LOW TEMPERATURE

OXIDATION OF LINSEED OIL

A Thesis Submitted for the Degree of
DOCTOR OF PHILOSOPHY

By

Juita, BEng, MM

November, 2011

Chemical Engineering
School of Engineering
Faculty of Engineering and Built Environment
The University of Newcastle
Callaghan, NSW 2308, Australia
Statement of Originality

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

Signature: Date:
Statement of Authorship

I hereby certify that the work embodied in this thesis contains published papers of which I am a joint author. I have included as part of the thesis a written statement, endorsed by my supervisor, attesting to my significant contribution to the joint publications.

Signature: Date:
Statement of Contribution of Others

We, the undersigned, attest that Research Higher Degree candidate, Juita, has carried out the experiments, result analysis and writing of all papers included in this thesis.

Professor Bogdan Dlugogorski  Date:

Professor Eric Kennedy  Date:

Professor John Mackie  Date:
Acknowledgements

I would like to take this opportunity to express my greatest gratitude to my supervisors, Professors Bogdan Dlugogorski, Eric Kennedy and John Mackie, for their advice, guidance, continuous support and encouragement throughout my study and during completion of this thesis. Their in-depth skills and knowledge, patience, attention to detail and focus on laboratory safety encouraged me to enhance my research ability, thoroughness and written communication skills.

I would like to thank the Australian Government for providing me with the Endeavour International Postgraduate Research Scholarship that covered my tuition fees, and the University of Newcastle for the Postgraduate Research Scholarship – a stipend which supported me during my PhD studies in Australia. I express my appreciation to the Australian Research Council for funding the project costs.

My appreciation is also extended to Dr Ian van Altena who assisted me with the FTIR analysis of films of the linseed oil. The support from Tony Rothkirch on the transesterification of linseed oil is sincerely acknowledged. I really appreciate the assistance of Dr Dominika Wojtalewicz in maintaining the GC-MS instrument. I also wish to thank Damian Pomeroy, Luke Dohrmann and Nick Basgallop from Agilent Australia for their professional advice on µGC and GC-MS instruments.

I would like to express my sincere gratitude to Professor Mohammednoor Altarawneh and Scott Molloy for many helpful discussions, and the staff in the
Priority Research Centre for Energy and the Discipline of Chemical Engineering, Rebecca Carey, Chi Crosskill, David Dlugogorski, Neil Gardner, Jane Hamson, Gillian Hensman, Darren McCarthy, Con Safouris, Tanya Shanley, Rohan Stanger and James Wilson for their technical and administrative assistance.

I am sincerely grateful to my research colleagues at the Priority Research Centre for Energy, Reehan Adne Ab Rahim, Reydick Balucan, Kai Chen, Joyeth Dorado, Wenfeng Han, Sazal Kundu, Mark Rayson, Ibrahim Suleiman, Sindra Summoogum, Wendy Venpin, and many others for their advice and assistance during my study.

Last but not least, I wish to extend my appreciation to my parents, my husband Agustinus Ratno and my son Richard Asher Valentino for their support, patience and encouragement over the last four years.
Abstract

This thesis presents a series of investigations into the complex phenomena of low temperature oxidation of linseed (flaxseed) oil designed to explain the oil’s potential to engender spontaneous ignition. Varieties of linseed oil commercially available have found numerous applications, especially, in painting and in wood treatment. The addition of transition metal dryers to the oil is a well established practice as it improves the drying rate of the paint. However, the presence of metal salts often induces self-heating and spontaneous ignition, when linseed oil is applied to lignocellulosic materials, such as cotton or timber. This phenomenon is also responsible for the emission of volatile organic compounds (VOC), causing health problems to building occupants.

The thesis studies the effect of transition metal salts on the rate of oxidation and self-heating of linseed oil, examines the gaseous products and VOC, develops the reaction mechanisms through the quantum chemical calculations and models important intermediates arising in the oxidation process. We constructed two experimental rigs: (i) a flow reactor for the measurement of gaseous oxidation products and for performing the ignition experiments; and, (ii) a batch reactor system for the determination of peroxide and unsaturation values, and headspace analysis of VOC.

Fourier transform infrared (FTIR) and gas chromatographic – mass spectrometric (GC-MS) analyses indicated the presence of carbon oxides, ethane, ethylene,
Low Temperature Oxidation of Linseed Oil

acetaldehyde, propionaldehyde, acrolein, crotonaldehyde and formic acid in the gaseous products. VOC products comprised aldehydes, ketones, alcohols, carboxylic acids and furans such as hexanal, 2-pentenal, 1-penten-3-ol, 2,4-heptadienal, 2,4-decadial, 3,5-octadien-2-one, ethanoic acid, hexanoic acid, 2-pentyl-furan. The majority of the species arose from the oxidation of linolenic glycerides, the most abundant esters of linolenic acid and glycerol, present at approximately 55% in linseed oil, while other species such as 2-propenal, pentanal, hexanal, 2,4-decadial and hexanoic acid formed from linoleic compounds. Moreover, we detected cross-linking or polymerised products in the oil following the oxidation process. This phenomenon is exploited in practice in paint drying.

Salts of cobalt(II) are the most effective catalysts among other transition metal salts, followed by manganese(II) and iron(II), indicated by the highest emission of oxidation products. Cobalt displays the highest activity for the decomposition of peroxides that form during oxidation of linseed oil, into reactive radicals, leading to the exponential increase in the oxidation rate. This is reflected in cobalt’s being frequently implicated in ignition of lignocellulosic materials impregnated with the oil. Nitrates augment the rate of decomposition of peroxides, as oppose to chlorides, which slow it down. As expected, higher temperatures increased the rate of peroxide decomposition. The overall activation energy of peroxide formation corresponds to $71 \pm 1 \text{ kJ mol}^{-1}$.

