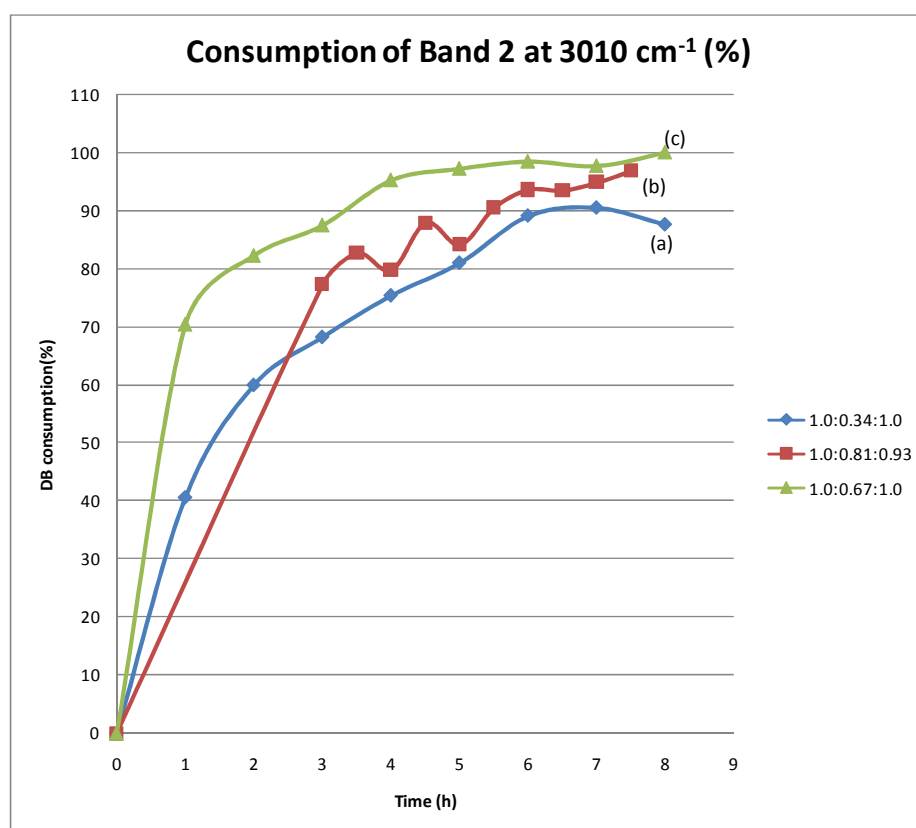


Figure 45 Comparison of the consumption of DB for three batches of EHO as determined by measuring the area under the curve at  $3010\text{ cm}^{-1}$ .

#### 4.6.2 Inspection of epoxidised HO using titration methods

Titration methods were used to determine quantitative values for each set of times samples. The percentage of oxirane oxygen was determined by the direct method with hydrobromic acid in acetic acid. The iodine value was obtained using the Wij's method.

##### Iodine value

The iodine value was obtained using the Wij's method. The iodine value for Eco-fibre HO was determined experimentally to be 133 (g iodine/ 100 h HO), which represents the starting point for both of the curves in figure 20. Curve (a) represents the lowest molar concentration of AA. The iodine value reaches a minimum of 45 (g iodine/ 100 h HO), at 8 hours. Observation of the curve shows that it is parabolic in appearance, and by 8 hours it is very close to reaching its minimum value. Curve (b) represents the highest molar concentration of AA used in these tests. The lowest iodine value is recorded on the last sample, being 22 (g iodine/ 100 h HO) after 8 hours. Its form is similar to that of (a), and based on the parabolic nature of the curve it is apparent that at this point the bottom of the curve has almost been reached. It is doubtful that a higher concentration of AA (or any other parameter shift for that matter) would have produced an iodine much lower as FTIR shows that at 8 hours a 99% consumption of DB had occurred.

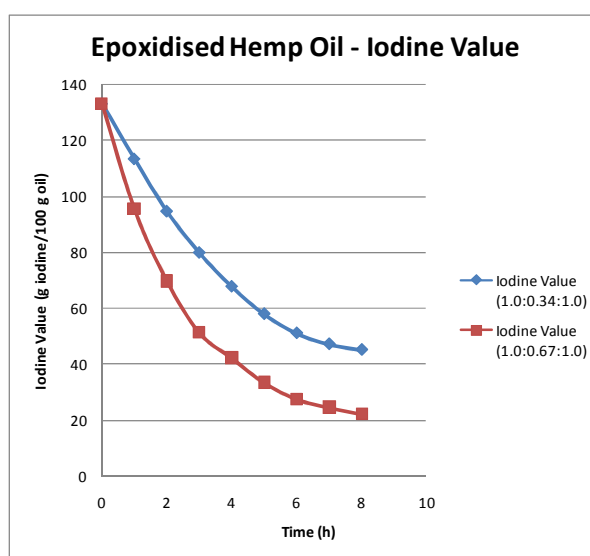


Figure 46 Iodine value for two batches of EHO with molar ratios (1.0:0.34:1.0) and (1.0:0.67:1.0), with samples taken each hour for 8 hours. The iodine value for the HO was measured to be 133 (g iodine/ 100 g HO). After 8 hours the iodine values were 45 and 22 (g iodine/ 100 g HO) for AA molar concentrations of 0.34 and 0.67 respectively.

