Mitigation of NO$_x$ with Pyrolysate Fragments of Solid Fuels and Their Surrogates

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This thesis is presented for the degree of

Doctor of Philosophy

Murdoch University

School of Engineering and Information Technology,
Murdoch University, Western Australia

2017
Declaration

I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

....................................

Ibukun OLUWOYE

February, 2017
Supervisory Statement

We, the undersigned, attest that Higher Research Degree candidate, Ibukun OLUWOYE, has devised and synthesised the experimental program, conducted experiments, analysed data, performed computational quantum-mechanical calculations and has written all papers included in this thesis. Professor Bogdan Z. DLUGOGORSKI and Dr Mohammednoor ALTARAWNEH provided the necessary advice on the experimental program, project direction and assisted with the editing of the papers, consistent with normal supervisors-candidate relations.

....................................

Professor Bogdan Z. DLUGOGORSKI

February, 2017

....................................

Dr Mohammednoor ALTARAWNEH

February, 2017
Dedications

To my families;

Both biologicals and within the congregation of Christ.
Acknowledgments

I appreciate GOD for the supreme assistance and strength – Dei sub numine viget.

The research work presented in this thesis reflects the help and support of many kind people around me, only to some of whom it is possible to give noteworthy salutations here.

I would like to thank my supervisors Professor Bogdan Z Dlugogorski and Dr Mohammednoor Altarawneh for their unwavering and exceptional support. Their understanding, mentorship, encouragement, dedication and magnanimity have provided a good fundamental driving force for the present study. Thank you again, your quick correspondences, corrections and gestures achieved the intended.

I am grateful to Murdoch University for the award of a postgraduate research scholarship which provided a valuable financial support for this research. This study has also been funded by the Australian Research Council (ARC) and Dyno Nobel Asia Pacific, with grants of computing time from the National Computational Infrastructure (NCI) and the Pawsey Supercomputing Centre in Perth, Australia.

Special thanks to Dr Jeff Gore of Dyno Nobel Asia Pacific Pty Limited, as well as Murdoch University’s Mr Kris Parker, Mr Andrew Foreman, Mr Kenneth Seymour, Mr Stewart Kelly, Mr John Boulton, Dr Marc Hampton and Mr Iafeta Laava for their professional and technical assistance.
I acknowledge my gratitude to my fellow student colleagues and staffs of the Fire Safety and Combustion Kinetics Research Laboratory: Zhe Zeng, Anam Saeed, Niveen Assaf, Ehsan Mohammadpour, Nassim Zeinali, Kamal Siddique, Arif Abdullah, Jomana Al-Nu’airat, Alaa Kamaluldeen, Sidra Jabeen, Sana Zahid, Pablo Fernández-Castro (University of Cantabria, Spain), Dr Juita and Dr Jakub Skut. Courtesy of you all, I experienced an exciting and fun-filled years of research and experiments.

I am highly privileged to receive the School of Engineering and Information Technology’s Graduate Poster Prize (2014), as well as the Western Australian Joint Chemical Engineering Committee (JCEC), i.e., the Institution of Chemical Engineers (IChemE) and the Engineers Australia’s (EA) selected finalist Postgraduate Research Excellence Award (2016).

Ultimately, I value the benevolent support of my family members – omnia vincit amor.
Abstract

This thesis presents a series of scientific studies exploring the thermal mitigation of nitrogen oxides (NO\textsubscript{x}) with solid fuel (waste polyethylene) and biomass surrogate (morpholine). These studies have revealed new mechanistic insights, have described the associated set of reactions, and have developed a sustainable means of reducing industrially formed NO\textsubscript{x}, for example, in combustion processes and during blasting of ammonium nitrate explosive.

Comprehensive quantum-mechanical calculations afforded the investigation of low-temperature oxidation of polyethylene (PE) film under representative NO\textsubscript{x} environments. Investigations of thermal reduction of NO\textsubscript{x} with recycled PE involved sample characterisation techniques, such as, carbon-hydrogen-nitrogen-sulfur (CHNS) elemental analyses, ion chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP-OES), as well as thermogravimetric experiments under practical NO\textsubscript{x} atmospheres. Innovative application of the on-line Fourier transform infrared (FTIR) spectroscopy and NO\textsubscript{x} chemiluminescence quantitated the reaction product species and established the removal efficiency of NO\textsubscript{x} by fragments of pyrolysing PE.

Studies on modelled surrogates, i.e., morpholine, resolved the fundamentals of thermal interaction of biomass with NO\textsubscript{x}. The experiment applied a flow-through tubular reactor coupled with FTIR spectroscopy and chemiluminescence NO\textsubscript{x} analysis, at constant pressure, reaction time, and representative fuel-rich condition. Furthermore, density-functional-theory (DFT) calculations uncovered new mechanistic insights into initial nitration reactions, and yielded their energetic characteristics, such as exothermic formation of nitro- and nitroso-adducts.
Results obtained in this study elucidated, for the very first time, initial products of low-temperature reaction of NO\textsubscript{x} with polymers and biomass, and determined the rate parameters, from the isoconversional degradation analysis, that are of great practical importance. A typical NO\textsubscript{x} removal efficiency (by fragments of pyrolysing PE) amounts to 80 % at moderate temperatures. Investigations employing a biomass surrogate revealed the sensitising role of NO\textsubscript{x} in combustion of biomass fuels. NO\textsubscript{x} reduction by biomass occurs only at temperatures in excess of 800 °C. The thesis also provides kinetic expression for process modelling. The results of the present work prove that, carbon-hydrogen-type waste polymers and biomass provide an effective means of mitigation of NO\textsubscript{x} emission in combustion processes. Furthermore, the scientific approach can be optimised to deploy solid fuels in bulk ammonium nitrate/fuel oil (ANFO)/emulsions explosive mixtures, so as to reduce the NO\textsubscript{x} formation during detonation of nitrate-based explosives in mining operations.
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  5.3.4. Thermodynamics and reaction kinetics

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6.2. Experimental Section

  6.2.1. Materials and sample characterisation

  6.2.2. Experimental methods

6.3. Results and Discussion

  6.3.1. Thermal decomposition of PE in NO\textsubscript{x} atmosphere and evolved gas analysis
6.3.2. Degradation kinetics

6.4. Conclusions

6.5. References

7. Paper V: Enhanced Ignition of Biomass in Presence of NO\textsubscript{x}

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7.2. Applied Methodologies

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7.2.2. Computational methods

7.3. Results and Discussion

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7.3.2. Initial steps in nitration of morpholine

7.4. Conclusions

7.5. References

8. Paper VI: Experimental Study on Thermal Reaction of Modelled Biofuel (Morpholine) with NO\textsubscript{x}

8.0. Abstract

8.1. Introduction

8.2. Applied Methodologies
Contribution towards Publication

The work embodied in this thesis contains published joint-authored papers as listed below. I am the principal contributor in the publications. I have included as part of the thesis a written statement, endorsed by my supervisors, attesting to my significant contribution to the joint publications.

**Paper I:** *Atmospheric Emission of NO\textsubscript{x} from Mining Explosives: A Critical Review*

Oluwoye, I.; Dlugogorski, B. Z.; Gore, J.; Oskierski, H. C.; Altarawneh, M.

*Atmospheric Environment (submitted)*

2015 impact factor: 3.459

**Paper II:** *Oxidation of Crystalline Polyethylene*

Oluwoye, I.; Altarawneh, M.; Gore, J.; Dlugogorski, B. Z.

*Combustion and Flame* 2015, 162, 3681-3690

DOI:10.1016/j.combustflame.2015.07.007

2015 impact factor: 4.168

**Paper III:** *Oxidation of Polyethylene under Corrosive NO\textsubscript{x} Atmosphere*

Oluwoye, I.; Altarawneh, M.; Gore, J.; Bockhorn, H.; Dlugogorski, B. Z.

*The Journal of Physical Chemistry C* 2016, 120, 3766-3775

DOI: 10.1021/acs.jpcc.5b10466

2015 impact factor: 4.509

**Paper IV:** *Thermal Reduction of NO\textsubscript{x} with Recycled Polyethylene*

Oluwoye, I.; Dlugogorski, B. Z.; Gore, J.; Vyazovkin, S.; Boyron, O.; Altarawneh, M.
Environmental Science and Technology 2017

DOI: 10.1021/acs.est.6b05560

2015 impact factor: 5.393

Paper V Enhanced Ignition of Biomass in Presence of NOx

Oluwoye, I.; Altarawneh, M.; Gore, J.; Dlugogorski, B. Z.

published as a Special Issue in the Fire Safety Journal 2017

DOI: 10.1016/j.firesaf.2017.03.042

2015 impact factor: 0.936

Paper VI: Experimental Study on Thermal Reaction of Modelled Biofuel
(Morpholine) with NOx

Oluwoye, I.; Dlugogorski, B. Z.; Gore, J.; Altarawneh, M.
(In preparation)

The list below itemises the publications to which I have contributed during the course of the PhD study, but which fall outside the scope of this thesis.

i: Formation of Environmentally Persistent Free Radicals on α-Al2O3

Assaf, N. W., Altarawneh, M., Oluwoye, I., Radny, M., Lomnicki, S. M., Dlugogorski, B. Z.

Environmental Science and Technology 2016, 50 (20), 11094–11102

DOI:10.1021/acs.est.6b02601

2015 impact factor: 5.393
ii: Phenol Dissociation on Pristine and Defective Graphene


*Surface Science* **2017**, *657*, 10-14

DOI: 10.1016/j.susc.2016.10.010

2015 impact factor: 1.931

iii: Inhibition and Promotion of Pyrolysis by Hydrogen Sulfide (H₂S) and Sulfanyl Radical (SH)

Zeng, Z., Altarawneh, M., Oluwoye, I., Glarborg, P., Dlugogorski, B. Z.


DOI: 10.1021/acs.jpca.6b09357

2015 impact factor: 2.883

iv: Formation of PCDDs and PCDFs in the torrefaction of biomass with different chemical composition

Gao, Q., Edo, M., Larsson, S. H., Collina, E., Rudolfsson, M., Gallina, M., Oluwoye, I.; Altarawneh, M., Dlugogorski, B. Z., Jansson, S.

*Journal of Analytical and Applied Pyrolysis* **2017**, *123*, 126-133

DOI: 10.1016/j.jaap.2016.12.015

2015 impact factor: 3.652
# Glossary of Abbreviations and Technical Terms

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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>AEISG</td>
<td>Australian Explosive Industry and Safety Group</td>
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<tr>
<td>AMD</td>
<td>Acidic mine discharge</td>
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<tr>
<td>AN</td>
<td>Ammonium nitrate</td>
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<tr>
<td>ANFO</td>
<td>Ammonium nitrate/fuel oil</td>
</tr>
<tr>
<td>AP</td>
<td>Ammonium perchlorate</td>
</tr>
<tr>
<td>ADN</td>
<td>Ammonium dinitramide</td>
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<tr>
<td>AOP</td>
<td>Acidity–oxidation potential measurements</td>
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<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
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<tr>
<td>BDH</td>
<td>Bond dissociation enthalpy</td>
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<tr>
<td>BEZ</td>
<td>Blast exclusion zones</td>
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<tr>
<td>CHNS</td>
<td>Carbon-hydrogen-nitrogen-sulfur</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>DNP</td>
<td>Numerical plus polarisation</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
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<tr>
<td>FMZ</td>
<td>Fume management zones</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalised gradient approximation</td>
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<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<tr>
<td>HEDM</td>
<td>High-energy-density material</td>
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<tr>
<td>HT-SEC</td>
<td>High temperature size exclusion chromatography</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>IC</td>
<td>Ion chromatography</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma emission spectroscopy</td>
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<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
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<tr>
<td>LST/QST</td>
<td>Linear synchronous and quadratic synchronous transit</td>
</tr>
<tr>
<td>MMD</td>
<td>Molecular mass distributions</td>
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<tr>
<td>NO\textsubscript{x}</td>
<td>Oxides of nitrogen</td>
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<tr>
<td>Nr</td>
<td>Reactive nitrogen</td>
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<tr>
<td>OB</td>
<td>Oxygen balance</td>
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<tr>
<td>OECD</td>
<td>Organization for Economic Cooperation and Development</td>
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<tr>
<td>PAC</td>
<td>Photoacoustic calorimetry</td>
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<tr>
<td>PAN</td>
<td>Peroxyacyl nitrates</td>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<tr>
<td>PE</td>
<td>Polyethylene</td>
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<tr>
<td>PM</td>
<td>Particulate matters</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surfaces</td>
</tr>
<tr>
<td>PPM</td>
<td>Parts per million</td>
</tr>
<tr>
<td>VOD</td>
<td>Velocity of detonation</td>
</tr>
<tr>
<td>SO\textsubscript{x}</td>
<td>Oxides of sulfur</td>
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<tr>
<td>STP</td>
<td>Standard temperature and pressure</td>
</tr>
<tr>
<td>ST</td>
<td>Shock tube</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetry apparatus</td>
</tr>
<tr>
<td>(T_{\text{MWL}})</td>
<td>Temperature of maximum rate of weight loss</td>
</tr>
<tr>
<td>TST</td>
<td>Transition state theory</td>
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CHAPTER 1

Introduction

This chapter sets the stage for the entire thesis, comprising detailed expression of research motivation, purpose, as well as concise outline of the dissertation...
1.1. General Overture

The recent expository report by the Intergovernmental Panel on Climate Change (IPCC)\textsuperscript{1} presented the global inventory of nitrogen oxides (NO\textsubscript{x}) in the environment. The report has established that, the anthropogenic emission of NO\textsubscript{x} adds substantially to overall discharge of reactive nitrogen species into the atmosphere. The term NO\textsubscript{x} refers to nitric oxide (NO), nitrogen dioxide (NO\textsubscript{2}) and other higher oxides based on the various possible oxidation states of nitrogen. Apart from its limited industrial and medical applications, NO\textsubscript{x} contributes to acid rain, eco-eutrophication, photochemical smog, ground level ozone, greenhouse effect, stratospheric ozone depletion, and health deterioration (e.g., chronic respiratory and obstructive pulmonary dysfunction) of predisposed organisms.\textsuperscript{2-6}

As industrial mitigation of NO\textsubscript{x} remains a prominent issue, most of the applied methods\textsuperscript{3,7-11} are designed solely for combustion systems. However, other emission sources, e.g. blasting of nitrate explosive in mining activities, require adequate and reliable NO\textsubscript{x} reduction technology. Practical technological limitations prevent the direct application of the post-combustion NO\textsubscript{x} mitigation techniques to blasting. These limitations comprise: (a) the fast dispersion of atmospheric air mixture, i.e., mixing of post-blast fume with air prevents its effective capturing, scrubbing, treatment and/or reprocessing; (b) nitrate blasting agents exhibit incompatibilities with materials (e.g., metal nitrides)\textsuperscript{12} that may serve, in the form of additives, to scavenge the generated NO\textsubscript{x}.

This thesis presents a series of scientific studies exploring both fundamental and practical aspects of the thermal mitigation of NO\textsubscript{x} with solid hydrocarbon fuel (waste polyethylene) and biomass surrogate (morpholine). It aims at developing new sustainable technologies for
reducing industrially formed NO$_x$, based on biomass and recycled plastics, especially for applications relevant to blasting of mining-grade ammonium nitrate (AN) based high-energy materials.

1.2. Research Motivation

Figure 1 presents the United Nations’ statistics on NO$_x$ emission per capita of different countries across the globe. Accordingly, and in consistent with the Organization for Economic Cooperation and Development (OECD) report, some countries (e.g. Australia) display high emission (127 kg for the year 2007 and 75 kg for the year 2012) of NO$_x$ per capita. This could be rationalised as a result of lack of mitigation of NO$_x$ emission in power plants, some industrial processes, combustion activities involving untreated fossil, bushfires and mining operations, especially large open cut mines that require significant movement of materials (including overburden) by diesel-driven excavators and trucks.
Figure 1.1. Global NO\textsubscript{x} emission per capita. The main source for NO\textsubscript{x} is burning of fuels, particularly petroleum products. In some countries agriculture and burning of savannas is also an important contributor.\textsuperscript{13} Anomalies associated with some countries such as Gabon, Niue, Paraguay, St. Vincent and the Grenadines, and Zambia are explicitly discussed in the cited reference.

Attention of environmental agencies and concerned citizens usually focuses on anthropogenic combustion of fossil fuel and/or biomass as the primary source of human-related NO\textsubscript{x} emission. Yet, according to some scientific studies available in open literature\textsuperscript{18-20} and in daily press\textsuperscript{21,22}, mining operations contribute significantly to the local emission of NO\textsubscript{x}. The AN explosive mixtures used in blasting processes may produce NO\textsubscript{x} because of imbalanced stoichiometry and intricacies of geological conditions. For instance, in open-cast mining, measurements reveal that the post-blast plume can comprise up to 500 parts per million (ppm) of NO\textsubscript{x} – primarily nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) – with the latter embodying the plumes with their orange hue.\textsuperscript{18-20}
CHAPTER 1 — Introduction

The current World Health Organisation air quality guidelines for NO\textsubscript{2} amount to a one hour level of 200 µg/m\textsuperscript{3} (1.88 µg/m\textsuperscript{3} of NO\textsubscript{2} = 10\textsuperscript{-3} ppm), and an annual average of 40 µg/m\textsuperscript{3}.\textsuperscript{23} The typical high concentrations of NO\textsubscript{x} in post-blast clouds, measuring between 5.6 to 580 ppm, exceed the safe limits by around 30 to 3000 times. These high emission values can lead to health deterioration of predisposed organisms.\textsuperscript{20} Consequently, emissions of NO\textsubscript{x} in mining operations have come under intense scrutiny by chief inspectors of mines and explosives or other health and safety authorities in the Australian jurisdictions, for example, the Chief Inspector of Coal Mines and the Chief Inspector of Explosives in the State of Queensland.\textsuperscript{24} The clouds of NO\textsubscript{x} from the detonation sites do not dissipate rapidly, and may drift outside mine boundaries into populated areas, in spite of stringent mining guidelines, causing protests of local residents.

Thus, the prime motivation behind the present study was to fill the existing gaps in knowledge and to find practical solutions to tackle the problems of NO\textsubscript{x} emissions from blasting of ammonium nitrate (AN) based explosives by developing new abatement technologies, gaining detailed knowledge of the fundamental mechanisms underpinning these technologies, and estimating the contribution of AN explosives to the total anthropogenic NO\textsubscript{x} formation.