FTIR analysis of oil film demonstrated the progressive decrease in the concentration of $cis$ non-conjugated double bonds, formation of $trans$ conjugated double bonds, appearance of hydroxyl groups and the broadening of the carbonyl peak in the
oxidation process, suggesting the consumption of unsaturated compounds in the oil and the formation of alcohols, aldehydes, ketones, carboxylic acids and esters. The overall rate of disappearance of double bonds follows first order kinetics with a rate constant of $0.030 \pm 0.007 \text{ h}^{-1}$ at $80^\circ \text{C}$.

Boiled linseed oil is the most reactive oil studied, followed by raw and refined linseed oils, with stand linseed oil as the least reactive. A very high reactivity of boiled linseed oil arises as a consequence of the addition of cobalt dryers, with the presence of cobalt confirmed by means of the inductively coupled plasma – optical emission spectroscopic (ICP-OES) analysis. Experiments with linseed oil applied to reactive (cotton) and unreactive (glass wool) supports have demonstrated the role of linseed oil in inducing the self heating of the reactive supports. Much more gaseous products formed in experiments with reactive than with unreactive supports.

The pathways of the oxidation of linseed oil comprise hydrogen abstraction from species of unsaturated fatty acids as the initiation reaction, followed by the interaction of allylic-type radicals with molecular oxygen to form peroxyl radicals, cyclisation reactions proceeding by intramolecular rearrangement through four and five-membered rings, and finally bond scission leading to the product formation. Quantum chemical calculations identified low energy cyclisation pathways resulting in the formation of major products, especially aldehydes and ketones. We calculated the overall exothermicity of the decomposition of the four and five membered rings as 78 and 93 kJ mol$^{-1}$, respectively.
The results of this thesis will find practical applications in formulating more accurate models of autoignition of lignocellulosic substrates impregnated with oils, the latter consisting of glycerol esters of carboxylic acids containing cis non-conjugated double bonds, such as fish oil and a number of vegetable oils with high linoleic content. The detailed measurements of the evolving VOC provide data for quantitative risk assessment of drying of paints based on linseed oil. The study on the catalytic effect of transition metal salts could be useful in applications ranging from catalysis to safety, considering that transition metals are common catalysts and the presence of transition metals can make chemical systems prone to run-away reactions. Finally, the knowledge of gaseous organic species produced in early stages of the self-heating process may be deployed in developing detection systems for warehouses storing large quantities of reactive oils.
List of Publications

Journal Articles


Conference Papers


Table of Contents

Statement of Originality  ii  
Statement of Authorship  iii  
Statement of Contribution of Others  iv  
Acknowledgements  v  
Abstract  vii  
List of Publications  xi  
Table of Contents  xii  
List of Figures  xix  
List of Tables  xxviii  
List of Abbreviations  xxx  

Chapter 1. Introduction  1  
1.1. Research Background  2  
1.2. Objectives of the Current Study  4  
1.3. Structure of the Thesis  5  
1.4. References  7  

Chapter 2. Literature Review  8  
2.1. Introduction  9  
2.2. Characteristics of Linseed Oil  11  
   2.2.1. Composition and Structure of Linseed Oil  11  
   2.2.2. Oxidation Process of Linseed Oil  15  
2.3. Experimental Methods to Test Oxidation and Self-Heating Reactions of Linseed Oil  19  
   2.3.1. Methods to Test the Spontaneous Ignition of Lignocellulosic Materials Soaked with Linseed Oil  19  
   2.3.2. Theory of Thermal Ignition and its Application to Linseed Oil  24  
   2.3.3. Measurements of Oxidation of Linseed Oil  30  

Low Temperature Oxidation of Linseed Oil  xii
2.4. Analytical Methods to Study the Oxidation Chemistry of Linseed Oil

2.4.1. Spectroscopic Techniques 35
2.4.2. Chromatographic and Mass Spectrometric Techniques 41
2.4.3. Parameters and Indices Assessing Progress of Oxidation of Linseed Oil 50
2.4.4. Measurement of Radicals Involved in Oxidation of Linseed Oil 54

2.5. Effect of Catalysts on Oil Oxidation 56

2.5.1. Role of Cobalt on Oxidation Reactions 57
2.5.2. Role of Other Metals on Oxidation Reactions 58
2.5.3. Inhibitors for Oxidation of Oils 61

2.6. Kinetics and Reaction Mechanisms of Oil Oxidation 61

2.6.1. Reaction Pathways Involved in Oxidation 61
2.6.1.1. Mechanism of Radical Chain Reactions 61
2.6.1.2. Isomerisation Reactions and Hydroperoxides as Important Intermediates 65
2.6.1.3. Mechanism of Epoxidation Reactions 70

