

KINETICS OF IN SITU EPOXIDATION OF HEMP OIL UNDER HETEROGENEOUS REACTION CONDITIONS: AN OVERVIEW WITH PRELIMINARY RESULTS

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Abstract: Epoxidised hemp oil (EHO) was synthesised in the laboratory by reacting hemp oil (HO) with peroxyacetic acid (PA) in a batch reactor. The peroxyacetic acid was formed *in situ* from acetic acid (AA) and hydrogen peroxide (H₂O₂) in the presence on an acidic ion exchange resin (Amberlite IR-120) as catalyst. The overall reaction can be thought of as having two components. The first being epoxidation, a homogenous reaction which occurs at the interface of the aqueous phase and the HO phase while the second is the formation of PA, a heterogeneous reaction at the interface of the aqueous phase and the solid catalyst phase. The overall reaction kinetics were modelled by applying the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model to heterogeneous reactions. Of the steps in the reaction it is postulated that the formation of PA is rate limiting, while the epoxidation occurs comparatively fast negating the requirement for an additional homogenous model. The diffusion steps in the reaction are also ignored in the kinetic model as it is believed that their effects are negligible due to intensive mixing in the batch reactor. Experiments were used to determine the optimal molar ratios of reactants and it was found that at these conditions 88% conversion of double bonds to epoxy groups occurred. The kinetic model was found to be in good agreement with the experimental results.

Key words: Epoxidation, hemp oil, reaction kinetics, hydrogen peroxide, peroxycarboxylic acid, ion exchange resin, batch reactor, heterogeneous reaction, Eley-Rideal mechanism, Langmuir-Hinshelwood-Hougen-Watson model.

1 INTRODUCTION

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 (Green, 2008). As a result opportunities have arisen to explore the development of more environmentally friendly and sustainable alternatives. One area that is currently receiving considerable attention is the synthesis of polymer resins from vegetable oils (VO) (Green, 2006).

As of 2006 the manufacture of plastics consumed 11 - 12% of all worldwide oil and gas produced. These fossil fuel feedstocks are limited and non-renewable. While some commentators claim that we are only decades away from peak global oil production (Flaris & Singh, 2009), others maintain that the world is currently experiencing peak oil production (Gallagher, 2011). 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 (Gandini, 2008).

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 & Hillmyer, 2008). However, strong examples do 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, Patwardhan, Goud, & Pradhan, 2008). Other commercially available products made from plant oils include plastic panels for John Deere machinery and foams for Ford truck seats (Wool & Sun, 2005).

1.1 Vegetable Oil Basics

The reason VOs are such an appealing alternative to crude oil for

the production of industrial chemicals and materials is because they are comprised of a structural unit called a triglyceride. Triglycerides are comprised of a carbon backbone in the form of a glycerol molecule which is bonded to three fatty acid (FA) chains. Through the process of esterification, a FA group is bonded to each of the hydroxyl groups (OH). With few exceptions these FA chains range from 14 to 22 carbon atoms in length. The formation of a triglyceride is shown in Fig. 01, where R represents functional groups which are the FA chains, examples of which are shown at the bottom of the figure.

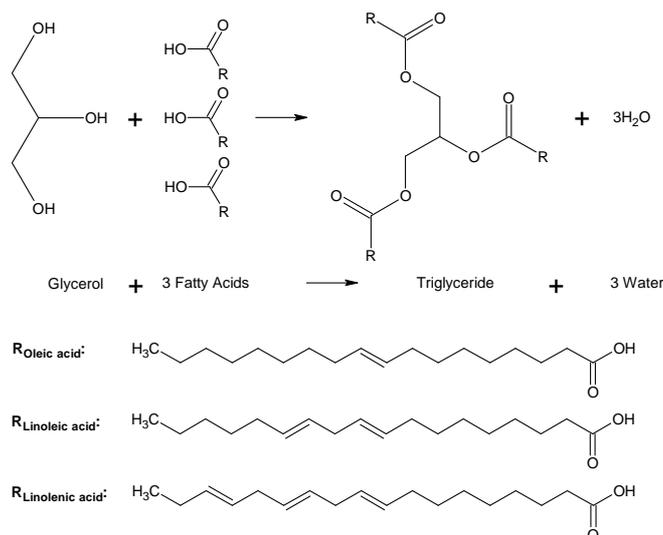


FIGURE 06: Structural formula for the formation of a triglyceride molecule. R represents the tail structure of the fatty acid chain, with three common types of unsaturated fatty acid chain given for reference