In the previous section we examined curves showing the decreasing iodine value as a result of the time evolution of the epoxidation process on two batches of HO. Although these curves present useful information concerning the consumption of double bonds, it is appropriate to re-present the curves to give an indication of the relative conversion DB into other groups. This is achieved by applying the following equation:

$$\% \text{ Conversion}_{\text{relative to IV}} = 100 \times \frac{IV_0 - IV_f}{IV_0}$$

where  $IV_0$  is the iodine value of the HO, and  $IV_f$  is the iodine value of the epoxidised sample. The results are plotted in figure 21. Curve (a) represents the lowest molar concentration of AA, and a maximum relative conversion is observed after 8 hours at 66%. Curve (b) represents the highest molar concentration of AA, and a maximum relative conversion is reached after 8 hours at 83%. A visual inspection of both curves gives the impression (due to the parabolic nature of the curves) that further time under reaction conditions would not have significantly improved the relative conversion.

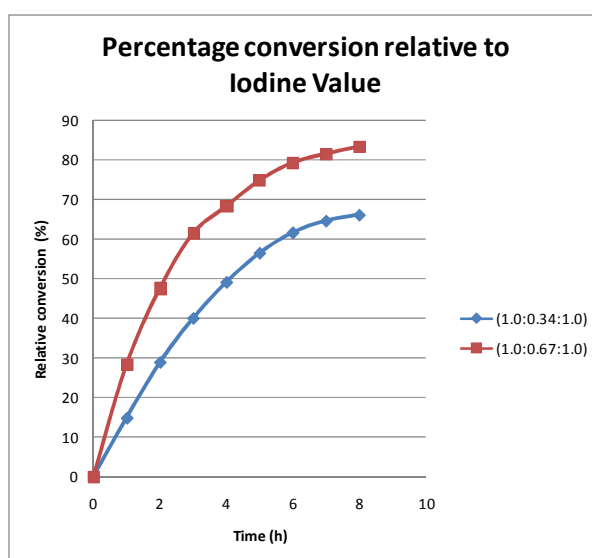


Figure 47 Relative conversion of DB for two batches of EHO with molar ratios (1.0:0.34:1.0) and (1.0:0.67:1.0). The maximum relative conversion after 8 hours was 66% and 83 % respectively.

### Oxirane Oxygen Content

Based on the suppliers specifications of the fatty acid composition of hemp oil, it was previously calculated that the iodine value (based on triglyceride content) is 163 (g iodine/100g HO). This was then used to determine that the theoretical maximum oxirane oxygen content of hemp oil is 9.3.

Once the oxirane oxygen content for each sample was determined by titration with hydrobromic acid in acetic acid, the percentage conversion could be calculated using

$$\% \text{ Conversion}_{\text{relative to } OO} = 100 \times \frac{OO_e}{OO_t}$$

where  $OO_e$  is the experimental value of oxirane oxygen and  $OO_t$  is the theoretical value. The results are plotted in figure 22. Curve (a) had the lowest molar concentration of acetic acid, and was reacted over 8 hours with samples taken every hour. The highest conversion was 64.4% and occurred at 7 hours. By 8 hours this had dropped back to 62.7%. Curve (b) had the highest molar concentration of acetic acid, and was reacted over 8 hours with samples being taken every hour. The highest conversion was 73.4% and occurred at 7 hours. By 8 hours it had dropped back to 72.9%. It should be remembered that the epoxy ring is highly strained and very unstable. This drop off after 7 hours can be attributed to the degradation of the epoxy groups into other groups such as alpha-glycols. If we refer back to the plots for percentage conversion relative to the iodine value it can be observed that by 7 hours the sample had not yet become fully saturated. This suggests that after 7 hours the epoxy groups are degrading at a higher rate than they are forming, and places emphasis on the fact that complete fatty acid saturation does not necessarily equate to maximum epoxy group formation. Acetic acid is the only variable in these batches, and the general shape of the curves is almost identical except that curve (b) is higher. This suggests that acetic acid plays a major role in the epoxidation reaction.