2.6.2. Catalytic Pathways Involving Transition Metals 71

2.6.2.1. Catalytic Mechanism of Decomposition of Hydroperoxides 72
2.6.2.2. Catalytic Mechanism of Complex Formation 75

2.6.3. Kinetic Parameters for Radical Chain Reactions 76
2.6.4. Effect of Temperature on Oxidation 80

2.7. Summary 81
2.8. References 84

Chapter 3. Experimental Summary 99

3.1. Apparatus 100

3.1.1. Flow Reactor 100
Chapter 4. Oxidation Reactions and Spontaneous Ignition of Linseed Oil

4.1. Introduction
4.2. Experimental
   4.2.1. Materials
   4.2.2. Experimental Apparatus
   4.2.3. Analytical Methods
      4.2.3.1. Micro Gas Chromatographic Analysis
      4.2.3.2. Fourier Transform Infrared Analysis
      4.2.3.3. Gas Chromatographic-Mass Spectrometric Analysis
   4.3. Results and Discussion
      4.3.1. Effect of Temperature
      4.3.2. Oxidation of Oleic, Linoleic and Linolenic Acids
      4.3.3. Formation of Aldehydes and Acids
      4.3.4. Autoxidation with Cross-Linking/Polymerisation (Drying) Reactions
      4.3.5. Effect of Metal Catalyst
   4.4. Conclusions
   4.5. References
Chapter 5. The Effect of Transition Metal Salts on the Peroxide Value: Spontaneous Heating and Ignition of Lignocellulosic Materials Impregnated with Linseed Oil

5.1. Introduction 157
5.2. Experimental 159
   5.2.1. Materials 159
   5.2.2. Experimental Apparatus 160
      5.2.2.1. Oxidation Experiments in Flow Reactor 160
      5.2.2.2. Oxidation in Batch Reactor 162
   5.2.3. Analytical Methods 162
      5.2.3.1. Micro Gas Chromatographic Analysis 162
      5.2.3.2. Fourier Transform Infrared Analysis 163
      5.2.3.3. Gas Chromatographic-Mass Spectrometric Analysis 167
      5.2.3.4. Peroxide Value Analysis 168
5.3. Results and Discussion 168
5.4. Conclusions 176
5.5. References 178

Chapter 6. Roles of Peroxides and Unsaturation in Spontaneous Heating of Linseed Oil

6.1. Introduction 181
6.2. Experimental 185
   6.2.1. Materials 185
   6.2.2. Experimental Apparatus 186
   6.2.3. Analytical Methods 187
      6.2.3.1. Micro Gas Chromatographic Analysis 187
      6.2.3.2. Fourier Transform Infrared Analysis 187
      6.2.3.3. Gas Chromatographic-Mass Spectrometric Analysis 188
      6.2.3.4. Peroxide Value Analysis 189
6.2.3.5. Iodine Value Analysis

6.3. Results and Discussion

6.4. Conclusions

6.5. References

Chapter 7. Linseed Oil and its Tendency to Self-Heat

7.1. Introduction

7.2. Experimental
   7.2.1. Materials
   7.2.2. Experimental Apparatus
   7.2.3. Analytical Methods

7.3. Results and Discussion

7.4. Conclusions

7.5. References

Chapter 8. Identification and Quantitation of Volatile Organic Compounds from Oxidation of Linseed Oil

8.1. Introduction

8.2. Experimental
   8.2.1. Materials
   8.2.2. Experimental Apparatus
      8.2.2.1. Transesterification Procedure
      8.2.2.2. Oxidation Procedure
      8.2.2.3. Sampling
   8.2.3. Analytical Methods
      8.2.3.1. GC-MS Analysis of Volatile Organic Compounds
      8.2.3.2. GC-MS Analysis of Fatty Acids in Linseed Oil

8.3. Results and Discussion
   8.3.1. Content of Fatty Acids in Linseed Oil
   8.3.2. Formation of Volatile Organic Compounds
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3.2.1. Different Sampling Time</td>
<td>236</td>
</tr>
<tr>
<td>8.3.2.2. Comparison between Separation on Polar and Non Polar Columns</td>
<td>238</td>
</tr>
<tr>
<td>8.3.2.3. Comparison between Direct and Indirect Sampling Methods</td>
<td>244</td>
</tr>
<tr>
<td>8.3.2.4. Comparison between Oxidation and Nitrogen Assisted Removal of VOC</td>
<td>247</td>
</tr>
<tr>
<td>8.3.2.5. Comparison of Oxidation of Raw and Boiled Linseed Oils</td>
<td>249</td>
</tr>
<tr>
<td>8.3.2.6. Comparison with Linoleic and Linolenic Acids</td>
<td>251</td>
</tr>
<tr>
<td>8.3.2.7. Mechanism of Product Formation</td>
<td>254</td>
</tr>
<tr>
<td>8.4. Conclusions</td>
<td>255</td>
</tr>
<tr>
<td>8.5. References</td>
<td>257</td>
</tr>
</tbody>
</table>

**Chapter 9. Mechanism of Formation of Volatile Organic Compounds from Oxidation of Linseed Oil**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1. Introduction</td>
<td>261</td>
</tr>
<tr>
<td>9.2. Computational Details</td>
<td>263</td>
</tr>
<tr>
<td>9.3. Results and Discussion</td>
<td>263</td>
</tr>
<tr>
<td>9.3.1. Non-Catalytic Pathways of Product Formation</td>
<td>263</td>
</tr>
<tr>
<td>9.3.2. Catalytic Pathways of Product Formation</td>
<td>274</td>
</tr>
<tr>
<td>9.4. Conclusions</td>
<td>275</td>
</tr>
<tr>
<td>9.5. References</td>
<td>277</td>
</tr>
</tbody>
</table>

**Chapter 10. Conclusions and Recommendations**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1. Conclusions</td>
<td>282</td>
</tr>
<tr>
<td>10.2. Recommendations</td>
<td>287</td>
</tr>
</tbody>
</table>
Appendices

Appendix A. Effect of Cobalt and Cerium on Self-Heating of Linseed Oil

A.1. Introduction

A.2. Experimental

A.2.1. Materials

A.2.2. Experimental Apparatus

A.2.3. Analytical Methods

A.2.3.1. Micro Gas Chromatographic Analysis

A.2.3.2. Fourier Transform Infrared Analysis

A.2.3.3. Gas Chromatographic-Mass Spectrometric Analysis

A.3. Results and Discussion

A.4. Conclusions

A.5. References

Appendix B. Supporting Information for Chapter 9

B.1. Coordinates of the Stable and Transition-State Species Included in Figs. 9.2, 9.3 and 9.7.