1.3. Objectives

The purpose of this research lies in its environmental and industrial implications. It aims to investigate the thermal reactions relevant to mitigation of NO\textsubscript{x} with waste plastics and biomass surrogate. To achieves this, the thesis targets fulfilling the following objectives:
i. Exploration of anthropogenic NO\textsubscript{x} formation: (a) To review the global NO\textsubscript{x} emission channels, in light of consequential environmental impacts and mitigation methods. (b) To introduce mining and infrastructure grade explosives, and overview of environmental impact of mining. (c) To evaluate the pollutant loads from blasting operations, to quantitate the NO\textsubscript{x} formation during detonation of ammonium nitrate blasting agents with valid explanation of different underlying mechanisms, as well as to assess their contributions with respect to the global nitrogen budget. (d) To present various abatement technologies, prevailing challenges, and outlooks on future developments regarding pollution-free blasting activities.

ii. Development of sustainable solid organic fuel for reduction of NO\textsubscript{x} emission: (a) To characterise waste polymer pellets towards their applicability for the intended purpose. (b) To measure the thermal decomposition pattern of neat and recycled polymer samples under controlled and representative NO\textsubscript{x} environments. (c) To develop a mechanistic insight explaining the formation of initial product, as well as to construct the necessary isoconversional kinetic parameter governing the thermal decomposition events. (d) To quantitate the NO\textsubscript{x} reduction efficiency of pyrolysing fragments of waste polymer, and hence provide optimum operating conditions in combustion systems.

iii. Investigation of thermal interaction of biomass with NO\textsubscript{x}: (a) To gauge the sensitising effect of NO\textsubscript{x} on biomass ignition/combustion. (b) To quantify the species produced during pyrolysis and combustion of modelled biofuel in NO\textsubscript{x} presence. (c) To establish the N-selectivity and NO\textsubscript{x} reduction profile as function of temperature. In order to avoid the complex nature of biomass residues, to perform experiments using representative model compounds, such as morpholine.
In agreement with principles of green chemistry and engineering,\textsuperscript{25, 26} thermal reduction of NO\textsubscript{x} by recycled polyethylene assigns value to minimisation of solid wastes by providing an ecofriendly exit route for excess plastic wastes in our society. Moreover, its application to NO\textsubscript{x} formation in combustion plants will promote the growth of innocuous degradation products, thereby enhancing low-emission technologies and effective energy recovery from polymeric waste materials. Furthermore, the scientific approach can be optimised to deploy waste polyethylene in bulk ammonium nitrate/fuel oil (ANFO)/emulsions explosive mixtures, so as to mitigate the NO\textsubscript{x} formation during detonation of nitrate-based explosives, for example, in mining operations. In view of the aforementioned tasks, the following section outlines the specific outcomes of the thesis.

\section*{1.4. Thesis Structure}

This dissertation represents a coordinated study assessing the thermal mitigation of NO\textsubscript{x} with solid fuels and their surrogates. The following chapter presents a comprehensive literature review designed to provide a balanced assessment of the contribution of mining-grade AN explosives to anthropogenic NO\textsubscript{x} formation, to explain the mechanism of emission of NO\textsubscript{x} in sensitisation and blasting of AN explosives, to describe the existing abatement technologies as compared to those developed in this thesis, and to point out the gaps in knowledge.

Chapter 3 illustrates the main experimental and computational techniques employed within the scope of this study.
Chapters 4 and 5 present systematic investigations of low-temperature interaction of polyethylene with NO\textsubscript{x}, discovering pathways leading to the formation of initial nitro and nitroso products. These pathways govern the mitigation of NO\textsubscript{x} by fragments of pyrolysed polymers.

Chapter 6 develops technology for mitigation of NO\textsubscript{x} formed in thermal processes using waste polyethylene. This chapter has two objectives: (a) to appraise the NO\textsubscript{x} reduction efficiency of fragments of pyrolysing PE; and, (b) to construct a kinetic mechanism that operate during the removal of NO\textsubscript{x} from the post-detonation gases.

Chapter 7 analyses the initial nitration steps and establishes the reasons for enhanced ignition of biomass in presence of NO\textsubscript{x}. This enhanced ignition represents an unintended consequence for process safety of using biomass for mitigation of NO\textsubscript{x}. This can be circumvented by proper (and separate) venting of NO\textsubscript{x} exhausts in organic dust-laden areas.

Chapter 8 focuses on high-temperature reaction of biomass surrogate (morpholine) with NO\textsubscript{x}, elucidating the N-conversion profiles, and NO\textsubscript{x}-reduction efficiency as compared to conventional hydrocarbon fuels.

Chapter 9 draws the concluding remark of this thesis, and makes suggestions and recommendations for future investigations.

Finally, Chapter 10 provides all necessary supplementary material.
1.5. References


CHAPTER 1 — Introduction


CHAPTER 2

Paper I: Atmospheric Emission of NO\textsubscript{x} from Mining Explosives: A Critical Review


The chapter presents a comprehensive focused review of one of the major influences of mining activities on atmospheric chemistry. It provides a balanced explanation on the contribution of AN explosives to anthropogenic NO\textsubscript{x} formation, describing in detail the underlying mechanisms and abatement technologies as compared to those developed in this thesis...
2.0. Abstract

High-energy materials such as emulsions, slurries and ammonium-nitrate fuel-oil (ANFO) explosives play crucial roles in mining, quarrying, tunnelling and many other infrastructure activities, because of their excellent transport and blasting properties. However, these explosives engender environmental concerns, due to atmospheric pollution caused by emission of nitrogen oxides (NO\(_x\)) from blasts that amounts up to 5 kg/(t AN explosive), on average. This first-of-its-kind review provides a concise literature account of the formation of NO\(_x\) during blasting of AN-based explosives, employed in surface operations. We estimate the total NO\(_x\) emission from AN-based explosives as 0.05 Tg (i.e., 5 \times 10^4 t) N per annum, which compares to the total global anthropogenic NO\(_x\) emissions of 41.3 \times 10^6 t N/y. Although the global budget is only on the scale of one per mille on a global scale, these emissions involve concentrated discharges characterised by NO\(_x\) concentration in the order of 500 ppm which can have workplace and local effects. The review describes different types of AN energetic materials for civilian applications, and summarises the essential properties and terminologies pertaining to their use. Furthermore, we recapitulate the mechanisms that lead to the formation of the reactive nitrogen species, and compare them with those experienced in other thermal and combustion operations. We also review the mitigation approaches, including guidelines and operational-control measures that minimise or manage the risk of post-blast NO\(_x\) fumes during mining operations. The review discusses the abatement technologies such as formulation of new explosive mixtures, comprising secondary fuels, spin traps and other additives, in light of their effectiveness and efficiency. We conclude the review with a summary of unresolved problems, identifying possible future developments and their impacts on the environment with emphasis on local and workplace loads.
2.1. Introduction

High-energy-density materials (HEDMs) have revolutionised the world’s mining, infrastructure and aviation industries. These materials generally consist of explosives, propellants and pyrotechnics. They generate high temperature and pressure via complex combustion phenomena involving physicochemical phase changes, complemented by rapid exothermic reactions.¹⁻³ Technically, the term “explosion” defines a sudden release of energy confined in (but not limited to) HEDMs, accompanied by dramatic discharge of expanding gases⁴ that enables impacting work done on the surroundings.

HEDMs fall into two broad categories, namely, the low and the high explosives. The salient features entrenched in this classification include the reaction velocities and pressures achieved during the combustion processes.¹⁻⁵ Low explosives, otherwise known as fast-burning or deflagrating substances, burn in a regular but less shattering manner, while exhibiting a relatively low reaction velocities between 0.01 – 400 m/s, and bar-range pressures. Typical examples of low explosives comprise black powders, smokeless powders, propellants and pyrotechnic mixtures. On the contrary, high explosives demonstrate superior rates of reaction, i.e., velocity of detonation (VOD) ranging from 1000 – 9000 m/s, as well as higher pressure of explosion. High explosives generate supersonic shock waves and perform relatively higher work on their surroundings. Sensitivity of high explosives to detonation serves as a convenient criterion to subdivide them into three main classes:²⁻⁶⁻⁷

(i) Primary high explosives (primers) represent extremely sensitive materials that easily explode with the application of shock, spark, fire, friction, impact and heat. They remain dangerous to handle and find use in comparatively small quantities in primers,
detonators and percussion caps. Examples of primary high explosives include mercury fulminate, lead azide, lead styphnate, silver azide, tetrazene, and diazodinitrophenol.

(ii) Secondary high explosives (base explosives) display relative insensitivity to mechanical shock, friction or flame, but shock waves of primary explosives can set them off, i.e., detonators. Common examples comprise nitro-glycerine, nitroglycol, nitromethane, dynamite, TNT, RDX, PETN, HMX, etc.

(iii) Tertiary high explosives (blasting agents) exhibit the least sensitivity. They cannot reliably detonate by application of practical quantities of primary explosive, requiring a booster of secondary explosives. This class consists of oxidisers such as ammonium nitrate (AN), ammonium perchlorate (AP), ammonium dinitramide (ADN), etc., and their corresponding fuel-composite mixtures.

Tertiary high explosives excel other high explosives for their stability, demanding more energy to set off. Blasting agents afford variety of civilian applications involving local displacement of earth crust, structural demolitions and building implosions, spanning large-scale mineral extraction, quarrying, tunnelling, and many other construction operations. AN-based blasting agents display desirable compromise between production, handling, safety, economic, and performance characteristics as compared to nitrated hydrocarbon compounds, i.e., molecular explosives.

AN-fused high energy products include emulsions, slurries and ammonium-nitrate-fuel-oil (ANFO) mixtures. Owing to their excellent transport and blasting properties, they represent nearly 90% of the total explosives employed worldwide in the civilian sector. A mixture of
a well-balanced bulk ANFO usually consists of 5.7 wt. % fuel oil in an oxidising AN matrix, whereas, formulations of emulsion and slurry explosives consist of additional components that improve the contact between the oxidising salt and the fuel, and sensitise these materials. For instance, emulsion explosives contain droplets of supersaturated aqueous phase of AN dispersed in continuous oil phase (mixture of fuel and emulsifier). The literature provides further information on the composition, manufacturing and underlying properties of these materials. Volatile oils give the greatest sensitivity towards the reaction. However, petroleum fractions with low flash points pose hazards. Therefore, the optimum choice incorporates fuel oils similar to those used in diesel engines, i.e., No 2 distillate fuel oil, biodiesel, etc. As seen by comparing the exothermicity of overall Equations (a) and (b), the fuel component of AN explosives increases their energy density.

\[
\begin{align*}
\text{NH}_4\text{NO}_3 & \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2(g), & \Delta H_r = -1440 \text{ kJ/kg} & \text{(a)} \\
3\text{NH}_4\text{NO}_3 + \text{CH}_2 & \rightarrow 3\text{N}_2(g) + \text{CO}_2(g) + 7\text{H}_2\text{O}, & \Delta H_r = -3900 \text{ kJ/kg} & \text{(b)}
\end{align*}
\]

Global (or overall) Equations (a) and (b) summarise a number of elementary steps that underpin each of these reactions. We use the right-headed arrows in the equations to stress their irreversibility. If a practical explosive formulation deviates from the stoichiometric requirements defined by Equation (b), the resulting fuel rich and lean fuel conditions lead to redox processes described in Equations (c) and (d), respectively.

\[
\begin{align*}
2\text{NH}_4\text{NO}_3(s) + \text{CH}_2 & \rightarrow 2\text{N}_2(g) + \text{CO}(g) + 5\text{H}_2\text{O}, & \Delta H_r = -3400 \text{ kJ/kg} & \text{(c)} \\
5\text{NH}_4\text{NO}_3(s) + \text{CH}_2 & \rightarrow 4\text{N}_2(g) + \text{CO}_2(g) + 11\text{H}_2\text{O} + 2\text{NO}, & \Delta H_r = -2500 \text{ kJ/kg} & \text{(d)}
\end{align*}
\]
Imbalanced stoichiometric reactions and intricacies in mineral deposits results in noxious footprint of ammonium nitrate explosives. For instance, in open-cast mining, observations reveal that, the post-blast plume can harbour more than 500 parts per million (ppm) of nitrogen oxides (NO₃),\textsuperscript{12-14} consisting mainly of nitric oxide (NO), which subsequently undergoes atmospheric oxidation to form nitrogen dioxide (NO₂) according to overall Equation (e).

\[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g), \quad \Delta H_r = -57 \text{ kJ/mol} \quad (e) \]

Orange-hue post-blast fumes indicate the presence of NO₂. Clouds of NOₓ from the detonation sites do not dissipate rapidly, and may drift outside mine boundaries into populated areas, in spite of stringent mining guidelines, causing protests of local residents. Managing exclusion zones by industry adds to the cost of mine operations. The average emission flux of NOₓ from blasts scales up to 5 kg/(t AN explosive).\textsuperscript{15-19}

This critical review presents a comprehensive summary of the influence of mining activities on atmospheric chemistry. We commence by introducing the main environmental impacts of mining, and then provide a critical evaluation of mechanisms of NOₓ formation. The review offers a balanced explanation on the contribution of AN explosives to anthropogenic NOₓ formation as generalised in Figure 2.1, emphasising the relevant abatement technologies. From this perspective, the review informs researchers and engineers across germane environmental disciplines and interested citizens on how to tackle unconfined NOₓ emissions with best-practice technologies.
Figure 2.1. Outline of NO$_x$ forming activities during the use of ammonium nitrate explosives in mining operations.

### 2.2. Environmental impact of mining

This section briefs the reader on the overall impact of mining on the environment, to set the scene for subsequent discussion:

(i) Typical air contamination: This category includes the emission of harmful gases, dust, explosive residues and particulate matters (PM). The major gaseous load from mining activities corresponds to NO$_x$, sulfur oxides, carbon oxides, photochemical oxidants, volatile organic compounds (VOCs) and methane. Overall, these emissions originate from either mobile, stationary or fugitive sources. The mobile sources involve vehicles and excavation equipment with on-board abatement techniques, such as catalytic converters. Stationary sources comprise large operations.
such as drying, roasting and smelting that allow post-activity emission treatments, whereas fugitive emissions result from rapid activities such as blasting and wind erosion preventing the gas clean-up by venting technologies.\textsuperscript{36-40}

(ii) Water resources impact: The environmental influence of mining on water resources embodies quantity- and quality-related issues. The former refer to drop and alterations in groundwater table.\textsuperscript{20} High water consumption in mining processes results in shortage of local water supplies.\textsuperscript{37, 41, 42} In the interest of public concerns for aquatic life, the quality of ground and surface water deteriorates as a result of suspended solids, leached contaminants (basically heavy metals), erosion of soil and mine wastes, and acidic mine discharge (AMD, formed when pyrite (FeS\textsubscript{2}) reacts with water and air to produce sulfuric acid and dissolved iron).\textsuperscript{20, 39, 43}

(iii) Land and soil infectivity: In addition to physical subsidence and topographical disturbances,\textsuperscript{20, 41, 44-46} mining operations contribute to soil contamination via chemical channels.\textsuperscript{47} The common contaminants include heavy metals and inorganic ions that can persist long after mine remediation.\textsuperscript{47, 48} Other environmental pathways operate through atmospheric deposition to affect the soil and water quality. The aftermaths of soil pollution disturbs the biological food chain, progressing from absorption of pollutants by plants to ingestion of plant material by individual organisms.

(iv) Miscellaneous issues: Other significant impact of mining includes thermal-related losses, waste treatment and disposal, ecological imbalance, noise and vibration pollution, resettlements, habitat loss and fragmentation, and economic waves.\textsuperscript{20, 37, 39, 41, 49-51}
Blasting activities result in formation of dust, primary particles and gaseous (basically NO$_x$) emissions. The air quality remains highly vulnerable as, unlike water or soil, practical considerations prevent reprocessing of atmospheric air mixtures. The post-blast fumes require adequate on-site control measures to reduce their negative impacts on the surrounding communities and the environment. The recent growth of mining industries, and continuous shift from underground mining to open-pit excavations have exacerbated the fume hazards. Other activities in mining operations also contribute to the formation of NO$_x$ species, however, this review focuses on emissions pertinent to direct use of AN explosives.

2.3. Overview of global NO$_x$ formation

On a global scale, reactive nitrogen (Nr) species arise from various human-related activities and natural terrestrial processes. Figure 2.2 demonstrates the speciation, environmental interactions and global sources of NO$_x$. The major Nr species comprise NO$_x$, ammonia, ammonium, nitrous oxide, nitrate and nitric compounds. Atmospheric NO$_x$ contributes substantially (nearly half) to the overall balance of Nr species, by trailing only the emission of ammonia. Also, Nr accumulates in the environment as a result of higher emission rates, relatively to denitrification to nonreactive N$_2$. 


Figure 2.2. Annual atmospheric emissions and interactions of NO$_x$. The data on the rightward figure, except for “others”, are extracted from IPCC 2014. All values are reported in Tg N/y. Conversion details: 1 Tg = $10^{12}$ g or $10^6$ tonnes. “Others” denotes emission sources with unknown global estimates, which may include aircraft ($\approx 0.7$ Tg N/y), 67 oxidation of NH$_3$ ($\approx 3.0$ Tg N/y), 68 and dispersed use of nitrate explosives (estimated to be $\approx 0.05$ Tg N/y). Total anthropogenic emission correspond to 41.3 Tg N/y.

2.3.1. Anthropogenic NO$_x$ emissions

Of all the sources of anthropogenic NO$_x$, combustion of fossil fuels induces the most emission, mainly due to the constituent nitrogenous heterocyclic species in the fuels’ structure. 70,71 During combustion processes, NO$_x$ and its precursors arise via the four routes: (a) the thermal process involving the Zeldovich reaction between atmospheric nitrogen and oxygen as a result
of high combustion temperature (above 1500 °C);\textsuperscript{72-74} (b) the fuel-N channel arising from oxidation of nitrogen compounds chemically bounded with the fuel organic matter. This corridor generates about 80 % of NO\textsubscript{x} emission in pulverised solid fuel combustion;\textsuperscript{73,75-78} (c) the prompt process characterising the reaction of atmospheric nitrogen with hydrocarbon radicals to form NO\textsubscript{x} precursors via a series of gas-phase reactions;\textsuperscript{73} (d) the heterogeneous route occurring as the result of the reactions of solid carbonaceous substance, i.e., char remaining after devolatilisation.\textsuperscript{70,78} The net amount of NO\textsubscript{x} formed from heterogeneous reactions depends on the intrinsic reactivity and the internal surface area of the char, as well as charring conditions.\textsuperscript{78-80} In addition, moderate nitrogen content of biofuels and lower temperature of biofuel combustion (in comparison to fossil-fuel combustion) decrease the release of NO\textsubscript{x} species in biomass firing.\textsuperscript{73,78,81-83}

Other human-related emission sources include agricultural activities, emission of NH\textsubscript{3} in chemical industry (e.g. from the Haber-Bosch process) and use of nitrate oxidisers in aviation, infrastructure and mining industries. Assessing the amount of NO\textsubscript{x} produced from a blast depends on the relative position (distance and angle) of the observer and the prevailing weather conditions.\textsuperscript{84} The Australian Explosive Industry and Safety Group (AEISG) has developed a viable qualitative chart,\textsuperscript{85} as seen in Table 2.1, to rate the post-blast NO\textsubscript{x} (typically NO\textsubscript{2}) on a simple scale of 0 to 5, but without linking the fume appearance to NO\textsubscript{x} concentration.
Table 2.1. Field colour chart for visual rating of blast-generate NO\textsubscript{x}.