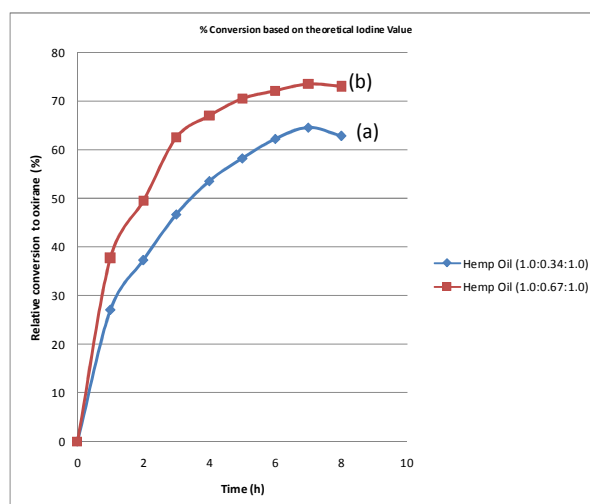


Figure 48 Relative conversion to oxirane for two batches of EHO with molar ratios (1.0:0.34:1.0) and (1.0:0.67:1.0). These curves are based on the iodine value of the hemp oil determined from the manufacturer's specifications of fatty acid composition. Maximum relative conversion to oxirane was 64.4% and 73.4% for curves (a) and (b) respectively.

The difference between these curves and the previous ones is that the iodine value used to calculate the theoretical maximum oxirane oxygen content was taken as 133 (g iodine/100 g HO). This was determined experimentally by the Wij's method titration. It seemed appropriate to replot the curves using this value, as the previous was determined using the manufacturers specified fatty acid composition for hemp oil, and there was no direct verification that they applied to the hemp oil being used. In this case; Curve (a) had the lowest molar concentration of acetic acid, and was reacted over 8 hours with samples taken every hour. The highest conversion was 77.4% and occurred at 7 hours. By 8 hours this had dropped back to 75.4%. Curve (b) had the highest molar concentration of acetic acid, and was reacted over 8 hours with samples being taken every hour. The highest conversion was 88.2% and occurred at 7 hours. By 8 hours it had dropped back to 87.6%.

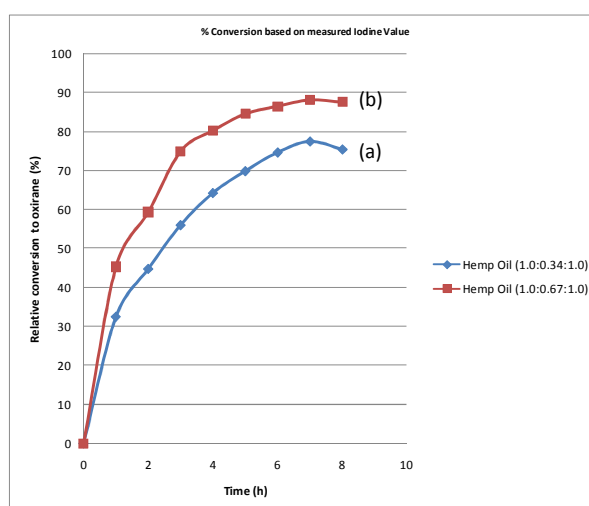


Figure 49 Relative conversion to oxirane for two batches of EHO with molar ratios (1.0:0.34:1.0) and (1.0:0.67:1.0). These curves are based on the iodine value of the hemp oil determined from titration via the Wij's method. Maximum relative conversion to oxirane was 77.4% and 88.2% for curves (a) and (b) respectively.

## 4.7 Conclusion

From the above discussion and results it is clear that optimum conditions found for the epoxidation of hemp oil is as follows.

**Molar ratio:** Hemp oil (1.0) : Acetic acid (0.67) : H<sub>2</sub>O<sub>2</sub> (1.0)

**Catalyst loading:** 15 wt% of HO

**Temperature:** 75 °C

This results in a maximum relative conversion to oxirane of 88%. A comparison of the results gained for HO against the reported results of other VO is given in Table 13. Hemp oil seems to stack up well against the other VO. It has the third highest relative conversion to oxirane and is only 2% lower than the highest. Epoxidation of HO requires the lowest molar concentration of H<sub>2</sub>O<sub>2</sub>, but uses slightly higher concentrations of AA. The reaction temperature is similar to that shown to be optimum for the others.