B.2. Computed Electronic and Zero Point Energies of the Species Included in Fig. 9.6.

B.3. The Structure of Bis(µ-hydroxo) Complex

Appendix C. Development of a Preliminary Kinetic Model of Peroxide Formation and Decomposition
List of Figures

Figure 2.1. Formation and further reactions of allylic hydroperoxides. 17

Figure 2.2. Temperature profiles inside spontaneously-heating materials based on the models of (a) Semenov; (b) Frank-Kamenetskii; (c) Thomas. 25

Figure 2.3. The kinetic compensation effect in the measurements of Worden. 28

Figure 2.4. Jet-stirred reactor for kinetic studies of oxidation reaction. 34

Figure 2.5. Laminar flow reactor system for oxidation study of captan. 35

Figure 2.6. H-NMR spectra of linseed oil. 38

Figure 2.7. The structure changes of ethyl linoleate observed by H-NMR during oxidation catalysed by AsA6p/Fe-eh, molar ratio 2. SOP and DB refer to secondary oxidation products and double bonds. 38

Figure 2.8. Identification of tryacylglycerol composition of linseed oil from Lower Austria, pressed at room temperature. Fatty acid chains in triacylglycerols are denoted as follow: Ln: linolenic acid, L: linoleic acid, O: oleic acid, S: stearic acid, P: palmitic acid. 44

Figure 2.9. Two-dimensional GC contour plot shows the separation of compound 22, 25 and 26 which corresponds to 1,8-cineole, 1-(2,2-dimethylcyclopentyl)-ethanone and 2,4-heptadienal, respectively. 45

Figure 2.10. The comparison of anisidine value profiles of several vegetable oils during oxidation at 70 °C in a convection oven with the exposure to the circulating air. 52

Figure 2.11. ESR spectra of polyunsaturated fatty acid-derived radicals generated by soybean lipoxygenase and linoleic acid using DMPO as the spin trap. 56

Figure 2.12. ESR spectra of alkoxyl radical generated by soybean lipoxygenase and linolenic acid using DMPO as the spin trap. 56

Figure 2.13. Reaction scheme of 1-OH addition to isoprene that operates at around 303 K in pristine forest (untouched forest which exists in its original condition without interference from human activities), characterised by high abundance of OH radicals. $E_r$ denotes the reaction energy. 69
Figure 2.14. Reaction mechanism of the chemo-enzymatic epoxidation.  

Figure 2.15. Epoxidation of α-pinene under autooxidation conditions.  

Figure 2.16. Activation of cobalt complexes through (a) coordinative and (b) radical pathways.  

Figure 3.1. Schematic diagram of the experimental apparatus with flow reactor for the oxidation of linseed oil.  

Figure 3.2. Schematic diagram of the experimental apparatus in a batch system for the oxidation of linseed oil.  

Figure 3.3. The calibration curve of cobalt obtained from the ICP-OES analysis at a wavelength of 230.786 nm.  

Figure 4.1. Schematic of linseed oil oxidation experimental apparatus.  

Figure 4.2. Schematic of copper reactor with the position of wool inside.  

Figure 4.3. Comparison of two profiles of (a) carbon dioxide and (b) ethylene formed during the oxidation of linseed oil at 100 °C (glass wool support and no catalyst).  

Figure 4.4. Chromatogram of the product gases emitted from the oxidation of linseed oil at 100 °C, as separated on the PoraPLOT Q column.  

Figure 4.5. Chromatogram of the product gases emitted from the oxidation of linseed oil at 100 °C, as separated on the Molsieve 5A column.  

Figure 4.6. Profile of (a) carbon monoxide; (b) water; (c) ethane; (d) ethylene; (e) acetaldehyde and (f) propionaldehyde formed during oxidation of linseed oil at 100 °C (glass wool support and no catalyst).  

Figure 4.7. (a) Effect of temperature to the evolution of CO₂ during oxidation of linseed oil; (b) Comparison of carbon dioxide formation of active components in linseed oil during oxidation at the oven temperature of 100 °C. Experiments were conducted using glass wool support.  

Figure 4.8. The position of double allylic and monoallylic hydrogens.  