<table>
<thead>
<tr>
<th>Level</th>
<th>Colour</th>
<th>Pantone number</th>
<th>Typical appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 0</td>
<td>Warm Grey 1C</td>
<td>(RGB 244, 222, 217)</td>
<td>![Image]</td>
</tr>
<tr>
<td>No NO\textsubscript{x} gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level 1</td>
<td>Pantone 155C</td>
<td>(RGB 244, 219, 170)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Slight NO\textsubscript{x} gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level 2</td>
<td>Pantone 157C</td>
<td>(RGB 237, 160, 79)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Minor yellow/orange gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level 3</td>
<td>Pantone 158C</td>
<td>(RGB 232, 117, 17)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Orange gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level 4</td>
<td>Pantone 1525C</td>
<td>(RGB 181, 84, 0)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Orange/red gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level 5</td>
<td>Pantone 161C</td>
<td>(RGB 99, 58, 17)</td>
<td>![Image]</td>
</tr>
<tr>
<td>Red/purple gas</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The pollutant release and transfer registers implemented since 1990s in all OECD countries do not provide estimates of the contribution of NO\textsubscript{x} from blasting to the total anthropogenic emission of this gas. For example, the Australian National Pollutant Inventory (NPI) reports combined emission of NO\textsubscript{x} from all activities at each mining facility, focussing on the amount of each pollutant rather than on establishing links between the amounts and the underlying discharge mechanisms.\cite{26,27} This is not a satisfactory situation. The increasingly prevalent open cut mines in Australia move large amount of overburden, an effort that tends to govern the NO\textsubscript{x} footprint of each mine. An additional, somewhat intractable, problem lies with the estimation approach itself that assumes emission factors that do not account for episodes of large discharge.
of NO\textsubscript{x} fumes from blasting. For this reason, in this article we adopt an average yield of NO\textsubscript{x} emission of 5 kg/(t AN explosive),\textsuperscript{25-29} as a first-order conservative approximation, and consider the global annual (for the year 2016) AN production of 58.2 million tonnes,\textsuperscript{87} of which 35% are deployed in the explosive industry,\textsuperscript{88} to arrive at a global annual emission of approximately 0.1 Tg/y of NO (i.e. 0.05 Tg N/y, or 5×10\textsuperscript{4} t N/y) generated as a result of mining-related blasting. This number is rather small in comparison to the total emissions of anthropogenic NO\textsubscript{x} from all sources that corresponds to 41.2×10\textsuperscript{6} t N/y (cf. Figure 2.2). Thus, in spite of its potential for large localised dispersive emission of NO\textsubscript{x} that may result in fatalities, blasting is not a major contributor to the environmental inventories of this pollutant.

2.3.2. NO\textsubscript{x} in the environment and mining workplaces: processes and health effects

2.3.2.1 Direct NO\textsubscript{x} health effects

Accumulation of atmospheric NO\textsubscript{x} can lead to various environmental and bio-related hazards. In the context of public health, NO\textsubscript{x} induces a number of chronic diseases. Low levels can irritate eyes, nose, throat and lungs, possibly leading to coughing and bleeding, shortness of breath, tiredness and nausea, and can also result in temporary build-up of lung fluids. Exposure to high concentration of NO\textsubscript{x} can cause pulmonary oedema as well as acquired or type II methemoglobinemia that exhibits symptoms of rapid burning, spasms and swelling of tissues in the throat and upper respiratory tract, reduced oxygenation of tissues, build-up of lung fluids, and possibly death.\textsuperscript{26,89} The current World Health Organisation air quality guidelines for NO\textsubscript{2} allow one hour-level safe limit of 200 µg/m\textsuperscript{3} (1.88 µg/m\textsuperscript{3} of NO\textsubscript{2} = 1 parts per billion), and an annual average of 40 µg/m\textsuperscript{3}.\textsuperscript{90} However, typical concentrations of NO\textsubscript{x} in post-blast clouds
can reach between 5.6 to 580 ppm, \cite{12,23,24} exceeding the safe limits by around 30 to 3000 times. Exposure of humans and wildlife to these high concentrations can lead to injuries \cite{24} and fatalities. \cite{91}

2.3.2.2 Atmospheric NO$_x$ processing and the consequential health impacts

The chemical reactivity of NO$_x$ in the presence of other atmospheric substances produces secondary pollutants. For instance, ground-level ozone, abundant in photochemical smog, arises as a result of chemical interaction of NO$_x$ with reactive hydrocarbons and other volatile organic compounds (VOC), in a process facilitated by heat and sunlight. \cite{74} Likewise, oxidation of NO$_x$ contributes to atmospheric formation of nitrate aerosols, \cite{66,92-95} and notably, the mineral particles and fugitive dusts synchronously present in post-blast fumes easily facilitate such reactions. Concerns about effects on human health include damage of lung tissue and dysfunction of respiratory system, such as emphysema and bronchitis. Furthermore, dissolved N in the form of nitrate species in groundwater have negative impacts on human health. \cite{66,96,97} Short-term exposure to nitrate in drinking water (contaminated by groundwater) at levels above the health standard of 10 mg/L nitrate-N remains a potential health problem, primarily for infants and people previously subjected to kidney dialysis treatment. In the human body, NO$_3^-$ converts into nitrite, which can cause methemoglobinemia by interfering with the ability of haemoglobin to take up O$_2$. Most cases of methemoglobinemia occur after consuming water with high concentrations of NO$_3^-$. \cite{98} Other health consequences of ingestion of nitrate at elevated concentrations include respiratory infection, reproductive risks, alteration of thyroid metabolism, and cancers induced by conversion of NO$_3^-$ to N nitroso compounds (especially
to nitrosamine, under certain conditions of gastric achlorhydria in the oral cavity, bowel or bladder) in the body.\textsuperscript{62,99,100}

2.3.2.3. Impact to ecosystems

With respect to impact on ecosystems, the wet (e.g., acid rain) and dry deposition of NO\textsubscript{x} increase the nitrogen contents in the soil and terrestrial water bodies. This leads to eutrophication and depletion of aquatic oxygen (hypoxia), as well as to rare anoxic conditions (anoxic conditions refer to severe hypoxia). Excessive level of these conditions affects marine life, causes leaf and root damage, and contributes to soil and water acidity.\textsuperscript{26,49,89} Other environmental impact of NO\textsubscript{x} includes stratospheric ozone depletion and corrosive effects of acid rain on life and property.

2.4. Mechanism of NO\textsubscript{x} formation during the use of AN explosives

Three distinct mechanistic pathways generate NO\textsubscript{x} during blasting of AN agents in various mining, civilian and infrastructural activities, as explored in the following sections; i.e., stoichiometrically unbalanced blasting, deflagration of AN prills and gassing of emulsion blends.
2.4.1. Stoichiometrically unbalanced blasting

The following general reaction\textsuperscript{101} balances the chemical species appearing in the blasting process:

\[(3x + 1)\text{NH}_4\text{NO}_3 + \text{C}_x\text{H}_{(2x+2)} \rightarrow (3x + 1)\text{N}_2 + (7x + 3)\text{H}_2\text{O} + x\text{CO}_2 \quad (2.6)\]

Equations 2.7 and 2.8 recast Equation 2.6 for the fuel oil and carbon residue, respectively, the two most common fuels comprised in the emulsion. In general, however, the fuel could be carbon-based\textsuperscript{8,101,102} or nonconventional, depending on fuel availability\textsuperscript{12,103-105}.

\[3\text{NH}_4\text{NO}_3 + \text{CH}_2 \rightarrow 3\text{N}_2 + \text{CO}_2 + 7\text{H}_2\text{O} \quad (2.7)\]
\[2\text{NH}_4\text{NO}_3 + \text{C} \rightarrow 2\text{N}_2 + \text{CO}_2 + 4\text{H}_2\text{O} \quad (2.8)\]

Alterations in bulk material composition, wicking of fuel content (i.e., removal of fuel by capillary suction of the surrounding rock), as well as intricacies of geological conditions such as moisture in blast hole (wet blast condition) and the presence of mineral matter prompt the formation of CO and NO. Manufacturers and end users often employ a characteristic property called “oxygen balance” (OB) to describe the reaction stoichiometry. The OB value of the constituent component of an explosive mixture expresses the amount of oxygen, in mass fraction unit (i.e., g O\textsubscript{2}/(g compound)), in excess or deficiency with respect to stoichiometry. It is calculated according to\textsuperscript{106}:

\[\text{OB} = \frac{16 \left( O - 2C - \frac{1}{2}H + M \right)}{MW} \quad (2.9)\]
where $MW$ refers to the molecular weight in g/mol of a compound (e.g., 80 g/mol for NH$_4$NO$_3$), and $O$, $C$, $H$ and $M$ correspond to the number of oxygen, carbon, hydrogen and metal atoms, respectively. A well-formulated commercial explosive must maintain an OB value close to zero. For example in ANFO mixture, AN has an OB of +0.20 ($=16 \times (3-1/2\times4)/80$), while the fuel oil retains a unit of –3.4 ($=16 \times (0-2\times1-1/2\times2)/14$). Hence, the optimised ratio of ANFO for a fully balanced bulk formulation corresponds to 94.3/5.7 (solve for $x$, the mass fraction of AN, $x\times0.2-(1-x)\times3.4=0$, $x=0.943$). OB influences detonation products, as illustrated in example Reactions 2.10 and 2.11:

\begin{align*}
\text{–OB} & \quad 2\text{NH}_4\text{NO}_3 + \text{CH}_2 \rightarrow 2\text{N}_2 + \text{CO} + 5\text{H}_2\text{O} & (2.10) \\
\text{(excess fuel)} && \\
\text{+OB} & \quad 5\text{NH}_4\text{NO}_3 + \text{CH}_2 \rightarrow 4\text{N}_2 + \text{CO}_2 + 11\text{H}_2\text{O} + 2\text{NO} & (2.11) \\
\text{(lean fuel)} && \\
\end{align*}

The NO gas oxidises rapidly in the atmosphere (via Reaction 2.12 with a rate constant of $2.08 \times 10^{-38} \text{ cm}^6/\text{molecules}^2 \text{ s at } 25 \degree \text{C}$)\textsuperscript{107,108} into orange-coloured NO$_2$, a relatively stable species that exists in equilibrium with its colourless linear dimer, N$_2$O$_4$. The equilibrium constant for Reaction 2.13 decreases with an increase in total pressure ($P$) of NO$_2$ + N$_2$O$_4$, and amounts to $7.1 \times 10^5 \text{ Pa}^{-1}$ at $P = 4.4 \times 10^3 \text{ Pa}$ and $T = 25 \degree \text{C}$.\textsuperscript{109}

\begin{align*}
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 & (2.12) \\
2\text{NO}_2 & \rightleftharpoons \text{O}_2\text{N–NO}_2 & (2.13)
\end{align*}
Figure 2.3 illustrates the effect of OB, fuel content and moisture on NO\textsubscript{x} formation from typical ANFO blends. The literature also provides information on the aspect of other parameters such as degree of confinement and emulsion additives.\textsuperscript{29,110}
Figure 2.3. Effect of oxygen balance (a) and percent fuel oil (b) on NO\textsubscript{x} formation from different ANFO blends, and the influence of water content (c) on NO\textsubscript{x} emission from 94/6 ANFO. Digitised data are sourced from Rowland and Mainiero’s study.\textsuperscript{18} NO\textsubscript{x} concentrations are recorded in (L at STP)/(kg bulk explosive).
Furthermore, as shown in Figure 2.4a, the interaction of fuel with AN under fuel-lean conditions leads to NO\(_x\) species via the nitrous acid, nitro- and nitroso-hydrocarbon intermediates. According to Oxley and co-workers, the NO\(_2\) generated during thermolysis of AN reacts with the fuel content, producing additional NO\(^{11}\)

**Figure 2.4.** (a) NO\(_x\) formation by interactions of fuel content of AN blasting agents during stoichiometrically unbalanced detonation. Deficiency of fuel results in positive oxygen balance. (b) Mechanism of NO\(_x\) formation as a result of N transformation in AN deflagration during blasting of bulk explosive mixtures. (c) NO\(_x\) formation during chemical gassing of emulsion explosives. Boxes denote the reactants and the dash-line circles the NO\(_x\) products.

“D”, in pane (c), represents diffusion steps across the oil films.

### 2.4.2. Deflagration of AN prills
Deflagration occurs in blasting of AN explosives when the fuel content is insufficient for a complete chemical reaction, and as a result, the AN prill provides a nitrogen based fuel source.\textsuperscript{110} This condition also arises as a consequence of fuel deficiency and/or mixture inhomogeneity due to inadequate integration of ANFO. Literature comprehensively reviews the properties of AN, especially those relevant to its use in explosive mixtures.\textsuperscript{8,9,112,113} Although various mode of decomposition chemistry of AN have been postulated,\textsuperscript{8,9,114} the complete mechanism remains poorly understood. The current consensus of opinion explains the thermal decomposition of solid AN to proceed by two channels in the condensed phase, ionic and radical. Species that leave the condensed phase participate in further radical reactions in the gas phases.\textsuperscript{13}

Except for evaporation of water, during heating, AN remains thermally stable until the temperature reaches the melting point. AN melts at around 169 °C, and then starts decomposing as the ionic species react with each other.\textsuperscript{115} This begins by an endothermic dissociation step (Equation 2.14), followed by decomposition of HNO$_3$ and subsequent oxidation of NH$_3$ according to Equations 2.15, 2.16 and 2.17, respectively.\textsuperscript{10,14,15,111,116} A broader list of reactions and their corresponding rate parameters in the liquid phase have been provided by Skalis’s et al.,\textsuperscript{15} though, the decomposition period depends on imposed heating rates and particle size.

\begin{align}
\text{NH}_4\text{NO}_3 & \rightarrow \text{NH}_3 + \text{HNO}_3 \\
\text{HNO}_3^+ + \text{HX} & \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{X}^- \\
\text{where } \text{HX} & = \text{NH}_4^+, \text{HNO}_3, \text{H}_2\text{O}, \text{and others} \\
\text{NH}_3 + \text{NO}_2^+ & \rightarrow \text{products (N}_2\text{O, H}_2\text{O)}
\end{align}

(2.14) \quad (2.15) \quad (2.16)
\[
\text{NH}_3 + X' \rightarrow \text{products (NO, NO}_2, \text{H}_2\text{O)} \quad (2.17)
\]

The gas-phase mechanism becomes noticeable at higher temperatures, when species emanating from the surface (above the melt front) undergo further radical oxidation and/or decomposition to form a relatively more stable products. Analysis of the rapid decomposition (at 4800 °C/min) products of AN by in situ Fourier transform infrared (FTIR) spectroscopy identified HNO\(_3\) as an intermediate species and revealed the formation of NO\(_2\) alongside N\(_2\)O and H\(_2\)O.\(^{117,118}\) As HNO\(_3\) transforms into the gas phase,\(^{119}\) it experiences successive homolysis of O–N bond, acting as the chain initiation reaction as shown in Equation 2.18.\(^{14,120,121}\)

\[
\text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2 \quad (2.18)
\]

The complex gas-phase mechanism propagates via reaction of NH\(_3\) with the decomposition products of HNO\(_3\) (from Equation 2.18), involving H and OH as the key chain carriers, whilst NH\(_x\) and NO\(_x\) (\(x = 1 – 3\)) serve as the major participants in the redox process.\(^{16,18,19,120,122-124}\)

The principal gas products comprise NO, NO\(_2\), N\(_2\)O and H\(_2\)O. Furthermore, reactions involving NH\(_3\), NO, and water form AN aerosol, as follows:\(^{117,125}\)

\[
3\text{NO} + \frac{3}{2}\text{O}_2 \rightarrow 3\text{NO}_2 \quad (2.19)
\]
\[
2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3 \quad (2.20)
\]
\[
\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \quad (2.21)
\]

Skalis et al.’s \(^{15}\) semi-empirical model combines the condensed- and gas-phase sub-mechanisms. Predictions from the model concur reasonably well with experimental measurements.\(^{126,127}\) Kinetic rather than thermodynamic considerations govern the
decomposition of AN. This is evident from the results of experiments and the Skalis et al. model and from the calculations of classical thermodynamics, say, using the Equilib program in the Chemkin-Pro distribution.\textsuperscript{128} In general, the formation of NO\textsubscript{x} during deflagration of AN prill depends on rates of condensed and gas-phase reactions that reflect the underlying conditions of temperature, heating rates, and pressure and confinement. Figures 2.4b and 2.5 portray the simplified mechanism of NO\textsubscript{x} formation at moderate heating conditions and the effect of heating rate on nitrogen selectivity in the gas-phase product species, respectively.