**Table 13 Comparison of process conditions and results of EHO to the results of other researchers for other EVO.**

Vegetable Oil	Iodine value	Maximum relative conversion to oxirane (%)	Molar concentrations			Temperature (degrees C)	Catalyst loading (wt%)
			VO	AA	H2O2		
Karanja oil	89	85	1	0.5	1.5	70	16
Canola oil	112	90	1	0.5	1.5	65	22
Mahua oil	88	89	1	0.5	1.1	70	16
Jatropha oil	105	73	1	0.5	1.5	85	16
Cottonseed oil	106	77	1	0.5	2	75	NA
Hemp oil	133	88	1	0.67	1	75	15



## 5 Conclusion

The premise of this research project was that the fatty acid structure of vegetable oils made them good candidates for conversion into polymeric materials. Currently the polymeric materials industry is reliant on the world's supplies of crude oil to derive its products. There is seen a need to wean these industries off crude oil in favour of more natural renewable alternatives. This is highlighted with research being currently done at CSIRO in developing oilseed crops which produce high quality vegetable oils (Green, A and Catizone I, 2009).

Because of the double bonds present in the fatty acid chain of vegetable oil triglycerides it was decided to focus on the epoxidation reaction. A review of the literature revealed that there has been some concentrated experimental research in this area, with the majority of it being published since 2006. Over that period from 2006 to the present a number of different approaches have been taken to epoxidised vegetable oils. All of these have relied on chemical synthesis, although the types and concentrations of chemicals have varied.

From this collective research, one method has emerged as being the most favourable amongst researchers. It involves epoxidising the vegetable oil with peroxyacetic acid formed *in situ* by the reaction of aqueous hydrogen peroxide and acetic acid in the presence of an acidic ion exchange resin as catalyst. It was decided that this method would be employed in this research project. The eventual goal of epoxidising vegetable oils in the literature and in this research project was to determine which chemical process conditions produce optimum results. To achieve this a trial and error approach was taken in which incremental changes to the chemical process conditions were made and the results examined.

As Queensland, and the Darling Downs region especially, is a large producer of vegetable oils it was decided to concentrate on local vegetable oils. Initially linseed oil and sunflower oil were experimented with. The process conditions used were those found to produce good results for other researchers. The results from these initial tests showed some poor results with the highest consumption of double bonds being 61.2% for linseed oil, and the lowest being 12.5% for sunflower oil, both with a molar ratio of 1.0:0.5:1.5 (vegetable oil : acetic acid : hydrogen peroxide)

A high quality hemp oil was later supplied by Eco-fibre, and since hemp oil was found to be under represented in the literature it was decided to make hemp oil the central focus of this research. Initial testing showed that for hemp oil the best results attainable were a 99% consumption of double bonds at a molar ratio of 1.0 : 0.41 : 1.27. By this point in the research the success of the

epoxidation reaction had only been assessed by determining what percentage of the double bonds in the original vegetable oil had been consumed by the reaction. Having determined whereabouts the optimum results for hemp oil occurred, it was then necessary to determine by direct methods what proportions of epoxy groups had formed, and at what stage in the reaction maximum amounts had occurred.

It was determined that optimum results for epoxidising hemp oil occurred at:

**Molar ratio:** Hemp oil (1.0 mole of double bonds) : Acetic acid (0.67 moles) : H<sub>2</sub>O<sub>2</sub> (1.0 moles)

**Catalyst loading:** 15 wt% of hemp oil

**Reaction time:** 7 hours

**Reaction temperature:** 75°C

At these conditions an 88% conversion of double bonds to epoxy groups was found to occur. This result was comparable to the results of other authors conducting similar research. The highest relative conversion to oxirane found in the literature was 90% for canola oil.

#### Further work

Further work would involve taking a closer look at the specific influence fatty acid structure and composition has on the epoxidation reaction. This correlation can then be carried forward into developing an understanding of how the fatty acid composition affects other outcomes like crosslinking during curing and the eventual material properties of the epoxy material. This would be most likely be achieved by characterising numerous locally produced vegetable oils with a method such as gas chromatography – mass spectrometry.

## 5.1 References

1. Green, A Catizone, I 2009, 'Helping wean the chemicals industry off crude oil' CSIRO media releases, viewed 26/10/09. <http://www.csiro.au/news/OilsForChemicalIndustry.html>