Figure 4.9. FTIR spectrum of linseed oil oxidation at 100 °C, using glass wool support.
Figure 4.10. Mechanism of formation of alkoxyl radical, followed by scission and creation of propionaldehyde, during oxidation of linseed oil. 141

Figure 4.11. (a) Comparison of carbon dioxide emission from cobalt-catalysed and uncatalysed oxidation of linseed oil on glass wool substrate at the initial temperature of 100 °C; (b) The effect of cobalt(II) and cobalt(III), on the catalytic effect of linseed oil oxidation at 80 °C on glass wool support. 144

Figure 4.12. (a) The effect of iron(II) and iron(III) on the catalytic effect of linseed oil oxidation at 80 °C on glass wool support compared to cobalt(II); (b) Comparison of carbon dioxide emission for oxidation of linseed oil at 80 °C on glass wool support between several transition metal salts. 145

Figure 4.13. (a) The effect of chromium(II) and chromium(III) salts on the emissions of carbon dioxide during oxidation of linseed oil at 80 °C on glass wool support; (b) Comparison of the effect of several copper(I) and copper(II) salts on the oxidation of linseed oil at 80 °C (glass wool support). 146

Figure 4.14. (a) Correlation between CO and CO$_2$ for oxidation of linseed oil at 80 °C on glass wool support, with and without metal catalysts; (b) The ratio of propionaldehyde to acetaldehyde formation during oxidation of linseed oil at 80 °C on glass wool support using several salts of transition metals. 147

Figure 4.15. Structure of 16-hydroperoxide-9,12,14-octadecatrienoic acid. 148

Figure 4.16. Effect of different anion on the ethylene production during oxidation of linseed oil at 80 °C on glass wool support. 149

Figure 4.17. Comparison of spectra of product gases evolved from linseed oil oxidation with and without metal nitrates present at 80 °C on glass wool support; Co(II) nitrate was used as metal salt. 149

Figure 4.18. The zoomed spectral range between 2050 and 2250 cm$^{-1}$ from Fig. 4.17. 150

Figure 4.19. Chromatograms of product gases evolved from the oxidation of linseed oil with and without metal nitrates present during oxidation. 151

Figure 4.20. Comparison of ethylene peak area (enlarged part) emitted during oxidation of linseed oil with and without metal nitrates. 151

Figure 5.1. Schematic diagram of the experimental apparatus with flow reactor for the oxidation of linseed oil. 161
Figure 5.2. FTIR spectrum of gaseous products from the oxidation of raw linseed oil in the presence of cobalt nitrate at 80 °C on the glass wool support.

Figure 5.3. (a) Identification of formic acid in the region of 1060 to 1144 cm\(^{-1}\); (b) The identification of acrolein and propionaldehyde in the band between 900 to 1000 cm\(^{-1}\) and 828 to 867 cm\(^{-1}\), respectively.

Figure 5.4. (a) The strongly overlapping bands between 1700 and 1800 cm\(^{-1}\) which consist of contributions from formic acid, acetaldehyde, propionaldehyde, acrolein and crotonaldehyde; (b) The overlapping bands between 2500 and 3100 cm\(^{-1}\) which show propionaldehyde, crotonaldehyde and ethane.

Figure 5.5. The spectral range between 2050 and 2250 cm\(^{-1}\) correspond to nitrous oxide overlap with carbon monoxide.

Figure 5.6. Comparison of the (a) emission of carbon monoxide from cobalt-catalysed and uncatalysed oxidation of linseed oil on glass wool substrate at an initial temperature of 100 °C; (b) Peroxide value built-up during oxidation of linseed oil at 100 °C between uncatalysed and using cobalt(II) nitrate catalyst.

Figure 5.7. (a) Mechanism of formation of alkoxyl and hydroxyl radical during oxidation of linseed oil; (b) The role of metal catalysts in hydroperoxide decomposition, radical recombination reaction and formation of propionaldehyde.

Figure 5.8. Comparison of the effect of several transition metal salt catalysts, cobalt(II) nitrate, cerium(III) nitrate and manganese(II) nitrate to the (a) peroxide value built-up during oxidation of linseed oil at 100 °C; (b) the concentration of carbon dioxide in the exhaust stream from the reactor, from oxidation of linseed oil on the glass wool support at 80 °C.

Figure 5.9. The comparison of the effect of several transition metal salt catalysts, cobalt(II) nitrate, cobalt(II) chloride, manganese(II) nitrate and manganese(II) chloride to the (a) peroxide value built-up during oxidation of linseed oil at 100 °C; (b) the concentration of carbon dioxide in the exhaust stream from the reactor, from oxidation of linseed oil on the glass wool support at 80 °C.

Figure 5.10. The comparison of the effect of several copper salts, copper(I) chloride, copper(II) chloride, copper(II) nitrate and uncatalysed to the (a) peroxide value built up during oxidation of linseed oil at 100 °C; (b) the concentration of carbon dioxide in the exhaust
stream from the reactor, from oxidation of linseed oil on the glass wool support at 80 °C.

Figure 6.1. (a) Peroxide value variation during oxidation of linseed oil in batch reactor at 100 °C uncatalysed and catalysed with cobalt(II) nitrate and manganese(II) nitrate; (b) Comparison of propionaldehyde produced from uncatalysed as well as cobalt and manganese catalysed oxidation of linseed oil on glass wool substrate in the flow reactor at the initial temperature of 80 °C.

Figure 6.2. Comparison of the effect of several transition metal salts catalysts, cobalt(II) nitrate, cerium(III) nitrate, manganese(II) nitrate and copper(II) nitrate on the (a) peroxide value during oxidation of linseed oil at 100 °C in the batch reactor; (b) the rate of carbon monoxide formation during oxidation of linseed oil on the glass wool support at 80 °C in the flow reactor.

Figure 6.3. (a) The effect of temperature on the peroxide formation during oxidation of boiled linseed oil; (b) logarithm of time to achieve maximum peroxide value as a function of inverse temperature.

Figure 6.4. The FTIR spectra of boiled linseed oil film (a) before reaction; (b) after 8 h reaction at 80 °C.