Triglycerides comprise both saturated and unsaturated FAs. Unsaturated means that the FA chain contains a number of double or triple carbon to carbon bonds. The designation for this is typically C=C and C≡C, respectively. Saturated means that all of

the carbon to carbon bonds are single bonds, indicated by C-C, and no more hydrogen atoms can be supported along the chain. Although saturated FAs such as palmitic acid and stearic acid are common constituents in VO triglycerides, they are predominantly comprised of varying percentages of the FAs oleic acid (C18:1), linoleic acid (C18:2), alpha-linolenic acid (C18:3) (the structures of which are given in Fig. 01) and gamma-linolenic acid (C18:3).

1.2 Overview of Epoxidation

Epoxidation occurs when a cyclic ether is formed at sites of ethylenic unsaturation (C=C) located along the FA chains by the addition of an oxygen atom. This epoxy group has the general structure shown in Fig. 02.

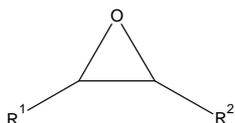


FIGURE 07: Epoxy group structure, where R¹ and R² represent the continuation of the fatty acid chain either side of the epoxy group.

The bond angles are about 60°, making the ring highly strained and highly reactive (Mungroo, Pradhan, Goud, & Dalai, 2008). The presences of these 'high strain energy' rings on the FA chains promote crosslinking when the epoxy resin is cured. The higher the amount of epoxy rings that are opened by the process, the more crosslinking can occur, and the higher the quality of the resulting plastic (Goud, Pradhan, & Patwardhan, 2006).

The method of epoxidising VO that has received the most attention in the literature is by reacting VO with peroxycarboxylic acid (Espinoza Perez, Haagenson, Pryor, Ulven, & Wiesenborn, 2009). The peroxycarboxylic acid donates the oxygen atom required to form the epoxy group and returns carboxylic acid to the bulk mixture.

Peroxycarboxylic acid is formed *in situ* by the reaction of carboxylic acid and hydrogen peroxide in the presence of an acidic ion exchange resin (AIER) as a heterogeneous catalyst (Goud, Patwardhan, & Pradhan, 2007; Mungroo et al., 2008; Sinadinovic-Fiser, Jankovic, & Petrovic, 2001; Campanella & Baltanas, 2007; Espinoza Perez, Wiesenborn, Haagenson, & Ulven, 2008). The *in situ* method is used because high concentrations of peroxycarboxylic acids can be unstable and explosive. By forming the peroxycarboxylic acid in the presence of a well dispersed oil phase, its consumption in the epoxidation reaction prevents regions of high concentration from occurring.

1.2.1 Choice of Carboxylic Acid

It is possible to use either formic acid or acetic acid as the carboxylic acid (Goud, Patwardhan, Dinda, & Pradhan, 2007; Petrovic, Zlatanic, Lava, & Sinadinovic-Fiser, 2002). However it was found that while the rate of formation of epoxide was higher with formic acid (Dinda et al., 2008) using acetic acid resulted in a 10% higher conversion of ethylenic unsaturation (EU) to epoxides (Mungroo et al., 2008) and a lower amount of undesirable by-products were 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 (AA) is that it is highly available, relatively cheap, has high epoxidation efficiency and is reasonably stable at moderate temperatures (Goud et al., 2007).

1.2.2 Choice of Catalyst

While peroxyacetic acid can be formed by solely mixing AA and

hydrogen peroxide, the kinetics are slow (Leveneuer, Warna, Salmi, Murzin, & Estel, 2009). To increase the speed of the reaction an acid catalyst is used. Inorganic liquid catalysts such as sulphuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) acid have been trialled as an acidic catalyst (Dinda et al., 2008), with sulphuric being the most effective. However due to epoxide ring opening caused by deleterious consecutive reactions they often hinder the attainment of high yields (Campanella & Baltanas, 2007). The reusability of homogeneous catalysts (liquid catalysts) is an issue as separation after reaction can be difficult. They can also be extremely hazardous to health, corrosive to equipment and an environmental pollutant. (Kiss, Bildea, & Grievink, 2010).

A "green chemistry" alternative is to use an AIER as heterogeneous catalyst (solid catalyst) as it can easily be reclaimed and often reused minimising the potential for waste. These catalysts are also less hazardous to people, the environment and equipment.