## 6 Appendix

## 6.1 Project specification

University of Southern Queensland

FACULTY OF ENGINEERING AND SURVEYING

**ENG4111/4112 Research Project**  
**Faculty of Engineering and Surveying**

- For: Tyson Cooney
- Topic: Polymer resin made from natural renewable resources (vegetable oils)
- Supervisors: Dr Francisco Cardona, Dr Hao Wang
- Project aims: Industrial plastics and polymer composites used for civil structures have traditionally been made from polymer resins derived from petrochemical feedstocks. The aim of the project is to investigate the creation of epoxidised resins from natural renewable resources (vegetable oils). The resin, once produced, will be tested to ascertain the success of the epoxidation reaction .
- Programme:
- 1) Convert the vegetable oil into epoxy resin. The initial aim will be to become familiar with the synthesis of Queensland based vegetable oils into epoxy resins. This will include:
    - Identifying the currently available raw materials; including vegetable oils, catalysts and other ingredients.
    - The operation of relevant laboratory equipment, including but not limited to: the reactor and the Fourier Transform Infrared Spectrometer.
    - Understand the mechanism of the reaction, the polymerisation and epoxidisation of the oils, and any other relevant chemical kinetics, and identify which key variables are likely to significantly affect the previously mentioned phenomenon.
  - 2) Once the basic processes have been identified, the end products (epoxidised oils and resin) will be examined in their pre and post processed condition. The properties of the products will be characterised. Properties that will be examined are:
    - Microstructure, namely the structure of the fatty acids present in the vegetable oils
    - Process conditions, the physical and chemical conditions used in the reaction and their effects
    - The degree of conversion of vegetable oil into epoxy resin
  - 3) Once steps (1) and (2) have been done, and the results tabulated, then the process conditions can be assessed with the aim of optimising the synthesis of vegetable oils into polymer resins suitable for the development of useful epoxy plastics. It may be possible to develop a suitable model capable of predicting optimum paths to a premium end product.

AGREED:

Tyson Cooney (student)		Date: ____ / ____ / 2009
Dr Hao Wang (supervisor)		Date: ____ / ____ / 2009
Dr Francisco Cardona (supervisor)		Date: ____ / ____ / 2009
Examiner/Co-examiner		Date: ____ / ____ / 2009

## 6.2 Experiment log

Initially, experimental runs on linseed oil and sunflower oil were designated Batch 01, Batch 02 and so on. When experimentation began on the hemp oil supplied by Eco-fibre, the designation changed to Batch 1H, Batch 2H etcetera, where the H stands for hemp. What follows is a brief log of experimental work carried out of various oils to date.

### Batch01

<b>Batch:</b>	01
<b>Date:</b>	16-03-09
<b>Vegetable oil (VO):</b>	Linseed oil (Diggers Raw Linseed Oil)
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:0.5:1.5
<b>Quantity of vegetable oil:</b>	800g
<b>Quantity of Acetic Acid (AA):</b>	120g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	620g
<b>Quantity of Amberlite IR120:</b>	80g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

### Batch 02

<b>Batch:</b>	02
<b>Date:</b>	17-03-09
<b>Vegetable oil (VO):</b>	Sunflower oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:0.5:1.5
<b>Quantity of vegetable oil:</b>	800g
<b>Quantity of Acetic Acid (AA):</b>	125g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	630g
<b>Quantity of Amberlite IR120:</b>	80g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

## Batch 03

<b>Batch:</b>	03
<b>Date:</b>	23-03-09
<b>Vegetable oil (VO):</b>	Sunflower oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:1.0:1.5
<b>Quantity of vegetable oil:</b>	800g
<b>Quantity of Acetic Acid (AA):</b>	250g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	630g
<b>Quantity of Amberlite IR120:</b>	80g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

Notes: The reaction that occurs due to the addition of the hydrogen peroxide is exothermic. This exothermic reaction, coupled with the increasing reactor temperature caused the overall temperature to peak, causing the mixture to boil, peaking at about 130°C. The pressure, as a result, rose in the reactor causing one of the reactor neck plugs to shoot out and break.

## Batch 04

<b>Batch:</b>	04
<b>Date:</b>	24-03-09
<b>Vegetable oil (VO):</b>	Sunflower oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:1.0:1.5
<b>Quantity of vegetable oil:</b>	400g
<b>Quantity of Acetic Acid (AA):</b>	125g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	315g
<b>Quantity of Amberlite IR120:</b>	40g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

Notes: The same molar ratio that was used in batch 03 was used here. The reason is because the results achieved in Batch 03 could have been affected by the fact that it boiled. On cleaning an emulsion occurred which was unable to be broken. No results were possible.

#### Batch 05

<b>Batch:</b>	05
<b>Date:</b>	31-03-09
<b>Vegetable oil (VO):</b>	Sunflower oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:1.5:1.5
<b>Quantity of vegetable oil:</b>	400g
<b>Quantity of Acetic Acid (AA):</b>	187.5g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	315g
<b>Quantity of Amberlite IR120:</b>	40g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

Notes: The batch, after completing the reaction process, sat in a beaker for two weeks over the semester one midterm break. It was observed that three distinct phases had formed. There was a thick layer on the bottom comprising mostly Amberlite IR120. The middle appeared to be resin, with a vegetable oil looking appearance, and on top a clearish gel like layer, presumably the peroxyacetic acid. This would imply that the resin should be easily separated.