Figure 6.5. (a) Variation of absorbance index of peaks 970 cm\(^{-1}\) and 987 cm\(^{-1}\) representing conjugated double bonds; (b) The profile of the absorbance index at 3472 cm\(^{-1}\) indicating the formation of hydroxyl groups during oxidation of boiled linseed oil at 80 °C.

Figure 6.6. (a) Variation of absorbance index of the peak at 1744 cm\(^{-1}\) representing the carbonyl group; (b) The profile of absorbance index of the 722 cm\(^{-1}\) peak attributed to the out-of-plane C-H bend of the methylene group bridging the double bonds during oxidation of boiled linseed oil at 80 °C.

Figure 6.7. (a) Variation of the absorbance index of 3010 cm\(^{-1}\) peak during oxidation of boiled linseed oil at 80 °C; (b) Natural logarithm of the 3010 cm\(^{-1}\) peak intensity (normalised value) as a function of time.

Figure 6.8. (a) Variation of iodine value during oxidation reaction of boiled linseed oil at 80 °C; (b) natural logarithm of the iodine value as a function of time.

Figure 6.9. (a) The relationship between iodine value and absorbance index of the 3010 cm\(^{-1}\) peak for oxidation of boiled linseed oil at 80 °C; (b) The comparison of iodine value profiles between boiled linseed oil and raw linseed oil in the presence of 0.1 % cobalt catalyst during oxidation at 80 °C.
Figure 6.10. The comparison of (a) peroxide value; (b) iodine value for oxidation of boiled linseed oil at 80 °C and 100 °C. 201

Figure 6.11. (a) Mechanism of formation of alkoxyl and hydroxyl radical during oxidation of linseed oil followed by a mechanism of double bond consumption. 202

Figure 6.12. (a) The role of metal catalyst in hydroperoxide decomposition; (b) The mechanism of radical recombination reaction. 203

Figure 7.1. Emission of gaseous products from the oxidation of raw, boiled, stand and refined linseed oils at 80 °C on glass wool support: (a) carbon dioxide; (b) carbon monoxide; (c) ethane; (d) ethylene; (e) acetaldehyde; (f) propionaldehyde. 216

Figure 7.2. The effect of substrate and linseed oil type on the (a) carbon dioxide; (b) carbon monoxide emission during oxidation of linseed oil at 100 °C. 219

Figure 7.3. Comparison of FTIR spectra of exhaust gases emitted during oxidation of raw linseed oil on cotton and glass wool substrates. 220

Figure 8.1. Oxidation reaction in a batch reactor with indirect method of SPME sampling. 231

Figure 8.2. Oxidation reaction in a batch reactor with direct method of SPME sampling. 232

Figure 8.3. The chromatogram of fatty acid methyl esters in raw linseed oil after transesterification process. TIC refers to total ion count. 235

Figure 8.4. GC-chromatogram of raw linseed oil analysed on ZB-5 column acquired under the following the extraction conditions: (a) room temperature for 30 min; (b) overnight, room temperature; (c) 80 °C for 30 min. The numbers on the graphs refer to the compounds shown in Table 8.1. 238

Figure 8.5. GC-chromatogram of the VOC extracted by SMPE from the headspace above raw linseed oil and analysed on ZB-5 column, extracted at 80 °C for 30 min. The peaks numbered in the figure refer to the compounds identified in Table 8.1. 239

Figure 8.6. Gas chromatogram of the VOC extracted by SMPE from the headspace above raw linseed oil and analysed on the FFAP column. Extraction was performed at 80 °C for 30 min. The peaks numbered in the figure refer to the compounds identified in Table 8.1. 240
Figure 8.7. Gas chromatogram of the VOC extracted by SMPE from the headspace above boiled linseed oil and analysed on the ZB-5 column. Extraction was performed at 80 °C for 30 min. The peaks numbered in the figure refer to the compounds identified in Table 8.2.

Figure 8.8. Gas chromatogram of the VOC extracted by SMPE from the headspace above boiled linseed oil and analysed on the FFAP column. Extraction was performed at 80 °C for 30 min. The peaks numbered in the figure refer to the compounds identified in Table 8.2.

Figure 8.9. Comparisons of concentration histories of important species in the oil (except for panes i and j), evolving during oxidation of raw linseed oil at 80 °C, from direct and indirect sampling methods. Closed and open symbols refer to the direct and indirect methods, respectively. Structures in panes (i) and (j) are provided only for illustrative purposes, as actual stereoisomers have not been identified.

Figure 8.10. The effect of inert atmosphere (i.e., no oxidation) on the concentration histories of oxygenates in the oil (except for panes i and j), evolving during heating of raw linseed oil at 80 °C, in comparison to the evolution of the same species under the oxidative atmosphere. Closed and open symbols refer to N₂/O₂ and N₂ atmospheres, respectively.

Figure 8.11. The comparison of concentration histories of species in the oil, from oxidation of raw and boiled oils at 80 °C. Closed and open symbols denote boiled and raw linseed oil, respectively.

Figure 8.12. Summary of the concentration histories of several species detected in gaseous products of the oxidation of boiled linseed oil at 80 °C, employing indirect sampling method. Relative area denotes the area of the peak associated with a species of interest divided by the area of the internal standard.

Figure 8.13. GC-chromatogram of the VOC extracted from the vapour space above linolenic acid and analysed on the FFAP column. Extraction was performed at 80 °C for 30 min. The peak numbers refer to the compounds listed in Table 8.3.