**Figure 2.5.** Impact of heating rate on nitrogen selectivity among gas-phase products. The calculations were done by performing temperature-programmed decomposition of 1 mg AN (pressure 1 atm, initial temperature 27 °C, bath gas helium, inlet volumetric flow rate 200 standard cm\textsuperscript{3} min\textsuperscript{-1}). The temperature reached at 50 % AN conversion (T\textsubscript{50}) is represented by a supplementary horizontal axis. Reproduced with permission from ref.\textsuperscript{15} Copyright 2014 Elsevier.
2.4.3. Chemical gassing of emulsion blends

Sensitisation of emulsion explosives with chemically-generated nitrogen bubbles (~ 400 μm in size)\textsuperscript{129} can also contribute to emission of NO\textsubscript{x}. A typical AN emulsion explosive involves a concentrated aqueous phase of oxidiser salts, consisting of droplet 10-20 μm in diameter, stabilised by an emulsifying agent; comprised in the continuous fuel phase (Table 2.2).\textsuperscript{8} In practice, solutions of sodium nitrite (NaNO\textsubscript{2}) and acid (e.g. acetic; CH\textsubscript{3}COOH) are injected into the pumped AN emulsion, during emulsion pumping into a blast hole. Once the bubbles grow to their desired size and emulsion reaches its target density, setting off a booster induces a shock wave to propagate through the emulsion column, adiabatically compressing the bubbles and providing a large number of hot spots to engender the explosion.
Table 2.2. Typical composition of AN emulsion explosive. This type of formulations are usually referred to as water-in-oil (W/O) emulsion.8

<table>
<thead>
<tr>
<th>Components</th>
<th>Percent quantity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrate</td>
<td>62</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>6</td>
</tr>
<tr>
<td>Sodium perchlorate</td>
<td>5</td>
</tr>
<tr>
<td>Calcium nitrate</td>
<td>8</td>
</tr>
<tr>
<td>Water</td>
<td>11</td>
</tr>
<tr>
<td>Fuel oil (oil phase)</td>
<td>3</td>
</tr>
<tr>
<td>Waxes</td>
<td>2</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>1.2</td>
</tr>
<tr>
<td>Atomised aluminium</td>
<td>0.8</td>
</tr>
<tr>
<td>Gassing agent</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Oxygen balance</strong></td>
<td><strong>Close to 0.0</strong></td>
</tr>
</tbody>
</table>

As shown in Figure 2.4c, generation of \( \text{N}_2 \) bubbles commences with molecular diffusion of \( \text{CH}_3\text{COOH} \) through the oil interface to droplets containing \( \text{NO}_2^- \) anions.130 Protonation of \( \text{NO}_2^- \) forms nitrous acid:

\[
\text{NO}_2^- + \text{H}^+ \rightleftharpoons \text{HONO}
\quad (2.22)
\]

The nitrous acid diffuses out of sodium nitrite droplet into the emulsion phase with three possible fates. It can react with strong nucleophilic species (X⁻) to from nitrosating agents of the form ONX,8,131 which reacts with amine substrate, such as thiourea, to produce nitrogen gas needed for the generation of hot spots. In practice, pH of the aqueous phase (see below) is
not high enough to deprotonated $\text{NH}_4^+$ and release ammonia. This limits the availability of $\text{NH}_3$ as substrate for $\text{N}_2$ formation.

\[
\text{HONO} + \text{X}^- + \text{H}^+ \rightleftharpoons \text{ONX} + \text{H}_2\text{O} \quad (2.23)
\]

\[
\text{ONX} + \text{SC(NH}_2)_2 \rightarrow \text{N}_2 + \text{SCN}^- + \text{X}^- + 2\text{H}^+ + \text{H}_2\text{O} \quad (2.24)
\]

The nitrosating agent (ONX) can also decompose to form nitric oxide. For example, when thiocyanate functions as a nucleophilic agent, nitrosyl thiocyanate (ONSCN) is formed as the resulting nitrosating agent. Other types of sulfur-bound amine substrates include aminothiones and thioacetamide.\textsuperscript{132,133} The unstable ONSCN decomposes at temperature approaching -60 °C to form nitric oxide.

\[
\text{HONO} + \text{SCN}^- + \text{H}^+ \rightleftharpoons \text{ONSCN} + \text{H}_2\text{O} \quad (2.25)
\]

\[
2\text{ONSCN} \rightarrow 2\text{NO} + (\text{SCN})_2 \quad (2.26)
\]

In addition, SCN\textsuperscript{-} reacts with ONSCN to form NO according to the following reaction: \textsuperscript{134}

\[
\text{ONSCN} + \text{SCN}^- \rightarrow \text{NO} + (\text{SCN})_2^- \quad (2.27)
\]

Without nucleophilic species, nitrous acid follows the second fate to produce nitrosating agent, dinitrogen trioxide ($\text{N}_2\text{O}_3$), under relatively mild acidic conditions (pH range ≈ 4-6) as a product of reaction of nitrous acid with nitrite ion.\textsuperscript{135} Dinitrogen trioxide represents the nitrosating agent that operates in practical emulsion explosives.

\[
\text{HONO} + \text{NO}_2 + \text{H}^+ \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O} \quad (2.28)
\]
The third fate operates at high rate in acidic conditions, at pH of 2 and below, where nitrous acid decomposes rapidly to form NO$_3$ via side Reaction 2.29:

$$2\text{HONO} \rightleftharpoons \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \quad (2.29)$$

As nitrosation (gassing) reactions accelerate at low pH, the dosing systems must include devices that prevent intentional (but undesirable) addition of extra acid to speed up the gassing process. Note that, one cannot eliminate completely the formation of NO$_x$ from HONO. Hence, all gassed emulsions always contain a small amount of NO$_x$. Most of that NO$_x$ remains dissolved in the aqueous phase but a fraction may enter the nitrogen bubbles.$^{130,135,136}$ Figure 2.4c demonstrates the NO$_x$ formation mechanism in chemical gassing of emulsion explosives.

2.5. Effective control measures and abatement techniques

2.5.1. Operation guidelines for controlling NO$_x$ emission in blasting operations

The Australian State of Queensland’s Guidance Note 20$^{84}$ provides useful precautionary measures for preventing, controlling and managing the formation of NO$_x$ fumes in open cast mining. Note 20 comprises standards for manufacturing, storage time-limit, selection of proper initiating devices, better design of mine shots and confinements, as well as appropriate planning and personnel training. At present, all major manufacturers of AN explosives offer formulations that can tolerate wet conditions, usually, with the resistance to these conditions related to the percent loading of emulsion in prill/emulsion (heavy ANFO) mixes. In practice,
selection of appropriate explosive formulation, dewatering of holes prior to loading and minimising the sleep time prior the detonation displays the largest impact on preventing the fume formation. Moreover, from a managerial perspective, Note 20 recommends considerations for establishing fume management zones (FMZ) and determination of blast exclusion zones (BEZ) that account for effects of meteorological (e.g., wind speed and direction, temperature, humidity, etc.) and geological conditions. FMZ represents an area likely to contain fumes after blast, requiring workers to remain outside the zone. For industry, managing exclusion zones adds to the cost of mine operations.

2.5.2. Abatement techniques

The NO$_x$ mitigation technologies employed in post combustion plants$^{78,137-140}$ do not carry over to blasting activities. This is because: (a) the post-explosion atmospheric air mixture do not yield itself to capturing, scrubbing, treatment and/or reprocessing; (b) AN exhibits incompatibilities with materials (Table 2.3)$^{141}$ that could serve for scavenging NO$_x$. However, strategic research into NO$_x$ abatement led to the development of the following mitigation technologies:
Table 2.3. Selected incompatibility of AN with some chemicals.118

<table>
<thead>
<tr>
<th>Substances</th>
<th>Effects on AN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powdered metals</td>
<td>Most metals react violently or explosively with fused ammonium nitrate below 200 °C. May also sensitise AN to shock.</td>
</tr>
<tr>
<td>Metal oxides</td>
<td>Lower the ignition temperature of AN-fuel mixtures.</td>
</tr>
<tr>
<td>Metal sulfides</td>
<td>Lead to runaway reaction, resulting in detonation at temperature below 40 °C, if the pH is less than 2.</td>
</tr>
<tr>
<td>Metal nitrite/nitrate</td>
<td>Magnesium nitrate may desensitise AN. Contact of AN with potassium nitrite causes incandescence.</td>
</tr>
<tr>
<td>Urea</td>
<td>Dehydrated AN mixtures containing 35 – 39 % urea can produce a residue capable of deflagration at 240 °C. The recommended processing temperature should not exceed 120 °C.</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Free ammonia may either stabilise, or tend to destabilise the AN salt depending on the condition.</td>
</tr>
<tr>
<td>Halide salts</td>
<td>Promote the thermal decomposition of AN. Lower the initiation temperature sufficiently to give a violent or explosive decomposition, i.e., premature spontaneous ignition.</td>
</tr>
<tr>
<td>Acids</td>
<td>Mineral acids destabilise. Concentrated acetic acid mixtures ignite on warming.</td>
</tr>
<tr>
<td>Organic fuels</td>
<td>Increases the heat of combustion. 2 – 4 % of organic fuel are used in commercial explosives.</td>
</tr>
</tbody>
</table>

(i) Alkalimetric neutralisation: One of the earliest studies on tackling the formation of NOx in blasting operation involved the use of neutralising additives. Azarkovich142 proposed the addition of inexpensive substances (to AN explosive charges) that possess the capacity of binding oxides of nitrogen. The author recommended additives that are
able to react as alkalis, viz., bases and salts of weak acids. Azarkovich et al. reported the neutralisation reaction of NO\textsubscript{2} occurring in a Dolgov bomb and an underground chamber, especially for additives such as slaked lime Ca(OH)\textsubscript{2}, chalk CaCO\textsubscript{3} and soda Na\textsubscript{2}CO\textsubscript{3}, uniformly spread into the charge in small aliquots of 0.1 – 0.2 mass %, or added into sand stemming. (Stemming denotes the practice of placing soil, sand or rocks on the explosives in the blast hole.). Equations 2.30 – 2.32 suggest the operation of the additives that reduce NO\textsubscript{2} emissions by 40 – 80 %, as monitored by an electromagnetically relayed air sampling vessel.\textsuperscript{142,143}

\[
\text{Ca(OH)}_2 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Ca(NO}_3)_2 + \text{H}_2\text{O} \quad (2.30)
\]

\[
\text{CaCO}_3 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Ca(NO}_3)_2 + \text{CO}_2 \quad (2.31)
\]

\[
\text{Na}_2\text{CO}_3 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons 2\text{NaN}_2\text{O}_3 + \text{CO}_2 \quad (2.32)
\]

(ii) Application of stabilising and scavenging additives: In the search of enhancing the stability of AN, Oxley et al.\textsuperscript{10} screened a large number of formulations comprising grounded sodium, potassium, ammonium and calcium salts of sulfate, phosphate, or carbonates as well as certain high-nitrogen organic compounds such as oxalate, formate, urea and guanidium salts at about 10 mol %. The authors revealed that, the more stabilising the additive, the lower the N\textsubscript{2}O/N\textsubscript{2} ratio, i.e., the more the N-selectivity favours N\textsubscript{2} formation. Although the Oxley et al.\textsuperscript{10} did not report measurements of NO and NO\textsubscript{2} concentration, the insight into the selectivity towards N\textsubscript{2} suggests NO\textsubscript{x} reduction. Opoku et al.\textsuperscript{144,145} inserted additive (non-ammonium) nitrates into the nanocrystalline structure of AN, and studied their effect on formation of NO\textsubscript{x} in deflagration of AN. The authors showed that additives, especially potassium nitrate
that forms 5 mol % K in the co-recrystallised AN salt, achieve up to 40 % reduction in NO emission.

(iii) Reburning-like technique: In boilers, reburning abates NO₅ by using a supplementary fuel to reduce NO₅,\(^{146}\) to achieve an overall decrease in NO₅ emission of about 50 – 85 %.

Reburning constitutes a three-stage process. In the first stage (primary zone), the main fuel burns under slightly fuel-lean condition. The produced NO₅ then reacts with supplementary hydrocarbon radicals in the “reburning zone” to form intermediate nitrogenous species, and then molecular nitrogen (N\(_2\)). Finally, addition of air in the last stage (burnout zone) completes the combustion process by oxidising all unreacted fuels and N-species.\(^{78,147}\) These interactions involve several elementary steps summarised in the following overall equation:\(^{147}\)

\[
\sum C_i H_j + NO \rightarrow HCN +... \quad (2.33)
\]

In excess NO₅, the HCN decays through series of intermediates, and ultimately reaches N\(_2\) via the reverse Zeldovich reaction (Equation 2.37):

\[
\begin{align*}
HCN + O & \rightarrow NCO + H \quad (2.34) \\
NCO + H & \rightarrow NH + CO \quad (2.35) \\
NH + H & \rightarrow N + H_2 \quad (2.36) \\
N + NO & \rightarrow N_2 + O \quad (2.37)
\end{align*}
\]

Many practitioners had applied reburning-like technology to reduce NO\(_5\) emission in blasting of AN explosives adding supplementary fuel (usually solid) of higher oxidation
stability compared to fuel oil used in AN explosives. As seen in Figure 2.6, the fuel with lower oxidation stability (fuel oil) participates solely in primary detonation reaction, with the resulting NO\textsubscript{x} species subsequently reduced to nitrogen. However, the excess fuel conditions, if they arise in the reburning of detonation-generated NO\textsubscript{x}, may lead to formation of CO, as shown in Equation 2.10.

![Figure 2.6](image)  

**Figure 2.6.** Conceptual schematic of the application of reburning-like method during blasting. The arrows indicate the direction of oxidation. Atmospheric O\textsubscript{2} completes the process by oxidising all unreacted fuels.

Sapko and co-workers\textsuperscript{25} demonstrated that the use of pulverised coal dust (mean particle size of 74 μm) as an additive mitigates the total NO\textsubscript{x} emission by 10 – 50 %. Likewise, biomass briquette and advanced reburning materials such as urea\textsuperscript{147} offer better NO\textsubscript{x}-mitigation performance.\textsuperscript{10,25} Other potential fuel additives may include non-hazardous waste polymers, such as polyethylene.\textsuperscript{148}
(iv) Chemical trapping: Spin traps can provide an effective reduction of in the overall release of nitric oxide in sensitisation (chemical gassing) of emulsion explosives. Spin trapping reaction remove radical species, such as NO, by forming stable adducts. Venpin et al. exploited the spin-trapping technique to develop NO scavengers to control NO\(_x\) emission from industrial processes, including sensitisation of emulsion explosives.\(^{149-151}\) In their experiments, they applied aromatic ortho substituted nitroso compounds, such as nitrosobenzene sulfonate (NBS), 3,5-dibromo-4-nitrosobenzene sulfonate (DBNBS), 3,5-dimethyl-4-nitrosobenzene sulfonate (DMNBS) and 3,5-dichloro-4-nitrosobenzene sulfonate, obtaining up to 70 % removal efficiency of NO during sensitisation of AN emulsion blends. The reaction pathways leading to the formation of N\(_2\) are shown in Equation 2.38 – 2.40:\(^{149}\)

\[
\begin{align*}
&\text{Aromatic nitroso sulfonate} & \quad \text{N} & \quad \text{Nitroso-NO adduct} \\
&X = \text{II, Br, CI, and Cl} \\
\end{align*}
\]

\[
\begin{align*}
&\text{(2.38)} \\
n&\text{NOS} \quad \text{NO} \quad \text{NOS} \quad \text{NOS} \\
&\quad \text{N} \quad \text{N} \\
&\quad \text{N} \quad \text{N} \\
&\text{X} \quad \text{X} \\
\end{align*}
\]

\[
\begin{align*}
&\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
&\quad \text{N} \quad \text{N} \\
&\quad \text{N} \quad \text{N} \\
&\text{X} \quad \text{X} \\
\end{align*}
\]

\[
\begin{align*}
&\text{Aryl diazenyl radical} & \quad \text{Aryl radical} \\
\end{align*}
\]

(v) Use of alternative oxidising agents: Even though the AN technologies have been established for applications in civilian explosives, there exist at least one non-nitrogen
based formulation. Araos and Onederra\textsuperscript{152} replaced AN with oxygenated water (hydrogen peroxide, H$_2$O$_2$, OW) and used micro balloons, rather than chemical gassing, to avoid NO$_x$ formation both in detonation and in emulsion sensitisation. Such OW/fuel blends detonate with similar heat release and VOD to AN explosives,\textsuperscript{152-154} but without NO$_x$ hazards. The technology requires further testing to verify its large-scale performance.

Some noteworthy patents include formulating the blasting agent to contain from about 1\% to about 20\% silicon powder,\textsuperscript{155} or appreciable amount of urea in the discontinuous oxidiser salt phase,\textsuperscript{156,157} improved composition of hydrogen peroxide based explosives,\textsuperscript{158} application of other nitrogen-free oxidisers,\textsuperscript{159} and appropriate gassing method.\textsuperscript{160}

2.6. Perspectives and future outlooks

We have identified the possibility of the formation of secondary pollutants (nitrate aerosols) as a result of atmospheric nitration of the mineral particles and fugitive dusts synchronously present in post-blast fumes. Development of new sampling methodologies should include the environmental monitoring of such species from blasting activities. Lightweight remote-controlled drone-sampling instrumentation, as well as surface sampling, could facilitate the measurements of nitrate aerosols, as well as other pollutants including supplementary Nr species (e.g. HNO$_3$, NH$_3$, and N$_2$O), hydrocarbons, nitrogenated analogues\textsuperscript{161} of dioxins and secondary contaminants such as peroxyacyl nitrates (PAN)\textsuperscript{162}. Understanding the mechanism of the formation and the survival of these pollutants in detonation of heavy AN explosives is crucial to achieve sustainable mining activities, as are further testing of OW emulsions and
bulking agents, and generating new knowledge on the exact mechanism of deflagration that involves the surface burning of AN particles.

2.7. References


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This chapter presents an overview of the main experimental and computational techniques employed within the scope of this study. Details of specific computational settings and experimental conditions are provided in subsequent chapters.
3.1. Computational Techniques

Computational ab initio methods have been used in this dissertation to study all necessary reaction steps. Ab initio (Latin for “from the beginning”) represents computation practices derived directly from theoretical principles without the inclusion of experimental data. This remains an approximate quantum mechanical calculation, reflecting only mathematical approximations, such as using a simpler functional form for a function or finding an approximate solution to a differential equation.\(^1\) The ab initio techniques solve the Schrödinger equation to predict the energy and optimum conformational structure of a molecule. Equation 3.1 depicts the Schrödinger equation, where \(\Psi\) represents the wavefunction, and \(m\), \(\hbar\), and \(V\) denote the mass of particle, Planck’s constant and the potential energy, respectively.\(^1,3\)

\[
\left\{- \frac{\hbar^2}{8\pi^2m} \nabla^2 + V\right\} \Psi(r, t) = \frac{i\hbar}{2\pi} \frac{\partial \Psi(r,t)}{\partial t} 
\]  \hspace{1cm} (3.1)

The accuracy of the final molecular energy relies on the level of assumptions made, as well as the precision of the numerical simulation – generally termed as “theory”. This work applies the density functional theory (DFT) within the framework of two selected model chemistries as enumerated below:

i. Three-dimensional slab model enabled the investigation of solid-gas interaction of polyethylene with oxidising species, such as atmospheric oxygen and NO\(_x\) gases. DMol\(^3\) package\(^4,5\) supported this kind of theoretical simulations, assisting all structural optimisations, and serving to calculate all energies and vibrational frequencies. In the optimisation of all stationary points, the theoretical approach comprised the generalised
gradient approximation (GGA) as the exchange-correlation potential alongside with the Perdew-Burke-Ernzerhof (PBE) functional. The total energy converged with a tolerance of $1 \times 10^{-6}$ Ha. The electronic core treatment included all electrons in the calculations while deploying a double numerical plus polarisation (DNP) basis set, and a global cut-off of 4.0 Å. The applied Brillouin zone involved automatic generation of $2 \times 3 \times 6$ and $1 \times 2 \times 1$ $k$-points for the unit cell and periodic slabs, respectively, through the Monkhorst-Pack grid scheme. The average computational cost, for each periodic slab typically amounts to 20 h on a 32 parallel processing cores. Where necessary, Tkatchenko and Scheffler’s semiemperical dispersion correction scheme offered the necessary measures to validate the compromise between the cost of evaluation of the dispersion terms and the need to improve non-bonding interactions in our system.

ii. Gas-phase reaction modelling allowed the development of theoretical insight into the formation of initial nitration products during thermal reaction of biomass surrogate (morpholine) with NO$_x$. Gaussian09 suite of programs implemented the complete-basis-set CBS-QB3 composite method to facilitate all structural optimisations, and served to calculate all enthalpies as well as vibrational frequencies using the tight convergence criteria and rigid-rotor/harmonic-oscillator approximations. In agreement with previous studies, the adopted computational method offered an accurate evaluation of thermochemical properties of all species studied herein.