A commonly used AIER catalyst is Amberlite IR-120 which is a cation exchange resin with a styrene-divinylbenzene matrix bearing sulphonic (SO₃) acid functional sites. The functional sites have a surplus negative electrical charge. So that the catalyst fulfils the electroneutrality principle it supports positively charged exchangeable H⁺ or Na⁺ ions called counterions. These counterions are free to move about within the structure, as well as leave the structure, providing their movement is compensated by the corresponding counter-movements of other similarly charged ions (Zagorodni, 2007). From here on in the considered counterion is the proton H⁺, which is the ionic form of the catalyst used in this research.

2 REACTION KINETICS

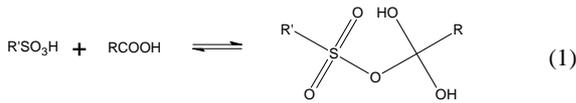
In formulating a set of differential equations that mathematically model the overall epoxidation reaction kinetics it is beneficial to work from the perspective of the rate limiting step (Fogler, 1999). The overall rate of reaction is defined by the rate-limiting step and is generally agreed to be the formation of peracetic acid (PA) (Sinadinovic-Fiser et al., 2001). The other reactions, such as epoxidation, occur quickly. It is therefore possible to determine the changing concentrations of EU and epoxide oxygen (EO) as a function of the formation of PA as opposed to examining the specific mechanism of the epoxidation reaction.

The production of PA centres around the Eley-Rideal mechanism of the catalyst and we will focus our attention here. Catalytic reactions are often broken down into a number of steps including diffusion steps and elementary reaction steps. It is assumed that the diffusion steps can be ignored as intensive mixing of the reactor has been shown (Goud, Patwardhan, & Pradhan, 2006) to make the resistance to mass transfer negligible. This will serve to significantly simplify the model and the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model is adopted for development of the overall reaction rate equations.

2.1 Reaction Steps

2.1.1 Step 1 – Adsorption

The first term on the left of (1) shows the sulphonic functional site bonded with the proton (R'SO₃H). As previously discussed the proton is free to move away from the functional site and protonates to the carbonyl group present in the AA (CH₃COOH) molecule. As a result of the protonation of the AA, it now has the same charge as the proton and can reattach to the functional site via the process of chemisorption.



In solution, AA contacts with active sites (s) on the surface of the catalyst and is adsorbed resulting in adsorbed acetic acid (AAs). The parameters of this reversible reaction are the adsorption reaction rate constants (k_a , k_{-a}). The reaction equation in (1) is redefined as:



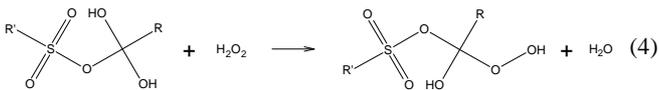
The rate expression for the non-dissociated adsorption of AA is provided by:

$$r_a = k_a \left(C_{AA} C_v - \frac{C_{AAs}}{K_{AA}} \right) \quad (3)$$

where C_i is the concentration of species i . This rate expression is formulated by the combination of the rate laws for each direction of the adsorption reaction and the ratio $K_{AA} = k_a/k_{-a}$ is the adsorption equilibrium constant.

2.1.2 Step 2 – Surface Reaction

The AAs on the catalyst surface contacts with suspended hydrogen peroxide (H_2O_2) and reacts to form adsorbed peroxyacetic acid (PAs) and water (H_2O) as a by-product. This is illustrated in the following equation.



The parameter of this non-reversible reaction is the surface reaction rate constant (k_{sr}).



The limiting reactant is considered to be H_2O_2 as AA is returned to the mixture after the formation of epoxy groups. The following outlines the method of determining the rate law for (5) based on the reaction of H_2O_2 .