Figure 8.14. GC-chromatogram of the VOC extracted from the vapour space above linoleic acid and analysed on the FFAP column. Extraction was performed at 80 °C for 30 min. The peak numbers denote species identified in Table 8.3.
Figure 9.1. The cyclisation pathways through the 4 and 5-membered ring involving triene structure as a model for the linolenic functional group. 266

Figure 9.2. Structures and atomic co-ordinates of stable species. 267

Figure 9.3. Structures and atomic co-ordinates of transition state species. 268

Figure 9.4. Variation of the electronic energy with increase in the carbon-carbon bondlength during the bond breakage of the 4-membered ring structure (II). 269

Figure 9.5. Structures of 4-membered ring compound (a) before and (b) after the oxygen-oxygen bond rupture. 269

Figure 9.6. The reaction potential energy surface for decomposition of peroxide compound via (a) four-membered ring; (b) five-membered ring. 271

Figure 9.7. Structures and atomic co-ordinates of optimised species. 272

Figure 9.8. The proposed mechanism for the products emission from linolenic compound. 273

Figure 9.9. The proposed mechanism for the products emission from linoleic compound. 273

Figure 9.10. Catalytic mechanism of hydroperoxide decomposition. 274

Figure A.1. Schematic diagram of the experimental apparatus for the oxidation of linseed oil. 298

Figure A.2. FTIR spectrum of linseed oil oxidation in the presence of cobalt nitrate at 80 °C on the glass wool support. 300

Figure A.3. The effect of cerium nitrate in comparison to the cobalt nitrate on the formation of gaseous product of linseed oil oxidation at 80 °C on glass wool support: (a) Carbon dioxide; (b) Carbon monoxide; (c) Ethane; (d) Ethylene; (e) Water; (f) Acetaldehyde. 303

Figure A.4. Examples of polymerisation reactions occurring during drying of linseed oil. 305

Figure A.5 (a). Formation of C$_2$H$_4$ and CO$_2$ from unimolecular (except for initiation) chain-propagating reactions involving linolenic and linoleic acids. The frames denote species identified in the product gases. 306
Figure A.5  (b). Formation of saturated and unsaturated aldehydes, involving transfer of radical site from linolenic acid to a molecule of unsaturated fatty acid. 307

Figure A.5  (c). Decomposition of oxetyl to CO and CO$_2$ by chain propagation. 308

Figure A.6. Correlation between CO and CO$_2$ for oxidation of linseed oil on glass wool support: (a) At 80 °C using cobalt nitrate and cerium nitrate; (b) At 60 °C and 100 °C with and without cobalt nitrate. 308

Figure A.7. Effect of temperature to the ratio of carbon dioxide to carbon monoxide for the oxidation of linseed oil on the glass wool support: (a) No catalyst; (b) Using cobalt nitrate. 308

Figure C.1. Evolution of peroxide concentration during oxidation of raw linseed oil in the batch reactor at 100 °C. 328

Figure C.2. Evolution of species during oxidation reaction of raw linseed oil, obtained from the model: (a) RH; (b) RO; (c) OH; (d) H$_2$O; (e) R; (f) ROO; (g) H; (h) ROOH; (i) O$_2$. 333
List of Tables

Table 2.1. Fatty acid composition of the major vegetable oils. 12
Table 2.2. A comparison of relative rates of autoxidation and photo-oxygenation of oleate, linoleate and linolenate compounds. 18
Table 2.3. The definition of symbol for the Frank-Kamenetskii model (Equation 2.3). 26
Table 2.4. Self-heating properties of linseed oil soaked cotton. 27
Table 2.5. Self-heating properties of several materials compared to cotton impregnated with linseed oil. 30
Table 2.6. Comparison of several analytical methods, reaction types observed and species detected during oxidation of linseed oil. 48
Table 2.7. Major hydroperoxides emitted during autoxidation of methyl oleate, linoleate and linolenate. 67
Table 2.8. Aggregated rate constants applied in the lipid peroxidation model. 78
Table 3.1. RMR of several gaseous products. 108
Table 3.2. The spectral bands of gaseous products analysed by FTIR. 110
Table 3.3. Absorption bands of liquid products in oil determined by FTIR. 111
Table 3.4. The comparison of hardware and operational conditions of GC/MS for analysis of gaseous products, volatile organic compounds (VOC) and fatty acid methyl esters (FAME). 112
Table 8.1. Species detected in the raw linseed oil, as adsorbed by headspace solid-phase microextraction, analysed using high (ZB-FFAP) and low (ZB-5) polarity columns and identified by quadrupole MS, supported by injection of authentic standards (marked with asterisks). 241
Table 8.2. Identification of gaseous species present evolved from boiled linseed oil, with the same analytical and experimental methodologies as described in the caption of Table 8.1. 243
Table 8.3. Identification of some compounds detected from vapour space of pure linolenic acid and linoleic acid analysed on ZB-FFAP column.

Table 8.4. Species detected in the oxidation of raw linseed oil with identification of their origin in oxidation of either linolenic or linoleic chains; positive identification is denoted by ×.

Table B.1. Computed electronic energies and zero point energies (in hartrees).

Table C.1. Peroxide built-up during oxidation of raw linseed oil at 100 °C in the batch reactor.