Furthermore, each chapter involving ab initio calculations contains a detailed description of the specific computational procedures.
3.2. Experimental Configurations

The experimental work of this thesis essentially investigates the conversion of NO\textsubscript{x} with polyethylene (PE, selected solid fuel), and morpholine as the chosen biomass surrogate. The following text describes the experimental rigs. Subsequent chapters elaborate the details of the applied methodologies.

3.2.1. Experiments involving thermal reaction of recycled polyethylene with NO\textsubscript{x}

i. Characterisation techniques:

- Fourier transform infrared (FTIR) spectroscopy: This method elucidated the major functional groups present in the polymer samples, using the Agilent Cary 670 equipped with the attenuated total reflectance (ATR, germanium crystal, Pike Technologies) accessory. Prior to analyses, samples were cryogenically pulverised to achieve reproducible measurements. The FTIR recorded the spectra at 4 cm\textsuperscript{-1} resolution, with accumulation of 32 scans per spectrum. The bands at 2916 cm\textsuperscript{-1}, 2848 cm\textsuperscript{-1}, 1470 cm\textsuperscript{-1} and 718 cm\textsuperscript{-1} correspond to CH\textsubscript{2} asymmetric stretch, CH\textsubscript{2} symmetric stretch, CH\textsubscript{2} scissors and CH\textsubscript{2} rock modes, respectively.

- Carbon-hydrogen-nitrogen-sulfur (CHNS) analysis: CHNS elemental analyser (Australia National University, Australia) provided a means for rapid determination of carbon, hydrogen, nitrogen and sulfur in the organic polymer matrices. Pulverised samples were fed into the pre-calibrated instrument (EuroVector EA3000) under dry helium and O\textsubscript{2} purge, and the combustion furnace operated at
approximately 1100 °C. The reactor functioned in a dynamic flash combustion mode, and contained both the oxidation zone represented by tungsten oxide and copper wired reduction zone. Two repeated runs resulted in precise measurements of the constituent elements.

- **Ion chromatography**: This method determined the trace concentration of halogens in polymers. Dissolved samples were injected into a DX-120 anion chromatograph.

- **Inductively coupled plasma emission spectroscopy (ICP-OES)**: Varian 715-ES ICP OES (University of Newcastle, Australia) served to measure the metal concentration in the sample. About 140 mg of the recycled PE were digested in microwave, and then transferred via Varian SPS 3 sample preparation system for analyses. High-purity ICP multi-element standard solution containing different metal cations in 2.0 % HNO₃ facilitated the necessary calibration.

- **High temperature size exclusion chromatography (HT-SEC) in TCB**: The HT-SEC (Université Claude Bernard Lyon 1, France) analyses operated on Viscotek system (from Malvern Instruments) equipped with three columns (Polefin 300 mm × 8 mm I. D. from Polymer Standards Service, porosity of 1000 Å, 100 000 Å and 1 000 000 Å). Sample solutions 200 µL in volume, with a concentration of 5 mg/mL, were eluted in 1,2,4-trichlorobenzene (1,2,4 TCB) with a flow rate of 1 mL/min at 150 °C. The mobile phase was stabilised with 2,6-di(tert-butyl)-4-methylphenol (200 mg/L). Online detection was performed with a differential refractive index detector and a dual light scattering detector (LALS and RALS) for absolute molar
mass measurement. The OmniSEC 5.02 software facilitated the calculation of the SEC parameters.

ii. Parametric and Temperature Profile of Experimental Setups

This aspect of the laboratory work involved three series of experiments. As shown in Figure 3.1, a standalone thermogravimetry apparatus (TGA)\textsuperscript{11-13} has been employed with the intention of eliminating any unwanted experimental artefacts that could be carried over into the subsequent kinetic evaluations. Furthermore, hyphenated infrared spectroscopy (TGA-FTIR, PerkinElmer Frontier) and chemiluminescence (TGA-NO\textsubscript{x}, Thermo Scientific model 42\textsuperscript{i}-HL) enabled the identification and quantitation of evolved gases.
Figure 3.1. Schematic diagrams of adopted experimental configurations for the TGA-FTIR-NO$_x$ analyses.

The reference standards for the mass and temperature calibration were selected according to the desired experimental range. Table 3.1 lists the measured values as compared to the expected quantities. The table also provides the calculated percent
error. During the entire duration of the study, replicate runs randomly carried out on different days quantified for the instrumental drift and reproducibility of experimental data.

Table 3.1. Verification of the Instrument’s (TGA-DSC) measured values

<table>
<thead>
<tr>
<th>Weight (mg)</th>
<th>Expected</th>
<th>Measured&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Measured&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified mass</td>
<td>54.37</td>
<td>54.59</td>
<td>54.36</td>
<td>7.36 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature&lt;sup&gt;3&lt;/sup&gt; (°C)</th>
<th>Expected</th>
<th>Measured&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Measured&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Percent error</th>
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</thead>
<tbody>
<tr>
<td>Indium</td>
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<td>156.21</td>
<td>156.45</td>
<td>9.58 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
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<tr>
<td>Zinc</td>
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<td>417.12</td>
<td>419.20</td>
<td>6.44 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Aluminium</td>
<td>660.10</td>
<td>662.67</td>
<td>660.30</td>
<td>3.03 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat flow&lt;sup&gt;4&lt;/sup&gt; (J/g)</th>
<th>Expected</th>
<th>Measured&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Measured&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
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<td>115.70</td>
<td>110.20</td>
<td>0.17 × 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Aluminium</td>
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<td>410.02</td>
<td>400.80</td>
<td>1.74 × 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>1</sup> Measured values before calibration.

<sup>2</sup> Measured values after calibration.

<sup>3</sup> Onset melting temperatures.

<sup>4</sup> Enthalpy of fusion ($\Delta H_f$).
3.2.2. Experiments involving thermal reaction of morpholine with NO\textsubscript{x}

This section of exploration involved a flow-through tubular reactor typically employed in similar studies.\textsuperscript{14-18} Figure 3.2 provides a schematic representation of the experimental setup in which a digital syringe pump delivered the reactant fuel (morpholine; TCI, purity > 99.0 %) into the preheated dilute stream of helium/NO\textsubscript{x}/oxygen flowing through the system. The concentration of morpholine in the diluted stream corresponded to 1000 ppm. An electrically heated three-zone horizontal split furnace accommodated the quartz reactor tube, and ensured a well-defined isothermal regime. The use of helium (99.999 %) as primary dilution gas facilitated better conductive heat transfer in the reaction zone, and also allowed quantitative measurement of N\textsubscript{2}. The stream concentrations, stoichiometric conditions, and other parametric details are provided in the subsequent relevant chapters.

\textbf{Figure 3.2.} Schematic representation of experiment rig for the study of the reaction of biomass surrogate with NO\textsubscript{x}.  

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As illustrated in Figure 3.2, product analyses involved three parallel stages. Firstly, FTIR spectroscopy (Perkin Elmer) facilitated online monitoring of product species exiting the tubular reactor. The setup incorporated an electrically heated transfer line (3.175 mm ID × 300 mm) linking the reactor to a small volume (100 mL) 2.4 m path-length online gas sampling cell (Pike) placed inside the FTIR compartment. The spectrometer averaged 64 accumulated scans per spectrum at 1 cm\(^{-1}\) resolution. Both the sample line and the sampling cell operated at 140 °C, to avoid the condensation of product volatiles prior and during the analysis. Furthermore, the chemiluminescence NO\(_x\) analyser (Thermo Scientific model 42i-HL) monitored the concentration of NO and NO\(_2\). Finally, the use of μGC (Agilent 490 micro-gas chromatography, 20 m MolSieve-5A column, heated injection) assisted N\(_2\) quantitation. The train of three impingers consisting of glass units filled with standardised 0.1 M H\(_2\)SO\(_4\), 1 M NaOH, and orange silica gel removed any contaminant species, e.g. ammonia and H\(_2\)O that could damage the GC column.

### 3.3. Data Analyses

Unless otherwise stated, Microsoft excel and Origin program served as the main numerical analysis tools for data presented in this thesis. The results from analytical instruments were processed in the respective software provided by the vendors. Regarding the FTIR spectra, QASoft database enabled the semi-quantitation of product species by their characteristic IR bands. Further details are provided in the subsequent chapters.
3.4. References


This chapter develops a systematic approach of investigating polymer-gas reactions. The interaction of $O_2$ with crystalline polyethylene have been studied, with appropriate comparison to analogous reactions in gas medium. This allows adequate investigation of the intended NO$_x$-polymer reaction later presented in Chapter 5 of this thesis...
4.0. Abstract

Auto-oxidation of polyethylene (PE) is of a common occurrence and could be triggered by several physical and chemical factors. In this study, for the first time, we report a comprehensive theoretical account on the initial oxidation of crystalline PE at low temperatures prior to its melting. We map out potential energy surfaces for large number of reactions, most notably, initial abstraction by \( \text{O}_2 \) molecules, formation of peroxy- and hydroperoxyl adducts, unimolecular eliminations of \( \text{HO}_2 \) and \( \text{H}_2\text{O} \) as well as C-C bond fissions. Rate constants have been estimated for all considered reactions over the temperature range of 300 – 800 K. We have discussed noticeable similarities between the oxidation of PE and that of gas-phase alkanes. Results presented herein provide new insights into the solid-state oxidation of PE and germane crystalline polyolefins/paraffins and pure carbon-hydrogen-type polymers.
4.1. Introduction

Polyethylene (PE) holds wide range of applications in the society. As a nontoxic low-priced polymer, PE resins have emerged as an important raw material for various industrial uses, frequently deployed, in substantial amount, in medical, automobile, food, pipeline, civil, and domestic sectors.\textsuperscript{1, 2} The key to the adaptability of PE lies in its adjustable semicrystalline morphology, giving rise to its existence in various forms. Major types of PE include high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and ethylene-vinyl acetate copolymer (EVA).\textsuperscript{1, 3} Due to their elevated calorific value and suitable combustion properties,\textsuperscript{1, 4, 5} used PE finds outlets in an extensive array of recycling processes, such as thermal energy recovery via incineration technologies, thermolytic conversion into liquid fuels\textsuperscript{6-9} and even pyrolytic conversion to low-carbon hydrocarbon gases for application in hybrid rocket propulsion systems.\textsuperscript{10, 11} Practical applications of thermal degradation of solid fuels often occur in oxidative environment,\textsuperscript{12} thus, it is important to understand the thermo-oxidative degradation mechanism of PE.

The thermal decomposition of PE arises by homolysis of C–C bond, unzipping, in successive enchained $\beta$-scission reactions, yielding monomer from the polymer. The decomposition then proceeds by free radical mechanism involving multistep chain reactions. This consists of consecutive H-abstraction and $\beta$ C–C scission, intramolecular hydrogen transfer (backbiting) and intermolecular hydrogen shift (random scission). At high temperature under pyrolytic conditions, PE undergoes both backbiting and random scission pathways.\textsuperscript{6, 13-16} The overall relatively high activation energy for the inert decomposition of PE (150 – 260 kJ/mol) is linked to a limiting step characterised by the initial random scission.\textsuperscript{6, 12, 17-20}
In presence of oxygen, the reactions proceed differently with lower activation energy of around 80 – 143 kJ/mol. Experiments on oxidation of low density PE and related polymers usually involve irradiation at low temperature (photo-oxidative accelerated weathering) or a temperature controlled air-circulated operation at moderate temperature of between 373 to 428 K (i.e., thermal ageing). Reactors and/or thermogravimetric analysers serve to perform high temperature oxidation experiments above 473 K (thermo-oxidative degradation).

Different pathways exist for the oxidation mechanism of PE. In the most general form, thermo-oxidative degradation begins by formation of radical sites initiated by induced temperature, but UV radiation as well as existence of trace peroxides and hydroperoxides also influence the initiation of photo-oxidative pathways. Oxygen reacts with the chain radical to form a peroxy-radical intermediate during the propagation step:

\[
\text{Initiation: } \quad RH \rightarrow R^\cdot + H^- \quad (a)
\]

\[
\text{Propagation: } \quad R^\cdot + O_2 \rightarrow ROO^\cdot \quad (b)
\]

The peroxy radical abstracts hydrogen to form hydroperoxide and a radical centre. The former yields an alkoxyl radical via a unimolecular or bimolecular decomposition mechanism. An alkoxyl radical can effectively abstract a hydrogen to form a hydroxyl group. Intermolecular and intramolecular H-abstractions lead to formation of new radical sites, thereby accelerating the oxidative degradation.

\[
\text{ROO}^\cdot + RH \rightarrow ROOH + R^\cdot \quad (c)
\]

\[
\text{ROOH} \rightarrow \text{RO}^\cdot + \text{OH} \quad (d)
\]

\[
\text{ROOH} + RH \rightarrow \text{RO}^\cdot + \text{R}^\cdot + \text{HOH} \quad (e)
\]
Amorphous zone of PE has more access to oxygen compared to the densely packed crystalline regions. The amorphous zone oxidises first and then acts as a buffer, protecting the crystalline region from attack during thermal degradation. Therefore, increasing the crystallinity lowers the oxidation rate and increases the sensitivity of mechanical properties of PE towards oxidation.\textsuperscript{31, 32}

While oxidative decomposition of PE mainly occurs in liquid media upon melting, auto-oxidation of solid PE at relatively low temperatures is a common phenomenon that could be triggered by many physical or chemical factors. These factors encompass presence of structural defects in PE, ultraviolet and ionising radiation, prompt heating, ultrasound, or direct exposure to catalysis, singlet molecular or atomic oxygen and ozone.\textsuperscript{33}

To this end, the present study deploys the density functional theory (DFT) to investigate initial steps encountered in the oxidation of crystalline PE. We analyse the reaction mechanisms pertinent to thermo-oxidative degradation of PE, and evaluate and compare the kinetic and thermochemical parameters with limited experimental measurements from the literature. Results presented herein provide improved insights into the solid-state oxidation of crystalline polyolefins/paraffins and carbon-hydrogen-type polymers. Such knowledge is instrumental to understand the auto-oxidation process of crystalline PE that underpins its natural ageing mechanism under thermo- and photo-oxidative conditions.
4.2. Methodology

4.2.1. Computational details

DMol³ package³⁴,³⁵ facilitates all structural optimisations, and serves to calculate all energies and vibrational frequencies. In the optimisation of all stationary points, our theoretical approach comprises the generalised gradient approximation (GGA) as the exchange-correlation potential alongside with the Perdew-Burke-Ernzerhof (PBE) functional. The total energy converges with a tolerance of $1 \times 10^{-6}$ Ha. The electronic core treatment includes all electrons in the calculations while deploying a double numerical plus polarisation (DNP) basis set,³⁴ and a global cut-off of 4.0 Å. Based on the subsequent thorough benchmarking against analogous experimental and theoretical values from the literature, we have found that, the adopted DFT functional and basis set offer a satisfying accuracy threshold for the system at hand. We carry out integration of the Brillouin zone via automatic generation of $2 \times 3 \times 6$ and $1 \times 2 \times 1$ $k$-points for the unit cell and periodic slabs, respectively, through the Monkhorst-Pack grid scheme. The average computational cost, for each periodic slab typically amounts to 20 h on a 32 parallel processing cores. Last of all, Tkatchenko and Scheffler’s semiemperical dispersion correction scheme³⁶ offers the necessary measures to validate the compromise between the cost of evaluation of the dispersion terms and the need to improve non-bonding interactions in our system.
4.2.2. Molecular and crystallographic structural parameters of polyethylene

Crystalline PE exhibits an orthorhombic crystal structure under all but the most exceptional circumstances. Its unit cell contains all crystallographic data needed for a complete crystallite. We generated the reference unit cell structure by optimising the orthorhombic crystalline arrangement reported by Avitabile et al. The primitive cell exhibits a Pnam space group that consists of twelve atoms, equivalent to two \(-\text{CH}_2-\) chains as shown in Figure 4.1.

![Figure 4.1](image)

**Figure 4.1.** Unit cell of ideal orthorhombic polyethylene; plan (left) and isometric (right) views.

Tables 4.1 and 4.2 report optimised structural parameters, i.e., lattice constants \(a\), \(b\), and \(c\), and the fractional atomic coordinates for the optimised PE unit cell. Our calculated lattice parameters are within the slightly scattered experimental measurements and computed values available in literature. Note a negligible difference in the fractional atomic coordinates, if compared with the analogous experimental values. Although, dispersion-correction approach reduces the lattice constants somewhat closer to experimental values, it also increases the computation time by approximately 20%. As dispersion corrections display importance in the modelling of some, but not all, physical systems. For the present
calculations, the application of the dispersion correction does not change the chemical interpretations of the results. Therefore, our chemical reaction modelling excludes the dispersion correction.

**Table 4.1.** Optimised geometrical parameter of crystalline polyethylene unit cell without (1) and with (2) dispersion correction as compared to experimental values. Unit conversion: 1 Å equals 0.1 nm.

<table>
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<tr>
<th>Parameters</th>
<th>Computational results</th>
<th>Experimental measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work (1)</td>
<td>LDA 41</td>
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<td></td>
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<td>GGA 41</td>
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<td></td>
<td></td>
<td>GGA 42</td>
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<td>Neutron scattering (4 K) 38</td>
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<td>Neutron scattering (90 K) 38</td>
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Table 4.2. Calculated fractional coordinates of atoms in the unit cell of orthorhombic PE. $\psi_1 = 0.0399761$, $\psi_2 = 0.0531014$, $\psi_3 = 0.1788820$, $\psi_4 = 0.0127033$, $\psi_5 = 0.0279984$, $\psi_6 = 0.2627310$.