During the cleaning process it was observed that although two phases presented quickly after agitation, when the contents of the separating funnel were allowed to settle, the aqueous layer developed on top, and a viscous milky coloured layer sunk to the bottom.

The emulsion was centrifuged to try and separate out the resin. At this point it was very thick and cloudy in appearance. It was centrifuged first for ten minutes at 1500 rpm, and the second time for 15 minutes at 1500 rpm. There was no real phase separation, but large droplets did form, evenly distributed throughout the top 30 mm of the vile. The lower levels were void of water droplets.



There were no results gained from this sample, though some time was afforded to trying to break the emulsion.

#### Batch 1H

<b>Batch:</b>	1H
<b>Date:</b>	20-04-09
<b>Vegetable oil (VO):</b>	Hemp oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:0.5:1.5
<b>Quantity of vegetable oil:</b>	600g
<b>Quantity of Acetic Acid (AA):</b>	93.75g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	472.5g
<b>Quantity of Amberlite IR120:</b>	60g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

**Reactor Setup:** The vegetable oil, acetic acid and Amberlite IR120 was stirred constantly at 80 rpm, while the reactor temperature was raised to 40°C. Once reaching this temperature, 473 g of hydrogen peroxide was added dropwise over a period of 1 hour. Once all the H<sub>2</sub>O<sub>2</sub> was dosed, the stirring speed was increased to 100 rpm, and the reactor temperature raised to 75°C over a period of 45 minutes. These conditions were held for 8 hours, and then the temperature was allowed to settle to ambient room temperature, while the stirring speed was maintained until the batch was removed from the reactor.

**Notes:** While cleaning phase separation occurred quickly. Cleaned four times and the centrifuged for 10 minutes at 1500 rpm. If let sit for more that 1 hour after shaking the separating funnel, the thick phase started sinking towards the bottom of the funnel, like a lava lamp.

#### Batch 2H

<b>Batch:</b>	2H
<b>Date:</b>	21-04-09
<b>Vegetable oil (VO):</b>	Hemp oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:1.0:1.5

<b>Quantity of vegetable oil:</b>	600g
<b>Quantity of Acetic Acid (AA):</b>	187.5g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	472.5g
<b>Quantity of Amberlite IR120:</b>	60g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

**Reactor Setup:** Same as Batch 1H

**Notes:** Running water is used to control the temperature of the reactor, and I forgot to turn on the water. The reactor dosed 170g of H<sub>2</sub>O<sub>2</sub> and then shut itself off.

#### Batch 3H

<b>Batch:</b>	3H
<b>Date:</b>	27-04-09
<b>Vegetable oil (VO):</b>	Hemp oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:1.0:1.0
<b>Quantity of vegetable oil:</b>	600g
<b>Quantity of Acetic Acid (AA):</b>	187.5g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (35 %):</b>	315g
<b>Quantity of Amberlite IR120:</b>	60g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

#### Batch 4H

<b>Batch:</b>	4H
<b>Date:</b>	28-04-09
<b>Vegetable oil (VO):</b>	Hemp oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:1.0:1.5
<b>Quantity of vegetable oil:</b>	600g

<b>Quantity of Acetic Acid (AA):</b>	187.5g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (32.5 %):</b>	432g
<b>Quantity of Amberlite IR120:</b>	60g
<b>Stirring Speed:</b>	100 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

**Notes:** This batch is a repeat of batch 2H, due to the fact that there was an interruption to that reaction process.

#### Batch 5H

<b>Batch:</b>	5H
<b>Date:</b>	05-05-09
<b>Vegetable oil (VO):</b>	Hemp oil
<b>Ratio (VO:AA:H<sub>2</sub>O<sub>2</sub>):</b>	1.0:0.81:0.93
<b>Quantity of vegetable oil:</b>	1000g
<b>Quantity of Acetic Acid (AA):</b>	313g
<b>Quantity of H<sub>2</sub>O<sub>2</sub> (30 %):</b>	675g
<b>Quantity of Amberlite IR120:</b>	100g
<b>Stirring Speed:</b>	110 rpm
<b>Temperature:</b>	75 °C
<b>Time:</b>	8 h

**Notes:** This batch is a repeat of Batch 4H. Higher quantities of constituents were used. The aim of this experiment was to remove samples over the period of the reaction process, so as to determine how the reaction evolves. The reaction process, as detailed in Batch 1H, was commenced at 12:20pm. It was initially decided that samples would be removed every half an hour, starting 30 minutes after the dosing of the hydrogen peroxide was completed. Time zero is regularly taken from when all the H<sub>2</sub>O<sub>2</sub> has been dosed (Mungroo et al, 2008), so in this case would be at 1:20 pm.