From (5) the irreversible surface reaction responsible for the formation of PA is an Eley-Rideal mechanism (Fig. 03) and the rate law is:

$$r_{sr} = k_{sr} \left(C_{AAs} C_{H_2O_2} - \frac{C_{PAs}}{K_S} \right) \quad (6)$$

where K_S is the surface reaction equilibrium constant. As it is not practical to determine experimental values of the concentrations of adsorbed species (C_{AAs} , C_{PAs}) and varying vacant sites (C_v), steps are taken to eliminate C_{AAs} , C_{PAs} and C_v . Since the surface reaction is considered rate limiting, then k_a and k_d (k_d is presented below in reaction step 3) are very large in comparison and it can be taken that:

$$\frac{r_a}{k_a} \cong 0 \quad \& \quad \frac{r_d}{k_d} \cong 0 \quad (7)$$

Applying (7) respectively to the rate laws given for adsorption (3) and desorption (13) we obtain the following relationships for adsorbed AA and PA.

$$C_{AAs} = K_{AA} C_{AA} C_v \quad \& \quad C_{PAs} = K_{PA} C_{PA} C_v \quad (8)$$

Recognising that the concentration of total active sites (C_t) is equal to the sum of the concentrations of adsorbed and vacant sites, and

substituting in the terms on the right of (8) the concentration of vacant sites is:

$$C_v = \frac{C_t}{1 - K_{AA} C_{AA} - K_{PA} C_{PA}} \quad (9)$$

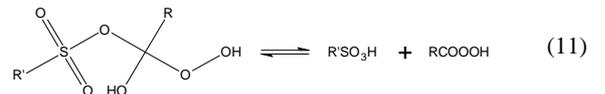
Substituting (8) and (9) into (6), and keeping in mind that the reaction is irreversible and no equilibrium condition exists for PA, we arrive at the general form of the rate law for an Eley-Rideal mechanism (Fogler, 1999).

$$r'_{H_2O_2} = - \frac{k C_{AA} C_{H_2O_2}}{1 + K_{AA} C_{AA} + K_{PA} C_{PA}} \quad (10)$$

where $k = k_{sr} C_t K_{AA} M_k$, and M_k is the mass of catalyst to mass of oil ratio, and is used to relate the reaction rates in the system. In (10) r' refers to the fact that this rate of reaction is a heterogeneous reaction with the units ($mol/s \text{ g catalyst}$).

2.1.3 Step 3 – Desorption

Once formed on the catalyst surface, the PAs (just as in the case of the adsorbed AA) is a reversible reaction and can desorb from the catalyst surface, and re-adsorb on to free active sites on the catalyst's surface. This is illustrated in the following reaction.



The parameters of this reversible reaction is the desorption reaction rate constants (k_d , k_{-d}).



The rate expression of this desorption reaction is:

$$r_d = k_d (C_{PAs} - C_{PA} C_v K_{PA}) \quad (13)$$

In summary, the overall reaction comprises three steps, namely (I) adsorption of the AA onto the catalyst active sites (II) reaction between the AAs and the suspended H_2O_2 and (III) desorption of the PA. These elementary reaction steps are shown in Fig. 03.

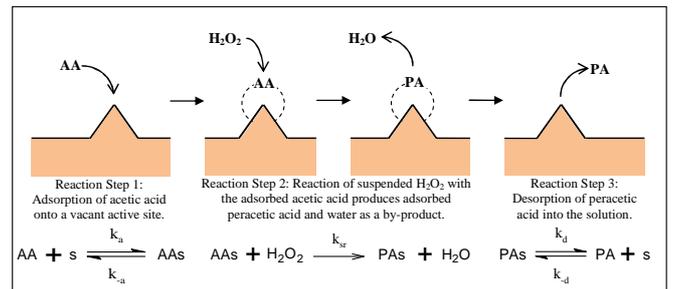
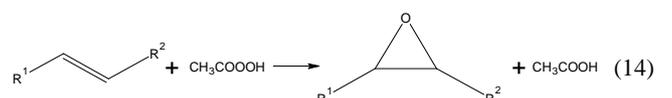


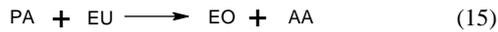
FIGURE 08: The Eley-Rideal mechanism responsible for the formation of peracetic acid. The adsorbed acetic acid molecule reacts with a H_2O_2 molecule from the aqueous phase. Water is released as a by-product and peracetic acid is desorbed back to the aqueous phase.

2.1.4 Epoxidation

The released PA contacts with the EU which reacts to form epoxide oxygen (EO) and AA. The general reaction is:



which is redefined as



where the parameter is the kinetic rate constant (k_3).