<table>
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<th>Atoms</th>
<th>Fractional coordinates</th>
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<tbody>
<tr>
<td>C</td>
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<tr>
<td>H</td>
<td>$\pm (\psi_3, \psi_4, \frac{1}{4})$</td>
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<tr>
<td>H</td>
<td>$\pm (\psi_5, \psi_6, \frac{1}{4})$</td>
</tr>
<tr>
<td>C</td>
<td>$\pm (\frac{1}{2} - \psi_1, \frac{1}{2} + \psi_2, -\frac{1}{4})$</td>
</tr>
<tr>
<td>H</td>
<td>$\pm (\frac{1}{2} - \psi_3, \frac{1}{2} + \psi_4, -\frac{1}{4})$</td>
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<tr>
<td>H</td>
<td>$\pm (\frac{1}{2} - \psi_5, \frac{1}{2} + \psi_6, -\frac{1}{4})$</td>
</tr>
</tbody>
</table>

4.2.3. Reaction modelling

A vacuum slab parallel to a plane defined by Miller index of (100) is constructed from the optimised unit cell to represent a PE(100) surface. Figure 4.2 depicts optimised geometry of the PE(100) surface. The vacuum slab has four repeated periodic layers. In all structural optimisations, we relax fully the two top layers and molecules, while the two bottom layers remain fixed at their corresponding bulk positions. A vacuum thickness of at least 10.0 Å (1 nm) separates each slab from its corresponding repeated images along the $z$ axis. This eliminates the interactions within the periodic images of the slab. A dipole correction, applied along the direction perpendicular to the surface, minimises any surface deformation owing to the dipole accumulation along the $z$ direction.
Search for transition states deploys the complete linear synchronous and quadratic synchronous transit approaches (LST/QST), as implemented in DMol³. Reaction rate constants are fitted to the Arrhenius equation (i.e., $k(T) = A \exp(-E_a/RT)$) in the temperature range of 298.15 – 800 K, according to the classical transition state theory (TST).\(^\text{47}\)

$$k(T) = \sigma_e \frac{k_B T}{h} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( \frac{-\Delta H^*}{RT} \right)$$  \(4.1\)

In Equation 4.1, $\sigma_e$ signifies the reaction degeneracy number, i.e., set to unity in all considered reactions (i.e. per C/H/O site). $\Delta S^*$ and $\Delta H^*$ refer to entropy and enthalpy of activation at temperature $T$, in that order. The remaining symbols, $k_B$, $h$, and $R$ denote Boltzmann’s, Planck’s and the universal gas constants, respectively. DMol³ package computes vibrational frequencies.
from which it obtains the temperature-dependent thermochemical parameters (\(\Delta H\), \(\Delta S\), \(\Delta H^\circ\) and \(\Delta S^\circ\)).

### 4.3. Results and Discussion

#### 4.3.1. Initiation reactions

Figure 4.3 presents energetics of two possible initiation pathways. Henceforth, we show only the two top layers (unrestricted layers) of all modelled slabs. The C–H bond dissociation enthalpy (BDH) (1a) in PE amounts to 416.2 kJ/mol. This value concurs with the corresponding BDH in secondary C–H bonds in alkanes.\(^{48, 49}\) Direct abstraction of an H atom by a triplet oxygen molecule (1b) entails a highly endothermic process of 351.1 kJ/mol at 298.15 K (all thermodynamic and kinetic parameters are calculated and discussed at this temperature). Thus, it is unlikely that, direct H abstraction by the triplet oxygen molecule from PE represents a significant initiation channel.
Figure 4.3. Initiation reactions in the oxidative decomposition of PE. The location of radical site is indicated by the bolded C atom.

Figure 4.4 portrays detailed mechanisms for subsequent oxidation steps. In real oxidation scenario, O/H radicals readily abstract an H from the CH site to form a radical centre. With the appearance of a radical site, oxygen molecule reacts in two modes; namely, direct addition and H abstraction. Figure 4.5 presents enthalpic profiles for these two reactions. Barrierless addition of $O_2$ (2a) to a $-\text{C(H)}-$ site forms a highly reactive peroxy adduct intermediate. In an ordered medium, such as a crystalline PE, there are restrictions to diffusion of oxygen. Calculations yield the exothermicity of this reaction as 131.2 kJ/mol. Corresponding values of the analogous reactions involving gaseous ethyl and butyl radicals amount to 141.8 kJ/mol and 136.0 kJ/mol, respectively.\textsuperscript{50, 51}
**Figure 4.4.** Reaction pathway for thermo-oxidation of crystalline polyethylene. Reactive hydrogen atoms are labelled $\alpha$, $\beta$, and $\gamma$, according to their position relatively to the peroxy group. Note the location of radical sites, for the figures that follow.

In the parallel competing pathway (2b), triplet oxygen abstracts an H-atom from the carbon atom adjacent to the radical centre. This reaction leads to formation of an alkene molecule and a hydroperoxyl radical. These two reactions constitute the major initiation channels in the low-temperature combustion of alkyl radicals. Calculations yield the enthalpy of activation for the abstraction channel as 212.5 kJ/mol and a modest reaction exothermicity of 44.2 kJ/mol, i.e., in a close agreement with the corresponding value for the formation of 1-butene + HO$_2$ from the n-butyl + O$_2$ reaction. Based on enthalpic values included in Figure 4.5, the formation of a peroxy adduct, via the addition channel (2a), represents a more preferred channel than the competing abstraction corridor (2b).
Figure 4.5. Reactions between oxygen and the alkyl-type radical of PE. Enthalpy values are calculated at 298.15 K and the bolded C atoms indicate radical sites.

Direct elimination of HO₂ from peroxyalkyl (3) constitutes a principal corridor for the formation of alkenes from peroxyalkanes at low temperatures. This reaction plays a crucial role in the oxidation process...
role by generating HO$_2$, a propagating radical that sustains the oxidation process via the reaction sequence (HO$_2$ + RH → H$_2$O$_2$ + R’ → 2OH + R’). In case of PE, our calculated value reveals endothermicity of 87.0 kJ/mol, and a reaction barrier of 97.4 kJ/mol (TS2). For the reactions of n-propyl radical with O$_2$ molecules, concerted elimination of HO$_2$ from RO$_2$ adduct implies endothermicity of 79.1 kJ/mol and a barrier height of 124.3 kJ/mol.$^{50}$

4.3.2. Formation of hydroperoxide group

Apart from its contribution to the generation of alkenes and HO$_2$ radicals, peroxy intermediate branches also into three other channels. Isomerisation of peroxy radical consists of intramolecular hydrogen transfer, driven principally by the conversion of alkyl peroxy species into alkyl hydroperoxide radicals.$^{52}$ A peroxy radical abstracts hydrogen atom intramolecularly from $\alpha$, $\beta$ and $\gamma$ positions (refer to Figure 4.4). Figure 4.6 represents potential energy surface (PES) for these reactions. Abstraction of hydrogen atom from the $\alpha$ position (4c) does not lead to formation of hydroperoxide species, rather yielding molecules of water and $\gamma$-alkyl ketone radical in an exothermic reaction. Despite of our best attempts, we were unsuccessful in locating a transition state for this reaction (4c). Previous studies attributed this reaction to formation of radical species that dissociate in microseconds into a long-range complex between a hydroxyl radical and an ester-type adduct.$^{24, 53, 54}$

On the other hand, H-abstraction from the $\gamma$ (4a) and $\beta$ (4b) position are endothermic by 66.9 kJ/mol and 69.3 kJ/mol and require activation enthalpies of 82.6 kJ/mol (TS3) and 91.9 kJ/mol (TS4), in that order. Barrier heights of TS3 and TS4 compare well with analogous values encountered in the intramolecular hydrogen-transfer reaction induced by alkyl peroxy
adducts.\textsuperscript{52} For instance, the analogous gas phase reaction \((\text{CH}_3\text{C(O}_2\text{)}\text{H(CH}_2)_3\text{CH}_3 \rightarrow \text{CH}_3\text{C(O}_2\text{)}\text{HCH}_2\text{C}’\text{HCH}_3)\) has endothermicity of 68.2 kJ/mol and activation energy of 89.1 kJ/mol.\textsuperscript{52}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4_6.png}
\caption{Intramolecular formation of hydroperoxide and ketone. Enthalpy values are calculated at 298.15 K and the bolded C atoms indicate radical sites. We could not locate the transition state for Reaction 4c.}
\end{figure}

In the intermolecular path as shown in Figure 4.7, a peroxy species abstracts a labile hydrogen from a neighbouring polymer chain (8). A computed reaction barrier displays prohibitively
high enthalpy value of 443.9 kJ/mol. From a view of a typical reaction coordinate, the geometry of the neighbouring chain constitutes the only factor that could be at play here, to make the barrier so high. The geometrical arrangement of PE might be highly constrained by the crystal structure, rendering the hydrogen atom inaccessible. It follows that, hydrogen abstraction from a neighbouring hydrocarbon chain carries negligible importance in auto-oxidation of PE.

![Reaction Coordinate](image)

**Figure 4.7.** Formation of hydroperoxide by intermolecular abstraction of H atom. Enthalpy values are calculated at 298.15 K and the bolded C atoms indicate radical sites.

However, at higher temperatures near the melting point, the chains acquire sufficient conformational flexibility to render the hydrogen atoms more accessible between chains, thereby substantially lowering the barrier. To provide a more realistic kinetic data germane to Reaction 8 near melting point of PE, we invoke an alternative procedure to account for the intermolecular H-transfer. Korcek et al.’s equation\(^\text{55}\) establishes a generalised linear
relationships among the activation energy, rate constant per hydrogen atom, and R–H bond strength for intermolecular H-abstraction by secondary peroxy radicals; $E_a = 0.55 \times (\Delta H^* - 62.5)$ and $\log(k) = 16.4 - (0.2 \times \Delta H^*)$, where $\Delta H^*$ is expressed in kcal/mol. This relationship allows obtaining approximate values of the activation energy and the rate constant for Reaction 8, from BDH of C-H bonds in PE of 416.2 kJ/mol.

4.3.3. Hydroperoxide decomposition and other reactions

Hydroperoxide from the $\gamma$ pathway undergoes a O–O bond dissociation and C–C $\beta$ scission ($5a_1$) to yield molecules of an alkene and an aldehyde. As shown in Figure 4.8, exothermicity of this process amounts to 19.9 kJ/mol with 116.0 kJ/mol (TS5) as its enthalpy of activation. The endothermic formation of alkyl oxetane ($5a_2$) represents a competing pathway. This reaction requires a barrier height of 89.0 kJ/mol associated with TS6. On the other hand, hydroperoxide from the $\beta$ channel decomposes through a similar barrier height of 92.9 kJ/mol (TS7), assuming structural rearrangement to form an alkyl epoxide in exothermic reaction ($5b$) of 27.1 kJ/mol.
Figure 4.8. Decomposition of intramolecular hydroperoxide species. Enthalpy values are calculated at 298.15 K and the bolded C atoms indicate radical sites.

Figure 4.9 portrays conventional barrierless unimolecular decomposition that either yields alkoxy radical (9a), through an endothermic reaction of 191.3 kJ/mol, or loses HO₂ (9b), to form alkyl radical with endothermicity of 292.7 kJ/mol. In comparison to similar reaction types, values of BDH of \( n\text{BuO}–\text{OH} \) and \( n\text{Bu}–\text{OOH} \) correspond to 189.1 kJ/mol and 293.7 kJ/mol respectively. The alkoxy radicals can ultimately generate alkyl hydroxide by
intramolecular hydrogen abstraction from $\gamma$ (10a$_1$) and $\beta$ (10a$_2$) sites. These reactions proceed with modest activation enthalpies of 90.4 kJ/mol (TS8) and 133.0 kJ/mol (TS9), respectively, as shown in Figure 4.10.

**Figure 4.9.** Decomposition of intermolecular hydroperoxide species. Enthalpy values are calculated at 298.15 K and the bolded C atoms indicate radical sites.
Figure 4.10. Formation of alkyl hydroxide species by intramolecular abstraction of H atom.

Enthalpy values are calculated at 298.15 K and the bolded C atoms indicate radical sites.

Barrierless addition of an oxygen molecule (6) at the $\gamma$ radical site, formed by peroxy group abstracting the H atom in Reaction 4a, is found to be exothermic by 98.5 kJ/mol and results in the formation of peroxyalkyl hydroperoxide radical (a chain comprising peroxy radical on the $\gamma$ carbon with respect to the hydroperoxide group). This radical can isomerise by internal transfer of hydrogen atom in an analogy to the well-documented process for the corresponding gas-phase reactions of alkanes to form alkyl dihydroperoxide radicals. Such rearrangements comprise mechanisms that are similar to that of $\alpha$, $\beta$ and $\gamma$ H shift. Herein, we investigate intermolecular abstraction of a hydrogen atom (7). The reaction is endothermic by 57.8 kJ/mol and associated with a modest reaction barrier of 85.4 kJ/mol. Figure 4.11 shows the PES for Reactions 6 and 7.
4.3.4. Kinetic considerations

Reactions passing through the initially-formed peroxy adducts play significant role in the overall low-temperature oxidation of PE, as depicted in Figure 4.4. Thermal oxidation of PE is typically modelled by adapting global reaction schemes. Reaction rate constants in oxidation of liquid or solid phase polymers originate from matching gas phase reactions with corrections due to inversion or transposition of the polymers into the liquid or solid phase. In this approach, $E_a$ values are corrected (i.e. lowered) by subtracting condensation heats of reactants. Correction in values of $A$ factors reflects the loss of degree of freedom when shifting from a gas to a solid or liquid phase. This loss is expressed by translational and rotational entropy contributions according to the following expression.
Likewise, rate parameters exist only for limited number of elementary kinetic steps and mechanistic schemes built from the elementary reactions rarely involve reactive pathways comprising intramolecular reactions.

We evaluate accuracy limits implicit in our calculated kinetic data based on a comparison with corresponding experimental values obtained by Vana Sickle and co-workers, for the intramolecular 1,5-hydrogen shift during auto-oxidation of liquid 2-peroxypentane. Our kinetic estimation for this reaction affords a barrier of 81.9 kJ/mol and log A of 13.1 s⁻¹; i.e., in agreement with the corresponding experimental assessment for this reaction, 82.4 kJ/mol and 11.5 s⁻¹, respectively.

Figure 4.12 depicts Arrhenius plots for several reactions investigated in this work, and Table 4.3 itemises reaction rate parameters in terms of activation energies (Ea) and the Arrhenius pre-exponential A factors. However, since molecular oxygen diffuses more easily in unordered medium, we expect higher rates in the amorphous and defected regions of PE. Values in Table 4.3 represent the first set of kinetic data that are calculated specifically for PE. Literature studies have adopted kinetic parameters of the corresponding gas-phase reactions. The overall rate-limiting step revolves around formation and decomposition of hydroperoxides that follow an experimental reaction rate expression of $k(T) = 1.5 \times 10^{10} \exp(-73/(R \cdot T))$ [L/(mol s)] and $k(T) = 2.5 \times 10^{14} \exp(-146/(R \cdot T))$ [s⁻¹] respectively. The latter accounts only for a typical unimolecular O–O bond fission (ROOH → RO⁻ + 'OH). As listed in Table 4.3, the decomposition of hydroperoxides follow three additional routes, in which the structural rearrangement of RO⁻ lowers the activation energies. Baum

\[ k_{\text{liq/solid}} = k_{\text{gas}} \exp\left(\frac{-\Delta H_{\text{gas-liq/solid}}}{RT}\right) \exp\left(\frac{\Delta S_{\text{gas-liq/solid}}}{R}\right) \]
explicitly followed the actual change in structure of PE during oxidation. At moderate temperature, the rate of formation of hydroperoxides proves that, the adducts rapidly reach their equilibrium concentration. Subsequently, their decomposition to free radicals accelerates the oxidation process. Essentially, while our calculated values describe auto-oxidation process in crystalline PE, they may also serve to model the oxidative decomposition of melted PE, provided that they are adjusted by the transposition approach.

Reaction rate parameters for channels 2a, 4c, 6, 9a and 9b cannot be computed by the conventional TST method because they appear barrierless. As an alternative approach, the variational transition state theory\textsuperscript{64, 65} affords a robust procedure in which the reaction rate constant is minimised as a function of temperature and reaction coordinate. However, application of such methodology in our system proves highly challenging in terms of computational cost. To the best of our knowledge, literature provides no application of the VTST on a periodic-boundary system. Nonetheless, as a limiting case scenario, one can assume the calculated enthalpies for these reactions as the energy term in the Arrhenius equation. A factors for these reactions follow from those of analogous gas-phase reactions of alkanes, corrected by the transposition method.
**Figure 4.12.** Arrhenius plots for the studied reactions.
CHAPTER 4 — Oxidation of Crystalline Polyethylene

Table 4.3. Kinetic parameters of reactions involving key radical intermediates.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ (s$^{-1}$); for Reactions 2b and 8, $A$ [L/(mol s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b: $R^+ + O_2 \rightarrow$ Alkene + HO$_2$</td>
<td>212.6</td>
<td>$1.72 \times 10^2$</td>
</tr>
<tr>
<td>3: $ROO^\cdot \rightarrow$ Alkene + HO$_2$</td>
<td>97.1</td>
<td>$5.90 \times 10^{12}$</td>
</tr>
<tr>
<td>4a: $ROO^\cdot \rightarrow R_\gamma^\cdot OOH$</td>
<td>84.0</td>
<td>$1.67 \times 10^7$</td>
</tr>
<tr>
<td>4b: $ROO^\cdot \rightarrow R_\beta^\cdot OOH$</td>
<td>91.3</td>
<td>$4.41 \times 10^9$</td>
</tr>
<tr>
<td>5a$<em>1$: $R</em>\gamma^\cdot OOH \rightarrow$ Alkene + RO + HO$^\cdot$</td>
<td>111.5</td>
<td>$1.30 \times 10^{13}$</td>
</tr>
<tr>
<td>5a$<em>2$: $R</em>\gamma^\cdot OOH \rightarrow$ RO$_{oxetane}$ + HO$^\cdot$</td>
<td>93.5</td>
<td>$1.67 \times 10^{18}$</td>
</tr>
<tr>
<td>5b: $R_\beta^\cdot OOH \rightarrow$ RO$_{epoxide}$ + HO$^\cdot$</td>
<td>95.9</td>
<td>$4.24 \times 10^{15}$</td>
</tr>
<tr>
<td>8$: $ROO^\cdot + RH \rightarrow$ ROOH + R$^\cdot$</td>
<td>85.4</td>
<td>$1.51 \times 10^{11}$</td>
</tr>
<tr>
<td>10a$<em>1$: $RO^\cdot \rightarrow R</em>\gamma^\cdot OH$</td>
<td>90.7</td>
<td>$8.50 \times 10^7$</td>
</tr>
<tr>
<td>10a$<em>2$: $RO^\cdot \rightarrow R</em>\beta^\cdot OH$</td>
<td>135.0</td>
<td>$1.36 \times 10^{11}$</td>
</tr>
</tbody>
</table>

* Estimated from linear relationship among R-H BDH, activation energy and rate constant for intermolecular H-abstraction by secondary peroxy radicals.