It was noted from observation that the stirrer in the reactor was not maintaining a homogenous mixture. It can be seen from the following photograph that there is a distinct oil phase on top, a turbulent multiphase in the centre and an aqueous phase on the bottom.

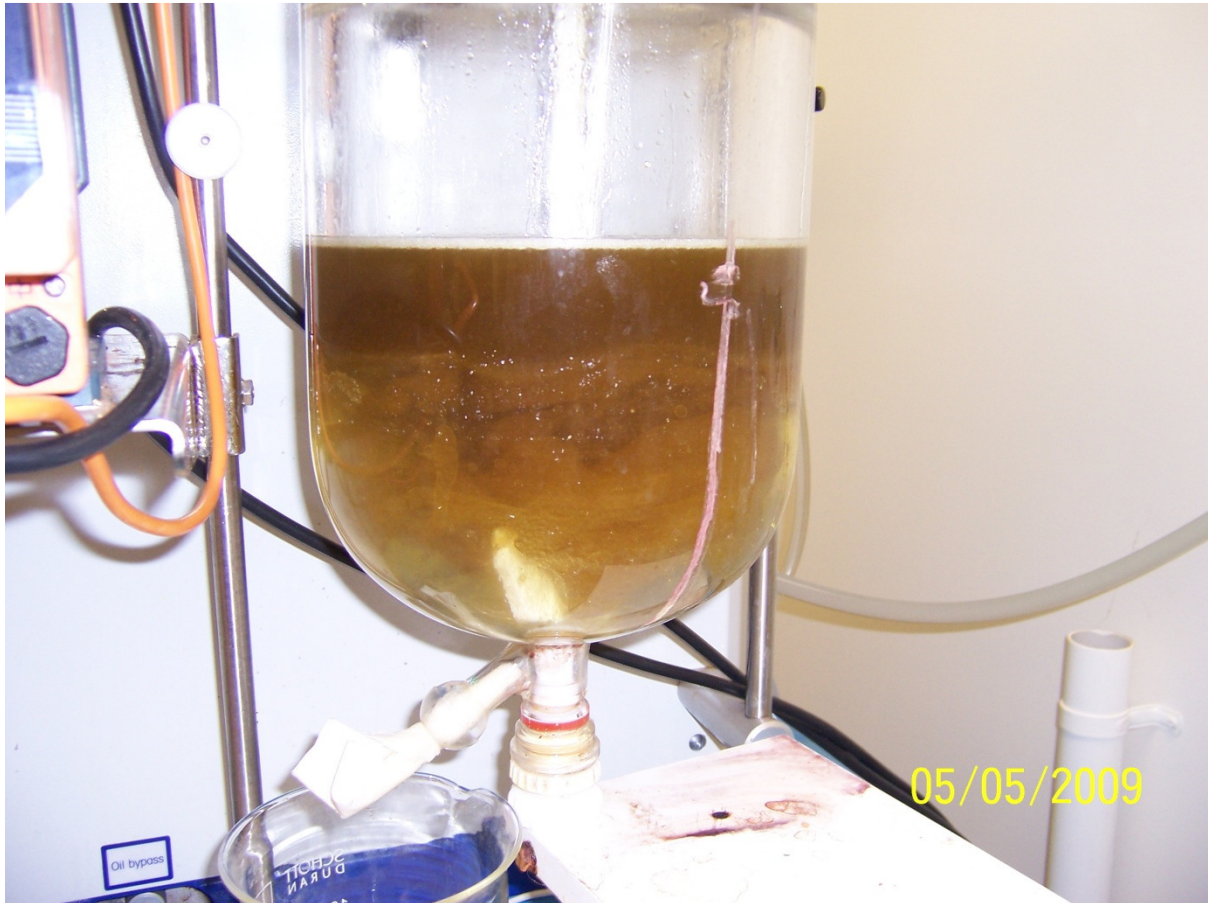


Figure 50 Picture of the reactor vessel. It can be noticed that the mixing is not homogenous.

Removing samples while the mixture was in this state would have born no useful results. On the advice of Dr Francisco Cardona, it was decided to wait until the reaction has reached a stage where all the reactants where homogenously mixed before starting to extract samples.

It was observed shortly after 4:00pm that the mixture was homogenous, and the first sample was removed at 4:20pm, three hours after time zero. Further samples were removed every half an hour thereafter. These samples have been through the cleaning process to date, but no testing has yet been done.

### 6.3 Chemical safety data

Commonly handled chemicals in the laboratory are acetic acid ( $\text{CH}_3\text{COOH}$ ), Amberlite IR120, potassium bromide, and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Safety precautions recommended by their materials safety data sheets are as follows.