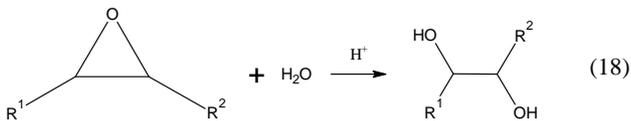
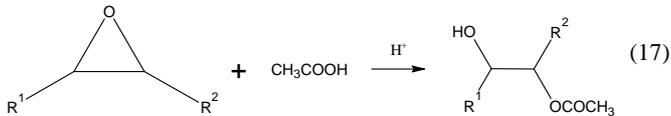
The rate law for (15) is:

$$r_{EU} = -k_3 C_{PA} C_{EU} \quad (16)$$

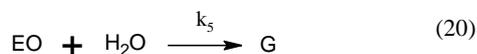
Ideally it is at this point in the overall reaction that the released AA would re-adsorb and the steps would be repeated until all the EU had been converted into EO. However the presence of the catalyst also causes the undesirable acid catalysed cleavage of the epoxide ring.

2.1.5 Undesirable Side Reactions

The rate of the overall epoxidation reaction is proportional to the total available surface area of catalyst in the reaction mixture. Higher loadings of catalyst allow more surface area and hence more surface protons which increases the rate of peroxy-carboxylic acid generation. However it has also been shown that deleterious degradation of the epoxide ring occurs upon interaction with the catalyst. The resin is hydrophilic and the oil phase, due to its large molecular structure, can't enter the AIER's polymer network. As a result, epoxide cleavage can only occur at the surface of the AIER (Campanella & Baltanas, 2007), with the likelihood of contact increasing with increased loadings of catalyst. Surface protons can cause epoxy ring cleavage by reaction with a number of chemicals present in the overall mixture, but for the purpose of a simplified model consideration is regularly restricted to AA and water (Sinadinovic-Fiser et al., 2001).



The undesirable products of these reactions are glycol (G), formed through hydrolysis of the oxirane ring, and its intermediate acetylated glycol (AG).



The rates of reaction for (19) and (20) are defined as:

$$r_{AG} = k_4 C_{EO} C_{AA} \quad (21)$$

$$r_{H_2O} = k_5 C_{EO} C_{H_2O} \quad (22)$$

In the case that the reaction is carried out in a batch reactor and mixing is considered to be perfect the reaction rates (10), (16), (21) and (22) can be used to obtain the following system of differential equations which model heterogeneous epoxidation reaction.

$$\frac{dC_{H_2O_2}}{dt} = -\frac{M_k C_t k_{sr} K_{AA} C_{AA} C_{H_2O_2}}{1 + K_{AA} C_{AA} + K_{PA} C_{PA}} \quad (23a)$$

$$\frac{dC_{AA}}{dt} = \frac{dC_{H_2O_2}}{dt} + k_3 C_{PA} C_{EU} - k_4 C_{EO} C_{AA} \quad (23b)$$

$$\frac{dC_{PA}}{dt} = -\frac{dC_{H_2O_2}}{dt} - k_3 C_{PA} C_{EU} \quad (23c)$$

$$\frac{dC_{EU}}{dt} = -k_3 C_{PA} C_{EU} \quad (23d)$$

$$\frac{dC_{EO}}{dt} = k_3 C_{PA} C_{EU} - k_4 C_{EO} C_{AA} - k_5 C_{EO} C_{H_2O} \quad (23e)$$

$$\frac{dC_{H_2O}}{dt} = -\frac{dC_{H_2O_2}}{dt} - k_5 C_{EO} C_{H_2O} \quad (23f)$$

$$\frac{dC_{AG+G}}{dt} = k_4 C_{EO} C_{AA} + k_5 C_{EO} C_{H_2O} \quad (23g)$$

3 EXPERIMENT AND MODEL VALIDATION

In order to determine the parameters and check the validity of the proposed model (23) laboratory experiments were conducted. Hemp oil (HO) was epoxidised in a well stirred batch reactor by the method so far outlined in this paper, with samples extracted each hour for 8 hours, being analysed. Hemp oil's high degree of unsaturation makes it an excellent candidate for the production of bio-resins by epoxidation and it is to date seriously underrepresented in the literature. Analysis was by titration methods (Paquot, 1979): the Wij's method for determining the iodine number which gives an indication of the degree of EU of the sample, and a direct method using hydrobromic acid solution which gives a measure of the epoxy group oxygen content.

Prior to applying the titration methods qualitative analysis of several batches was carried out using Fourier Transform Infrared Spectroscopy (FTIR). The aim was to determine the optimum process conditions for: (a) molar ratios of reactant (b) weight percent of catalyst and (c) operating conditions such as stirring speed, reactor temperature and time. The FTIR spectrums for each batch were compared against that of the raw HO. Primary consideration was given to the peak present at wavenumber 3010 cm^{-1} which indicates the presence of EU. The formation of epoxide groups is the predominated mechanism by which this peak will diminish. A sample comparison is given in Fig. 04.