Table C.2. Fitted reaction rate constants for the model.
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amp</td>
<td>2-Aminomethylpyridine</td>
</tr>
<tr>
<td>AOCS</td>
<td>American Oil Chemists’ Society</td>
</tr>
<tr>
<td>APE</td>
<td>Allylic Position Equivalent</td>
</tr>
<tr>
<td>AsA6p</td>
<td>Ascorbic acid 6-palmitate</td>
</tr>
<tr>
<td>AV</td>
<td>Anisidine Value</td>
</tr>
<tr>
<td>BAPE</td>
<td>Bis-Allylic Position Equivalent</td>
</tr>
<tr>
<td>CAR/PDMS</td>
<td>Carboxen/Polydimethylsiloxane</td>
</tr>
<tr>
<td>CFAM</td>
<td>Cyclic Fatty Acid Monomers</td>
</tr>
<tr>
<td>Co(II)(acac)$_2$</td>
<td>Cobalt(II) acetylacetonate</td>
</tr>
<tr>
<td>Co-EH</td>
<td>Cobalt(II)-2-ethylhexanoate</td>
</tr>
<tr>
<td>CW/DVB</td>
<td>Carbowax/Divinylbenzene</td>
</tr>
<tr>
<td>CyH</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>DHS-TD</td>
<td>Dynamic Headspace-Thermal Desorption</td>
</tr>
<tr>
<td>DMPO</td>
<td>5,5-Dimethyl-1-pyrroline N-oxide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DNPH</td>
<td>2,4-Dinitrophenylhydrazine</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>DVB/CAR/PDMS</td>
<td>Divinylbenzene/Carboxen/Polydimethylsiloxane</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray Ionisation- Mass Spectrometry</td>
</tr>
<tr>
<td>ESI-MS/MS</td>
<td>Electrospray Ionisation- Mass Spectrometry/ Mass Spectrometry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Name</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty Acid Methyl Esters</td>
</tr>
<tr>
<td>Fe-eh</td>
<td>Fe-2-ethylhexanoate</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>GC-TOFMS</td>
<td>Gas Chromatography- Time-of-Flight Mass Spectrometry</td>
</tr>
<tr>
<td>Hdpm</td>
<td>Dipivaloylmethane</td>
</tr>
<tr>
<td>Hmp</td>
<td>2-hydroxymethylpyridine</td>
</tr>
<tr>
<td>HMTETA</td>
<td>1,1,4,7,10,10-hexamethyl triethylenetramine</td>
</tr>
<tr>
<td>H-NMR</td>
<td>Hydrogen-Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>H$_2$tbpppy</td>
<td>2-[(bis(2-hydroxy-3,5-di-tert-buty1benzyl)aminomethyl]pyridine</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectrometer</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>IRC</td>
<td>Intrinsic Reaction Coordinate</td>
</tr>
<tr>
<td>JSR</td>
<td>Jet-Stirred Reactor</td>
</tr>
<tr>
<td>LC-MS</td>
<td>Liquid Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>LC-MS/MS</td>
<td>Liquid Chromatography-Mass Spectrometry/ Mass Spectrometry</td>
</tr>
<tr>
<td>LOXes</td>
<td>Linoleate:Oxygen Oxidoreductase</td>
</tr>
<tr>
<td>MALDI-MS</td>
<td>Matrix-Assisted Laser Desorption/Ionisation-Mass Spectrometry</td>
</tr>
<tr>
<td>MALDI-RTOF-MS</td>
<td>Matrix-Assisted Laser Desorption/Ionisation-Reflectron Time of Flight-Mass Spectrometry</td>
</tr>
</tbody>
</table>
| MDN          | Methyl-N-Duryl Nitro
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeTACN</td>
<td>Polyamines 1,4,7-trimethyl-1,4,7-triazacyclononane</td>
</tr>
<tr>
<td>NFPA</td>
<td>National Fire Protection Association</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NTP</td>
<td>Normal Temperature and Pressure</td>
</tr>
<tr>
<td>ODO</td>
<td>Olfactory Detector Outlet</td>
</tr>
<tr>
<td>PA</td>
<td>Polyacrylate</td>
</tr>
<tr>
<td>PDMS-DVB</td>
<td>Polydimethylsiloxane-Divinylbenzene</td>
</tr>
<tr>
<td>PUFA</td>
<td>Polyunsaturated Fatty Acid</td>
</tr>
<tr>
<td>RMR</td>
<td>Relative Molar Response</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>SOP</td>
<td>Secondary Oxidation Products</td>
</tr>
<tr>
<td>SPME</td>
<td>Solid Phase Microextraction</td>
</tr>
<tr>
<td>SPME-GC-MS</td>
<td>Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>TD-GC-O/MS</td>
<td>Thermal Desorption Gas Chromatography combined with Olfactometry and Mass Spectrometry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TGA-DSC</td>
<td>Thermogravimetric Analysis- Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>TGA-DSC-FTIR</td>
<td>Thermogravimetric Analysis- Differential Scanning Calorimetry- Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>TGA-DSC-MS</td>
<td>Thermogravimetric Analysis- Differential Scanning Calorimetry- Mass Spectrometry</td>
</tr>
<tr>
<td>TGA-DTA</td>
<td>Thermogravimetric Analysis- Differential Thermal Analysis</td>
</tr>
<tr>
<td>TOFMS</td>
<td>Time-of-Flight Mass Spectrometry</td>
</tr>
<tr>
<td>TR-FTIR</td>
<td>Time Resolved-Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>TS</td>
<td>Transition States</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>UHT</td>
<td>Ultra High Purity</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>ZDC</td>
<td>Zinc dialkyldithiocarbamate</td>
</tr>
<tr>
<td>ZPVE</td>
<td>Zero Point Vibrational Energies</td>
</tr>
<tr>
<td>µGC</td>
<td>Micro Gas Chromatography</td>
</tr>
</tbody>
</table>