#### *Acetic Acid*

**Conditions to be avoided:** Strong heating.

**Substances to be avoided:** Anhydrides / water, aldehydes, alcohols, halogen-halogen compounds, oxidizing agents (i.a.  $\text{CrO}_3$ ,  $\text{KMnO}_4$ , peroxi compounds, perchloric acid, chromosulfuric acid), metals alkali hydroxides, non-metallic halides, ethanolamine.

**Hazardous decomposition products:** In the event of fire : Acetic acid vapours.

**Further information:** Exposable with air in vapour / gaseous state.

#### Health Hazard

**Inhaled:** Irritation symptoms in the respiratory tract, pneumonia bronchitis. Inhalation may lead to the formation of edemas in the respiratory tract.

**Skin:** Contact with the skin causes severe burns.

**Eye:** Burns. Risk of blindness. Risk of corneal clouding.

**Ingested:** Ingestion is followed by burns, severe pain (risk of perforation), nausea, vomiting and diarrhea.

**Toxicity data:** LD50 3310 mg/kg (using 25% solution) oral in rat.

**Carcinogenicity:** No specific data.

### First Aid

**Inhaled:** Remove from exposure to fresh air. Obtain medical attention.

**Skin:** Wash off with plenty of water. Dab with polyethylene glycol 400. Immediately remove contaminated clothing. Obtain medical attention immediately.

**Eye:** Rinse out with plenty of water for at least 10 minutes with the eyelid held wide open. Obtain medical attention immediately.

**Ingested:** Make victim drink plenty of water, avoid vomiting (risk of perforation). Obtain medical attention immediately. Do not attempt to neutralize.

### Protective Measures

**Fire extinguishing agents:** Water, CO2 foam, powder.

**Fire special risks:** Vapour heavier than air. Formation of explosive mixtures possible with air. The following may develop in event of fire : Acetic acid vapours.

**Ventilation:** Well, cool, dry, out of direct sunlight.

#### **Personal protection equipment:**

- **Respiratory protection:** Required when vapours / aerosols are generated.
- **Hand protection:** Required.
- **Eye protection:** Required.
- **Skin and body protection:** Protective barrier cream. Wash hands and face after working with substance.
- **Other protection equipment:** Acid – resistant protection clothing.
- **Industrial hygiene:** Change contaminated clothing.

### *Potassium Bromide*

#### Health Hazard

**Inhalation:** Dust may cause irritation to the respiratory tract. Symptoms may include coughing, sore throat, and shortness of breath.

**Ingestion:** May cause nausea, vomiting and abdominal pain. Ingestions are usually promptly rejected by vomiting, but sufficient absorption may occur to produce central nervous system, eye and brain effects. Symptoms may include skin rash, blurred vision and other eye effects, drowsiness, irritability, dizziness, mania, hallucinations, and coma.

**Skin Contact:** Dry material may cause mild irritation. Solutions may cause irritation, redness, pain, and skin burns.

**Eye Contact:** May cause irritation, redness and pain.

**Chronic Exposure:** Repeated or prolonged exposure by any route may cause skin rashes (bromaderma). Repeated ingestion of small amounts may cause central nervous system depression, including depression, ataxia, psychoses, memory loss, irritability, and headache.

**Aggravation of Pre-existing Conditions:** Persons suffering from debilitation, depression, alcoholism, neurological or psychological disorders may be more susceptible to the effects of this compound.

#### First Aid

**Inhalation:** Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

**Ingestion:** Induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. Call a physician.

**Skin Contact:** In case of contact, immediately flush skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. Call a physician.

**Eye Contact:** Wash eyes with plenty of water for at least 15 minutes. Call a physician.

### Personal Protective Equipment

**Airborne Exposure Limits:** None established.

**Ventilation System:** A system of local and/or general exhaust is recommended to keep employee exposures as low as possible. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

**Personal Respirators (NIOSH Approved):** For conditions of use where exposure to dust or mist is apparent and engineering controls are not feasible, a particulate respirator (NIOSH type N95 or better filters) may be worn. If oil particles (e.g. lubricants, cutting fluids, glycerine, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-face positive-pressure, air-supplied respirator. **WARNING:** Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

**Skin Protection:** Wear protective gloves and clean body-covering clothing.

**Eye Protection:** Use chemical safety goggles. Maintain eye wash fountain and quick-drench facilities in work area.

It is recommended by Goud et al that utmost care should be exercised keep the reaction mixture at a constant stirring speed. Voids of high concentration peroxide should be avoided because they could lead to explosive mixtures with the organic materials present (Goud et al, 2007).