4.4. Conclusions

This chapter has analysed the initial elementary steps occurring during the low-temperature oxidation of PE, locating optimised geometries and estimating thermodynamic properties of all plausible products and transition structures. Aldehydes, epoxides, oxetanes and ketones appear as a consequence of intramolecular H-transfer from three adjacent –CH$_2$– sites, on the same hydrocarbon chain, to the outer oxygen atom in the initially-formed peroxy adduct. Secondary alkoxy and hydroxy groups arise from intermolecular H-transfer from a neighbouring chain, with a generalised linear relationship deployed to estimate the respective activation energy and
rate constant of H-transfer. Moderate activation energies accompany intermolecular reactions if compared with intramolecular reactions. Thermochemical and kinetic parameters obtained in this study provide an understanding of the solid-state auto-oxidation of PE and afford insights into oxidation of other crystalline polyolefins.

4.5. References


40. Pnam Space Group. [http://img.chem.ucl.ac.uk/sgp/large/062bz1.htm](http://img.chem.ucl.ac.uk/sgp/large/062bz1.htm)


55. Korcuk, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U., Absolute rate constants for hydrocarbon autoxidation. XXI. Activation energies for propagation and the correlation of


CHAPTER 5

Paper III: Oxidation of Polyethylene under Corrosive NO\textsubscript{x} Atmosphere


The paper has been reformatted for Australia English.

This chapter describes the low-temperature interaction of polyethylene with NO\textsubscript{x}. It investigates the relevant pathways leading to the formation of initial products, hence, furnishes insights into the experimental observation reported in Chapter 6...
5.0. Abstract

This chapter reports the results of comprehensive quantum-mechanical calculations of low-temperature oxidation (i.e., below the softening point) of polyethylene (PE) film in a corrosive NO\textsubscript{x} environment, by mapping out the potential energy surface for a large set of reactions, developing thermokinetic parameters for each elementary reaction and discussing in detail the most energetically-favourable paths. Remarkably, addition of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) results in formation of C-nitroso and nitro species, respectively, and successively leads to internal tautomerisation or concerted elimination of nitroxyl (HNO) and nitrous acid (HNO\textsubscript{2}). We demonstrate that, the presence of molecular oxygen sustains the formation of O-nitroso compounds, organic nitrites and nitrates. Reaction rate parameters have been established for all considered reactions over the temperature range of 300 K to 800 K. The results presented herein provide new insights into the solid-state polymer-gas reactivity of PE in NO\textsubscript{x} atmosphere pertinent to thermal recycling of materials laden with PE and to co-combustion of PE with a nitrogen-rich fuel such as biomass. The results will find application to systems that involve oxidative decomposition of germane crystalline polyolefins/paraffins and pure carbon-hydrogen-type polymers induced by aggressive gases such as NO and NO\textsubscript{2}. 
5.1. Introduction

Long-established and widespread use of polymers necessitates the study of their reactivity, thermal stability, degradation and decomposition under conditions typical of their intended function. Polyethylene (PE), for example, as one of the major non-toxic commercially available polymer, serves in wide range of applications; from household utensils to industrial and medical paraphernalia.\(^2,3\). The deployment of PE had encouraged a great deal of research on its pyrolysis, oxidation and chemical reactivity.\(^4-10\) This research has mainly aimed to understand the decomposition behaviour of PE for application related to thermal recycling of materials laden with PE and energy recovery of main stream municipal wastes, often loaded with significant amounts of pure carbon-hydrogen-type polymers.

Regarding thermal studies, a clear distinction rests between thermal degradation and thermal decomposition. The former describes a process wherein certain defining properties of a polymeric material deteriorate under heat exposure, while the latter is characterised by a variation in the chemical structure or an extensive change in chemical identity caused by heat.\(^11\) Although, to a reasonable extent, both phenomena for PE had been understood under oxidative O\(_2\) conditions,\(^12-15\) the literature lacks detailed demonstrations on how PE decays in other reactive fumes.

In the 1950s, Ogihara pioneered the study of reaction of nitrogen dioxide with PE.\(^16,17\) Afterwards, Jellinek and collaborators investigated reactions of different classes of polymers with air pollutants, such as oxides of sulfur (SO\(_x\)) and nitrogen (NO\(_x\)).\(^18,19\) At low atmospheric concentration and standard conditions, the aggressive pollutants (NO\(_x\)) exert limited effect on vinyl polymers. However, a slight increase in concentration and temperature induces a
pronounced interactions within their macromolecular structure.\textsuperscript{20} In fact, this kind of conditions becomes practically important when industrial applications deploy PE in processes characterised by elevated concentration of NO\textsubscript{x}. For instance, in high-voltage systems, polymer insulators could suffer NO\textsubscript{x} attack during a coronal discharge.\textsuperscript{21-24} Likewise, a discharge treatment of oxidative corona of PE films in air yields an unsaturated surface, abundant in oxygenated species such as ketones, aldehydes, alcohols, and esters, with large numbers of macroradicals,\textsuperscript{3, 25, 26} which can possibly react with oxides of nitrogen, produced concurrently in the course of the same process.\textsuperscript{27, 28} Furthermore, in another type of surface modification (hydrophilic plasma treatment), a stream of reactive nitrogen oxides implants nitrogen-bearing functional groups on the surface of a polymeric material.\textsuperscript{29, 30} In addition, oxidation of PE in fuming nitric acid (HNO\textsubscript{3}) also incurs the contributions of nitrogen-oxide functionalities.\textsuperscript{31, 32} Furthermore, the polyethylene-enhanced selective catalytic reduction (SCR) of NO\textsubscript{x}\textsuperscript{33} and co-combustion of PE with a nitrogen-rich fuel could serve as additional examples for the co-existence of O\textsubscript{2} – NO\textsubscript{x} – PE.

Primarily, NO\textsubscript{x} includes nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}). Because of the toxicity of NO and NO\textsubscript{2},\textsuperscript{34} their study remains a thematic research topic among environmentalists, chemists and engineers. Gas-phase reaction of NO\textsubscript{x} with hydrocarbons attracts much interest, as it plays an important role in combustion, as well as in atmospheric and tropospheric chemistry.\textsuperscript{35-44} However, results from such findings cannot fully describe analogous condensed-phase reactions. For instance, reaction of NO\textsubscript{2} with alkene experiences different competitive pathways in solutions.\textsuperscript{45} In gas-solid systems, molecules have insufficient conformational flexibility that restricts mobility of constituent chains.
To this end, in the present chapter, we provide the first comprehensive theoretical evidence of oxidative decomposition of PE under corrosive NO\(_x\) atmosphere. By deploying the density functional theory (DFT), from mechanistic and kinetic viewpoints, we analyse primary initiation reactions of NO\(_x\) with modelled PE species. Results presented herein provide new physical insights into the solid-state oxidation of crystalline polyolefins/paraffins and carbon-hydrogen-type polymers in NO\(_x\) environment. In addition to the aforementioned systems, in which NO\(_x\) interferes with PE oxidation, our mechanistic and kinetic analyses are of broad interest in understanding the role of nitrogen oxides during an auto-oxidation process of crystalline PE, as apparent in its natural ageing mechanism under thermo- and photo-oxidative conditions.

Finally, this work should not be confused with the so-called pinking or yellowing (discolouring) of PE. This colour change arises from the reaction of NO\(_x\) with a phenolic antioxidant present in the resin. The surface oxidation leads to formation of quinone-like structure that can be easily reversed in UV light.\(^{46,47}\)

### 5.2. Methodology

The reaction modelling rests on a similar approach applied in our recent theoretical investigation of the oxidation of crystalline polyethylene by molecular oxygen.\(^1\) DMol\(^3\) package\(^{48,49}\) enables all structural optimisations, and serves to calculate all energy and vibrational frequencies. As illustrated in Figure 5.1, we develop a PE(100) surface defined by the (100) Miller index, by employing an optimised form of a primitive orthorhombic crystalline arrangement reported by Avitabile et al.\(^{50}\)
Figure 5.1. Illustration of the adopted methodology. The prior study\textsuperscript{1} provides the complete crystallographic structural parameters of the unit cell.

The vacuum distance between each periodic slab sufficiently eliminates any interactions within the recurring images, while accommodating all target species, as well as dissociative products. For the purpose of representation in this paper, we show only the major singular PE chain in all potential energy surfaces (PES).

The DFT exchange-correlation potential employs the generalised gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional, with the tolerance on the convergence of the total energy of $1 \times 10^{-6}$ Ha. In the calculations, the electronic core treatment includes all electrons while applying a double numerical plus polarisation (DNP) atomic basis set, confined within a global cut-off of 4.0 Å. The integration of the Brillouin zone involves automatic generation of $2\times3\times6$ and $1\times2\times1$ $k$-points for the unit cell and periodic slabs,
respectively, through the Monkhorst-Pack grid scheme. The average computational cost typically amounts to 20 h (on 32 parallel processing cores) for each periodic slab. Our earlier study\textsuperscript{1} revealed that, the selected choice of DFT functional and basis set offers a satisfying accuracy threshold for the system at hand, even without semiempirical dispersion correction scheme.

Furthermore, as implemented in DMol\textsuperscript{3}, the complete linear synchronous and quadratic synchronous transit approaches (LST/QST) locate all necessary transition states. Reaction rate constants are fitted to the Arrhenius equation (i.e., $k(T) = A \exp(-E_a/RT)$) in the temperature range of 298.15 K to 800 K, according to the classical transition state theory (TST)\textsuperscript{51}:

$$k(T) = \sigma_e \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$  \hspace{1cm} (5.1)

DMol\textsuperscript{3} package computes vibrational frequencies from which it obtains the temperature-dependent thermochemical parameters. In Equation 5.1, we set the reaction degeneracy number $\sigma_e$ to unity (i.e. per C/H/O/N site) in all considered reactions. $\Delta S^*$ and $\Delta H^*$ refer to entropy and enthalpy of activation at temperature $T$ in that order, $k_B$, $h$, and $R$ symbolise Boltzmann’s, Planck’s and the universal gas constants, respectively. The implicit accuracy limit for the calculated reaction rate parameters have been validated by intramolecular 1,5-hydrogen shift during auto-oxidation of liquid 2-peroxypentane. Our kinetic estimation for this reaction affords a barrier of 81.9 kJ/mol and log $A$ of 13.1 s\textsuperscript{-1}; i.e., in reasonable agreement with the corresponding experimental assessment for this reaction of 82.4 kJ/mol and 11.5 s\textsuperscript{-1}, respectively.\textsuperscript{52, 53}
5.3. Results and Discussion

5.3.1. Initiation reactions and formation of radical species

Figure 5.2 portrays the energetics of the three initiation pathways. According to reaction (1a), the bond dissociation enthalpy (BDH) of a secondary C‒H bond in PE amounts to 416.2 kJ/mol. This value agrees well with the corresponding values for gas-phase alkanes; i.e., 410.0 – 416.0 kJ/mol.\textsuperscript{54, 55}

\[
\text{RH} \rightarrow \text{R}^- + \text{H} \quad \text{(1a)}
\]

Elevated temperature, UV radiation as well as mechanical or chemical factors may overcome the sizable enthalpic requirement for the barrierless fission of a C‒H bond, permitting the appearance of infinitesimal fraction of radical sites in the polymer matrix, ready for further reaction.\textsuperscript{1}

Earlier experimental studies speculated the initiation reactions to involve direct hydrogen abstraction by NO\textsubscript{2}.\textsuperscript{19} Generally, such mechanism could take the form:

\[
\text{RH} + \text{NO} \rightarrow \text{R}^- + \text{HNO} \quad \text{(1b)}
\]
\[
\text{RH} + \text{NO}_2 \rightarrow \text{R}^- + \text{HONO} \quad \text{(1c)}
\]

In this mechanism, the oxides of nitrogen abstract H atom from a polymer chain. Our calculated results at 298.15 K (all reaction and activation enthalpies are discussed at this
temperature) elucidate (1b) as a highly endothermic process, requiring 342.9 kJ/mol, in like manner to H-abstraction by triplet oxygen.\textsuperscript{1} Incurring a high reaction barrier of 380.7 kJ/mol (TS1), it is unlikely that, direct H-abstraction by the NO free radical from PE represents a significant initiation channel. However, direct secondary H-abstraction by a NO\textsubscript{2} molecule proves to be somewhat more feasible. It entails moderate reaction enthalpy (86.5 kJ/mol), over a barrier height of 337.2 kJ/mol (TS2). Analogous abstraction of secondary hydrogen from C\textsubscript{3}H\textsubscript{8} incurs similar reaction enthalpy of 83.2 kJ/mol, but sufficient conformational flexibility experienced in gas phase prompts a lowered barrier height of 136.1 kJ/mol.

![Figure 5.2. Initiation reactions by H-dissociation (1a) and H-abstraction (1b and 1c).](image)

Enthalpy vales are calculated at 298.15 K.

The presence of oxygen results in the generation of the reactive H/O radical pool in addition to the formation of peroxy adducts. The latter triggers the formation of different stable species such as aldehydes, epoxides, oxetanes, ketones and hydroxyl, mainly via intramolecular and intermolecular H-transfer from adjacent –CH\textsubscript{2}– sites. As it is the case for alkanes,\textsuperscript{56} reactions of H/O radicals with PE may also generate free alkyl sites. At lower temperatures, hydroperoxyl radicals play a crucial role in driving the low-temperature oxidation cycle.\textsuperscript{57, 58}
In subsequent steps, hydroxyl and hydroperoxyl radicals could add to vacant radical sites in the PE chain. Consequently, oxidation of PE produces three main radical-type species; namely, alkyl, hydroxyalkyl and hydroperoxyalkyl. In a rich NO\textsubscript{x}\textsuperscript{-}environment, oxides of nitrogen potentially react with three PE-type radicals as depicted in Figure 5.3. As the next sections demonstrate, the reactivity of these radicals varies based on the characteristics of vicinal functional groups.

**Figure 5.3.** Reaction pathways for primary initiations during oxidation of crystalline polyethylene in NO\textsubscript{x} atmosphere.

### 5.3.2. Addition reactions and fate of consequential N-derivative species

The appearance of radical sites allows subsequent reactions. Remarkably, barrierless additions of NO (2, 13 and 23) and NO\textsubscript{2} (4, 15 and 25) are exothermically competitive. As shown in Figure 5.4, these reactions lead to the formation of C-nitroso and nitro adducts, and respectively
release 164 – 192 kJ/mol and 383 – 411 kJ/mol, depending on the functionality of neighbouring chemical groups, i.e. alkyl, hydroxyalkyl and hydroperoxyalkyl.

Figure 5.4. Addition of molecular oxygen, nitric oxide and nitrogen dioxide to different carbon radical sites on a PE chain. Enthalpy values are calculated at 298.15 K.

Generally, nitroso compounds convert into more thermodynamically stable oxime tautomers by migration of an \( \alpha \) H atom (i.e., from the same carbon atom attached to NO) to the nitroso group.\(^{59}\) According to Figure 5.5, transformation of nitrosoalkyl in a PE chain (3a) reveals exothermicity of 49.9 kJ/mol and a reaction barrier of 328.4 kJ/mol (TS3). However, availability of hydroxyl (14) and hydroperoxyl groups (24), closely located on the same PE chain, moderates the reaction barrier to 201.1 kJ/mol (TS4) and 231.1 kJ/mol (TS5), respectively. On the other hand, with the exemption of nitromethanes, nitroalkanes exist as highly versatile stable compounds.\(^{59,60}\) As a result, in PE, tautomerisation of nitroalkyl into its
aci form (5a) proceeds via the enthalpy of activation of 285.6 kJ/mol with endothermicity of 73.1 kJ/mol. In addition, the presence of a hydroxyl group on the same chain (16) significantly lowers the barrier to 132.4 kJ/mol, but existence of hydroperoxyl group (26) raises the barrier up to 434.9 kJ/mol, with a significant change in the endothermicity of the reactions. Based on results from our recent work on dehydrohalogenation of ethyl halides, we envisage that the presence of the vicinal hydroxyl and hydroperoxyl functional groups alters the activation energies via modifying the charge distribution environment around the transferred H atom. Nevertheless, the exact effect of introducing these groups requires further scrutiny.

Figure 5.5. Tautomerisation of nitroso- and nitroadducts. Enthalpy values are calculated at 298.15 K.
Owing to sizable activation enthalpy associated with the intramolecular H transfer in reactions 3a and 5a, the initially formed N-derivative species must have competing exit routes. In Figure 5.6, each of the two NO\textsubscript{x} species departs the PE chain simultaneously with a $\beta$-hydrogen atom. This results in concerted eliminations of nitrooxyl (3b) and nitrous acid (5b), with modest endothermic reaction enthalpies of 112.7 kJ/mol and 84.0 kJ/mol, in that order. The reactions lead to the formation of alkenes, over moderate barrier heights of 124.1 kJ/mol (TS9) and 165.4 kJ/mol (TS10).

Figure 5.6. Concerted elimination of nitrooxyl (HNO) and nitrous acid (HONO) from the initial N-derivative species. Enthalpy values are calculated at 298.15 K.