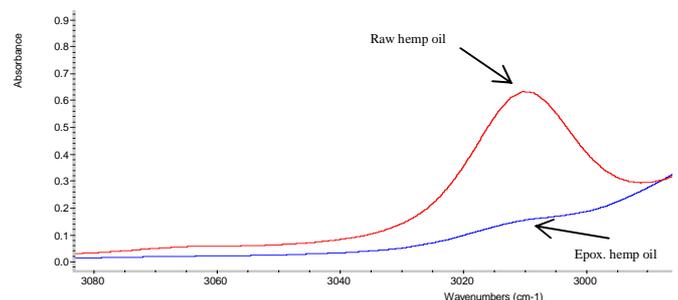


FIGURE 09: FTIR spectrum of VO against EVO showing a 97.6% consumption of band 2 at 3010 cm^{-1}

The curve identified as raw HO shows a raised peak at 3010 cm^{-1} indicating the presence of EU. The second curve, identified as epoxidised HO, shows the presence of EU after the epoxidation reaction. It can be noted that some peak still exists, though it has almost been completely consumed by the reaction. This is an indication that most of the EU has potentially been converted to epoxy groups.

It was found that optimum conditions occurred under the following conditions. (a) For the molar ratios of HO : AA : H₂O₂, between 1.00:0.35:1.00 to 1.00:0.70:1.00. (b) 15 wt% of catalyst to HO and (c) stirring speed = 150 rpm, temperature = 75°C and time = 8 hours maximum.

3.1 Materials and apparatus

Hemp Oil was supplied by Ecofibre (Maleny, Queensland, Australia). Its major properties are: Experimental iodine number = 133 (g I₂/100 g oil); Listed iodine number = 165 (g I₂/100 g oil); moles of EU in 100 g HO = 0.64; saponification value = 193. Its fatty acid concentrations are: oleic acid = 12%; linoleic acid = 57%; alpha-linolenic = 19%; gamma-linolenic = 1.7%; other FAs = 10.3%.

The glacial AA was by LabServ (Biolab, Australia) and was of analytical grade with a minimum concentration of 99.7%. The hydrogen peroxide was by LabServ (Biolab, Australia), was analytical grade with a concentration of 30%. The amberlite IR-120 was by Fluka (Sigma-Aldridge, Australia) and was of the ionic form H⁺.

The reactor used was a Mettler Toledo LabMax Automatic Lab Reactor, with a 4 L jacket glass tank stirred by a low profile ship's anchor stirrer.

3.2 Procedure

3.2.1 Experimental

The constituents were added to the reactor, stirring was set to an intermediate speed, and the reaction sequence was activated. Initially the temperature of the reactor is raised so that the mixture had a uniform temperature of approximately 40°C. The H₂O₂ was then dosed in a drop-wise fashion over a period of 1 hour. Once dosing was complete the stirring speed and temperature were increased to their operational values of 150 rpm and 75°C. These conditions were then maintained for 8 hours, at which point the reaction was terminated. Samples were removed every 30 minutes for analysis.

Each sample needed to be cleaned to remove the aqueous phase and catalyst. First the sample was washed with cool water by manually shaking in a separating funnel, repeating twice; first with near boiling water and then cool water again. It was found that an emulsion often occurred if the shaking action was too vigorous.

Next the sample was centrifuged and subsequently aerated. Aeration tended to be more effective if conducted at 60 – 70 °C. Finally the sample was dried with anhydrous sodium sulphate in the proportion of 1 to 2 g per 10 g of sample. Once the anhydrous sodium sulphate is added to the resin it was placed in an oven at 50 °C. The mixture was stirred vigorously and then filtered using Whatman No. 40 Filter Paper (Ashless, 110 mm dia).

TABLE 05: Parameters for the reaction kinetics model

Parameters	Units	Values
C _t k _{sr}	mol (s) / s · g(cat)	3.2
k ₃	100 g oil/(s mol)	2.8
k ₄	100 g oil/(s mol)	0.25
k ₅	100 g oil/(s mol)	3.0 x 10 ⁻⁴
K _{pA}	mol/L	50
K _{AA}	L/mol	0.98

3.2.2 Model Solution

The model in (23) was solved with a fourth Runge-Kutta method implemented with MATLAB's ode45 solver. The parameters were estimated by fitting the experimental values obtained from the titration methods using a nonlinear regression program based on the Levenberg-Marquardt algorithm (Tab. 01).

3.3 Results

In the two batches analysed the molar concentration of AA was the only variable. It can be seen from Fig. 05 that the concentration of EU is considerably reduced with the higher AA concentration. The starting value of 133 (g I₂/100 g oil) was determined from application of Wij's method to the raw HO. The lowest concentration of EU was 22 (g I₂ / 100 g oil) after 8 hours. The FTIR analysis of this same sample showed that a 99% consumption of the band at 3010 cm⁻¹ had occurred.

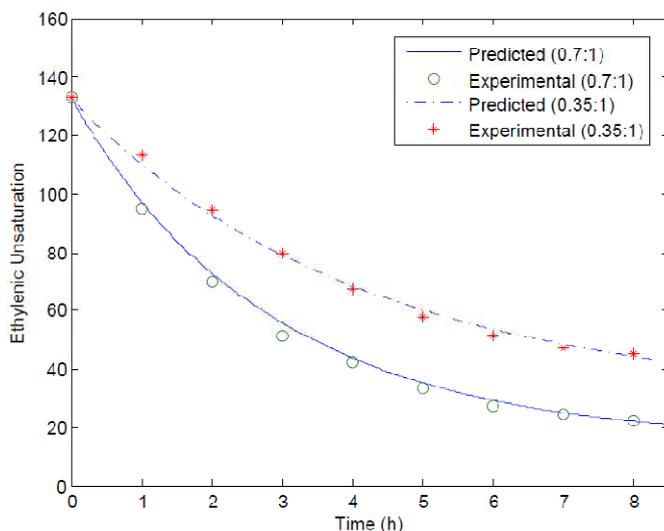


FIGURE 05: Iodine number as a measure of ethylenic unsaturation. The iodine value (g I₂/100 g oil) for two batches of epoxidised hemp oil. The starting iodine value was 133. Acetic acid concentrations were 0.35 to 1.00 of oil and 0.7 to 1.00 of oil.

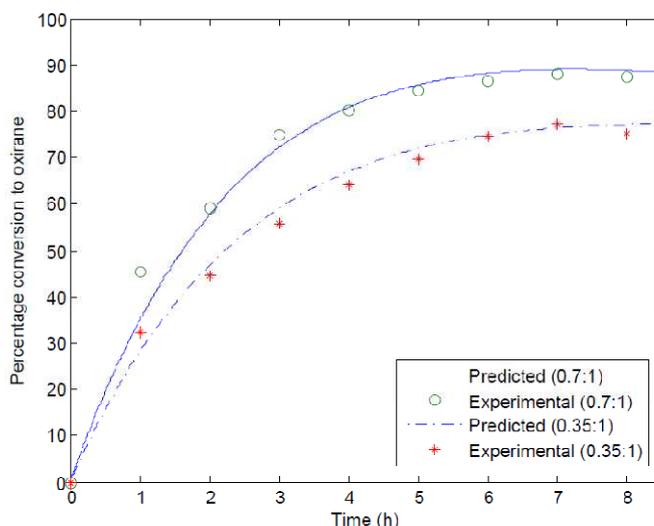


FIGURE 06: The relative percent conversion to oxirane for two batches of epoxidised hemp oil. Acetic acid concentrations were 0.35 to 1.00 of oil and 0.7 to 1.00 of oil. The highest percentage conversion was 88% after 7 hours.

In Fig. 06 the best results occurred after 6 hours for the batch with the higher concentration of AA, where an 88% conversion to epoxide oxygen had occurred. After 7 hours the curve tends to slope downwards. This is an indication the epoxide cleavage due to the presence of the catalyst is occurring.

For both instances the kinetic model tends to provide a good fit to the experimental data suggesting that the proposed mechanism is accurate and that the rate limiting step is indeed the formation of the peracetic acid on the surface of the catalyst.

4 CONCLUSIONS

An overview of the mechanisms and reaction kinetics involved in a popular method for epoxidising VO was presented. A system of differential equations was obtained that model the overall reaction. Experiments were conducted and samples analysed to measure the consumption of EU and the formation of epoxides over an 8 hour period. These results were then compared to curves produced from the model. It was found that the model generally agreed with the experimental data.

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