5.3.3. Formation of organic nitrites and nitrates

As previously established, the presence of oxygen produces a peroxy adduct. Along this corridor, NO or NO\textsubscript{2} bond with the outer oxygen atom of peroxy species. In urban areas with high NO\textsubscript{x} concentration, addition of NO/NO\textsubscript{2} remains the major sink for ROO$^-$ radicals.\textsuperscript{40, 62, 63} In gas phase, considering the typical rate parameters for this set of reactions,\textsuperscript{64, 65} and excessive NO\textsubscript{x} level, the pseudo-first-order rate will predominate over the unimolecular reactions of
Figure 5.7 illustrates the formation of alkylperoxy nitrates (7a and 7b) and alkylperoxy nitrates (8), by respective exothermic addition of NO (-131.7 kJ/mol and 117.0 kJ/mol) and NO\(_2\) (-261.0 kJ/mol) to the peroxyl group. Alkylperoxy nitrite has two conformers; namely, the *cis-* and the relatively less stable *trans-*structures, depending on the arrangement of the ROO-NO link. Structural rearrangement of *cis*-alkylperoxy nitrite (9a\(_2\)) is exothermic by 128 kJ/mol, requiring a barrier height of 96.8 kJ/mol (TS11a). Likewise, similar reaction for *trans*-alkylperoxy nitrite species (9b\(_2\)) reveals exothermicity of 142 kJ/mol, and a reaction barrier of 118 kJ/mol (TS11b). Furthermore, dissociation of NO\(_2\) from the alkylperoxy nitrite conformers (9a\(_1\) and 9b\(_1\)) or alkyl nitrates (10) remain less probable due to the relatively high endothermicity of the reactions involved.
Figure 5.7. Formation of organic nitrites and nitrates. Reactions with $a_1$ and $b_1$ subscripts represent NO$_2$ dissociation from the cis- and trans-peroxy adducts respectively, according to Figure 5.3. Enthalpy values are calculated at 298.15 K.
The progress of NO or NO\textsubscript{2} addition to an OH-functionalised PE chain (18a – 21) follows the same profile, with slight alterations in energetics. However, in OOH-functionalised PE chain, structural transformation of \textit{trans}-peroxy nitrite adduct appears barrierless, expressing the reaction as concerted elimination and re-addition of NO\textsubscript{2}. Also, dissociation of NO\textsubscript{2} leads to the formation of hydroxyalkyl peroxy, as the H atom of the OOH group preferentially migrates to the adjacent alkoxy end.

The usual O\textsubscript{2} oxidation route contributes to the formation of alkoxy species\textsuperscript{1,56}. These species combine with NO molecules to form alkyl nitrites. As shown in Figure 5.8, such reactions exhibit exothermicity of 178.8 kJ/mol (11), and the presence of neighbouring hydroxyl and hydroperoxyl functional groups reduces the exothermicity of the reactions to 140.5 kJ/mol (22) and 113.1 kJ/mol (32), respectively.

\textbf{5.3.4. Thermodynamics and reaction kinetics}

Figure 5.9 presents changes of thermodynamic potentials of reactions involving addition of NO and NO\textsubscript{2} molecules as function of temperature. Over the considered temperature range, the exothermic reaction enthalpies display weak dependence on temperature. However, on a $\Delta_r G^\circ$ scale, the reactions become gradually less spontaneous as temperature increases. Such occurrences can be attributed to the orderliness of the system (negative change of entropy) due to disappearance of gaseous species, and from a thermodynamic outlook, the spontaneity of these reactions requires low temperature. In a more practical sense, at high temperature, the rate of kinetic processes increases, and the system can more easily attain equilibrium, as both forward and backward reactions operate at higher rates.
Figure 5.8. Addition of NO molecules to alkoxy species. Enthalpy values are calculated at 298.15 K.
Figure 5.9. Variation of enthalpy (a), entropy (b) and Gibbs energy (c) with temperatures, for all reactions attributed to addition of NO and NO\textsubscript{2}. Refer to Figure 5.3 for the corresponding reaction sequences.
Reactions of polymers with NO\textsubscript{x} constitute an important factor responsible for deterioration and chemical transformation of their macromolecular structures. Concerning carbon-chain polymers containing no carbon–carbon double bonds, pioneering studies\textsuperscript{16, 17} have confirmed that, NO\textsubscript{2} cannot abstract secondary and tertiary hydrogen atoms from PE and polypropylene (PP) at 298 K, however at temperatures above 373 K, direct H-abstraction may occur.\textsuperscript{19, 20, 67} On the other hand, NO cannot abstract tertiary or allylic hydrogen from organic molecules, but it readily reacts with free radicals to form nitroso compounds by addition to vacant radical sites.\textsuperscript{20}

Figure 5.10 depicts Arrhenius plots for several reactions comprising key radical intermediates, and Table 5.1 assembles their respective reaction rate parameters in terms of activation energies ($E_a$) and the Arrhenius pre-exponential $A$ factors. Based on reaction rate constants reported in Table 5.1, concerted eliminations of HNO (3b) and HONO (5b) dominate the fate of initially formed nitroso- and nitroadducts, and tautomerisation of nitrosoalkyl compounds favours their oxime derivatives. In case of nitroalkyls, the position of equilibrium lies towards the nitro form. In addition, the rate parameters reveal that, alkylperoxy nitrites exhibit rapid structural transformation into the corresponding alkyl nitrate species. While the rate parameters listed in Table 5.1 remain valid for crystalline PE, they can also serve to describe similar reactions in melted PE provided that, the $E_a$ and $A$ are accurately adjusted by considering the inversion or transposition of the polymer into the liquid phase:

$$k_{liq} = k_{solid} \exp \left( \frac{-\Delta H_{\text{solid-liq}}}{RT} \right) \exp \left( \frac{\Delta S_{\text{solid-liq}}}{R} \right)$$
Unlike gas-to-liquid transposition, the energy term represents the heat of fusion required to melt the polymeric material, and the positive change in entropy increases the $A$ factor as the system becomes more disordered in liquid phase.

**Figure 5.10.** Arrhenius plots for the studied reactions.
Table 5.1. Kinetic parameters of reactions involving key radical intermediates.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ (s$^{-1}$); for Reactions 1b and 1c, $A$ [cm$^3$/(mole s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b: $\text{RH} + \text{NO} \rightarrow \text{R}^\cdot + \text{HNO}$</td>
<td>425.0</td>
<td>$7.11 \times 10^{19}$</td>
</tr>
<tr>
<td>1c: $\text{RH} + \text{NO}_2 \rightarrow \text{R}^\cdot + \text{HONO}$</td>
<td>383.6</td>
<td>$1.57 \times 10^{13}$</td>
</tr>
<tr>
<td>3a$_{\text{forward}}$: $\text{RNO} \rightarrow \text{RNOH}$</td>
<td>332.0</td>
<td>$1.39 \times 10^{14}$</td>
</tr>
<tr>
<td>3a$_{\text{backward}}$: $\text{RNOH} \rightarrow \text{RNO}$</td>
<td>382.0</td>
<td>$1.71 \times 10^{14}$</td>
</tr>
<tr>
<td>3b: $\text{RNO} \rightarrow \text{R}^\cdot + \text{HNO}$</td>
<td>125.3</td>
<td>$9.79 \times 10^{11}$</td>
</tr>
<tr>
<td>5a$_{\text{forward}}$: $\text{RNO}_2 \rightarrow \text{RNO}_2\text{H}$</td>
<td>290.0</td>
<td>$8.91 \times 10^{14}$</td>
</tr>
<tr>
<td>5a$_{\text{backward}}$: $\text{RNO}_2\text{H} \rightarrow \text{RNO}_2$</td>
<td>220.0</td>
<td>$1.09 \times 10^{19}$</td>
</tr>
<tr>
<td>5b: $\text{RNO}_2 \rightarrow \text{R}^\cdot + \text{HONO}$</td>
<td>167.4</td>
<td>$6.54 \times 10^{11}$</td>
</tr>
<tr>
<td>9a$_2$: cis-$\text{ROONO} \rightarrow \text{RONO}_2$</td>
<td>85.4</td>
<td>$1.21 \times 10^{5}$</td>
</tr>
<tr>
<td>9b$_2$: trans-$\text{ROONO} \rightarrow \text{RONO}_2$</td>
<td>104.3</td>
<td>$4.36 \times 10^{3}$</td>
</tr>
<tr>
<td>14$_{\text{forward}}$: $\text{OH}^\cdot\text{RNO} \rightarrow \text{OH}^\cdot\text{RNOH}$</td>
<td>207.0</td>
<td>$3.19 \times 10^{15}$</td>
</tr>
<tr>
<td>14$_{\text{backward}}$: $\text{OH}^\cdot\text{RNOH} \rightarrow \text{OH}^\cdot\text{RNO}$</td>
<td>270.5</td>
<td>$1.33 \times 10^{17}$</td>
</tr>
<tr>
<td>16$_{\text{forward}}$: $\text{OH}^\cdot\text{RNO}_2 \rightarrow \text{OH}^\cdot\text{RNO}_2\text{H}$</td>
<td>133.8</td>
<td>$3.50 \times 10^{10}$</td>
</tr>
<tr>
<td>16$_{\text{backward}}$: $\text{OH}^\cdot\text{RNO}_2\text{H} \rightarrow \text{OH}^\cdot\text{RNO}_2$</td>
<td>67.0</td>
<td>$3.87 \times 10^{12}$</td>
</tr>
<tr>
<td>20a$_2$: cis-$\text{OH}^\cdot\text{ROONO} \rightarrow \text{OH}^\cdot\text{RONO}_2$</td>
<td>64.3</td>
<td>$1.20 \times 10^{8}$</td>
</tr>
<tr>
<td>20b$_2$: trans-$\text{OH}^\cdot\text{ROONO} \rightarrow \text{OH}^\cdot\text{RONO}_2$</td>
<td>83.9</td>
<td>$7.16 \times 10^{10}$</td>
</tr>
<tr>
<td>24$_{\text{forward}}$: $\text{OOH}^\cdot\text{RNO} \rightarrow \text{OOH}^\cdot\text{RNOH}$</td>
<td>223.1</td>
<td>$1.31 \times 10^{5}$</td>
</tr>
<tr>
<td>24$_{\text{backward}}$: $\text{OOH}^\cdot\text{RNOH} \rightarrow \text{OOH}^\cdot\text{RNO}$</td>
<td>289.1</td>
<td>$1.08 \times 10^{8}$</td>
</tr>
<tr>
<td>26$_{\text{forward}}$: $\text{OOH}^\cdot\text{RNO}_2 \rightarrow \text{OOH}^\cdot\text{RNO}_2\text{H}$</td>
<td>437.2</td>
<td>$1.73 \times 10^{11}$</td>
</tr>
<tr>
<td>26$_{\text{backward}}$: $\text{OOH}^\cdot\text{RNO}_2\text{H} \rightarrow \text{OOH}^\cdot\text{RNO}_2$</td>
<td>358.8</td>
<td>$1.15 \times 10^{13}$</td>
</tr>
<tr>
<td>30a$_2$: cis-$\text{OOH}^\cdot\text{ROONO} \rightarrow \text{OOH}^\cdot\text{RONO}_2$</td>
<td>52.5</td>
<td>$9.55 \times 10^{8}$</td>
</tr>
</tbody>
</table>

As an extra note, hydroperoxide species constitute reactive intermediates in the oxidative decomposition of polymers. Apart from their usual disappearance route, nitrogen oxides...
induce autoaccelerated decomposition of polymeric hydroperoxides. For instance, in PP, NO2 dimer initiates ROOH decomposition, resulting in the generation of a thermally unstable peroxy nitrite\textsuperscript{20,69} that undergoes fast intracage conversion into nitrate as in (9), (20) or (30) of our proposed mechanism.

### 5.4. Conclusions

This contribution has analysed the primary initiation reactions occurring during aggressive low-temperature oxidation of PE. In the NO\textsubscript{x}-laden atmosphere, formation of diverse nitrogen-containing species ultimately accompanies the free-radical processes in solid PE. Nitroso and nitroalkyl species appear as a result of respective addition of NO and NO\textsubscript{2} molecule to a carbon radical site in PE chain. Availability of a neighbouring chemical functional group alters the thermodynamic and kinetic properties of the reactions. Concerted elimination of HNO and HONO from nitroso- and nitroadducts, respectively, requires moderate activation energies, compared with unimolecular tautomerisation of the adducts. The presence of molecular oxygen induces the formation of per oxy species, that subsequently bond with NO and/or NO\textsubscript{2}, thereby serving as a potential source of organic nitrites and nitrates. In comparison with previous studies that substantiated the addition of nitrogen oxides to solid polymer resins, the current investigation delivers the concrete thermodynamic evidence of such events, and provides the reaction channels describing the fate of consequential nitrogenous species. On this note, the thermochemical and kinetic parameters obtained in this study offer an improved understanding of the polymer-gas reactions, and present insights into similar reaction sequences in other crystalline polyolefins.
5.5. References


CHAPTER 6

Paper IV: Thermal Reduction of NO$_x$ with Recycled Plastics


The paper has been reformatted for Australia English, and the Supporting Information is placed as Appendix I in Chapter 10.

The chapter develops technology for mitigation of NO$_x$ formed in thermal processes using waste polyethylene. It assesses the NO$_x$ reduction efficiency of fragments of pyrolysing PE, providing the kinetic evaluations for the thermal reactions...
6.0. Abstract

This study develops technology for mitigation of NO$_x$ formed in thermal processes using recycled plastics such as polyethylene (PE). Experiments involve sample characterisation, and thermogravimetric decomposition of PE under controlled atmospheres, with NO$_x$ concentration relevant to industrial applications. TGA–Fourier transform infrared (FTIR) spectroscopy and NO$_x$ chemiluminescence serve to obtain the removal efficiency of NO$_x$ by fragments of pyrolysing PE. Typical NO$_x$ removal efficiency amounts to 80 %. We apply the isoconversional method to derive the kinetic parameters, and observe an increasing dependency of activation energy with the reaction progress. The activation energies of the process span 135 kJ/mol – 226 kJ/mol, and 188 kJ/mol – 268 kJ/mol, for neat and recycled PE, respectively, and the so-called compensation effect accounts for the natural logarithmic pre-exponential ln ($A$/min$^{-1}$) factors of ca 19 – 35 and 28 – 41, in the same order, depending on the PE conversion in the experimental interval of between 5 and 95 %. The observed thermal delay of recycled PE reflects different types of PE in the plastic, as well as possible molecular rearrangements during the recycling processes. These measurements also provide data for kinetic modelling of both isothermal and non-isothermal decomposition of PE in NO$_x$ atmosphere in practical situations.
6.1. Introduction

Apart from its limited industrial and medical applications, oxides of nitrogen (NO\textsubscript{x}) contribute to acid rain, eco-eutrophication, photochemical smog, ground level ozone, greenhouse effect, stratospheric ozone depletion, and health deterioration (e.g., chronic respiratory and obstructive pulmonary dysfunction) of predisposed organisms. Primarily, NO\textsubscript{x} consists of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}). Typical anthropogenic emission of NO\textsubscript{x} (comprising mostly NO) amounts up to 800 ppm in untreated combustion systems burning fossil/nitrogenous fuels for power generation, and can soar as high as 500 ppm during decomposition of nitrate oxidisers in some aviation propellants and mining-grade explosives.\textsuperscript{1-11}

The quest for reliable NO\textsubscript{x} reduction has led to implementation of strict environmental regulations and development of industrial-scale technologies. In combustion systems, these technologies include fuel pre-treatment, combustion modification and post-treatment techniques.\textsuperscript{12-14} Although post-flame gas clean-up remains viable, strategic modification of combustion processes often controls NO\textsubscript{x} emission more economically.\textsuperscript{2,15,16}

Noticeably, fuel reburning provides a commercially available technological retrofit that appears more effective than alternative modifications of combustion processes. The process abates NO\textsubscript{x} by using fuel as a reducing agent.\textsuperscript{17} Since 1950s, a number of practical and experimental studies investigated the reburning technique,\textsuperscript{4,18-24} including a collateral effect of SO\textsubscript{2} reduction.\textsuperscript{25} Conceptually, reburning occurs in three stages (see Figure 6.1) to achieve between 50 % and 85 % reduction in the total NO\textsubscript{x} emission. In the first stage (primary zone), the main fuel burns under slightly fuel-lean condition. Afterwards, the produced NO\textsubscript{x} reacts with supplementary hydrocarbon radicals in the “reburning zone” to form intermediate
nitrogenous species, and then molecular nitrogen (N₂). Finally, addition of air in the last stage (burnout zone) completes the combustion process by oxidising all unreacted fuels and reduced N-species.²⁴

**Figure 6.1.** Schematic diagram of the three stages of the reburning process.

Although, large-scale reburning systems usually rely on hydrocarbon gases (e.g., methane), carbonaceous solid residues have proven equally suitable. Spliethoff et al. employed the pyrolysate fragments of coal as a reburn fuel to mitigate NOₓ formation in a bench-scale reburning facility, and attained good reduction efficiency of about 80 %.²⁶ Likewise, demonstrations of application of coal reburning in commercial boilers achieved excellent NOₓ control averaged at around 70 % reduction efficiency.²⁷-³⁰ Biomass fuels such as wood, straw, rice husk, bio-oil, sewage sludge, and carbonised municipal solid waste also provide effective means of reducing NOₓ formation (50 – 75 %) in combustion systems.³¹-⁴⁰ Yet surprisingly, only a few studies assessed the performance of polymeric materials (e.g., waste tyres⁴¹-⁴³) as a secondary reburn fuel for NOₓ remediation.
Unlike coal or biomass, plastics, such as polyethylene (PE), lack nitrogen functionalities that can further contribute to fuel-NO\textsubscript{x} formation within the reburning zone. Owing to its high calorific value, good volatile content and favourable combustion rate,\textsuperscript{44-46} waste PE finds outlets in recycling processes such as thermal energy recovery, as it burns without prompting environmental concerns, e.g., formation of pollutants and fire-related hazards.\textsuperscript{47,48} Measurements of pyrolytic conversion of PE to low-carbon gases in hybrid rocket propulsion\textsuperscript{49,50} indicate the suitability of the polymer in reburning applications, and as a potential NO\textsubscript{x} reductant during detonation of ammonium nitrate-based explosives in open-cut mining operations.

To this end, the current study presents a series of experimental investigations of thermal mitigation of NO\textsubscript{x} with PE. We hypothesis that, waste PE can potentially serve to reduce NO\textsubscript{x} emission in industrial activities. We aim at solving two crucial environmental problems, to develop a sustainable solution to NO\textsubscript{x} emission, and to provide additional means of dealing with excessive plastic wastes in the society. In particular, we report the result of thermal decomposition of PE in NO\textsubscript{x} atmosphere, providing a detailed analysis of reaction products. The insights from the present study apply equally to abatement of NO\textsubscript{x} with materials laden with PE, polyolefins/paraffins and pure carbon-hydrogen-type polymers, as well as to co-combustion/pyrolysis of PE with nitrogen-rich fuels such as biomass and coal.
6.2. Experimental Section

6.2.1. Materials and sample characterisation

The experiments involved recycled polyethylene received in form of extruded black cylindrical pellets, around 2.5 mm in diameter and 2 mm in length. We sliced the pellets into thin oblong particles of uniform size distribution of between 250 μm and 400 μm. Sigma-Aldrich, USA, provided neat low-density polyethylene, employed in control studies, to gauge the effect of impurities in the recycled PE on its thermal and NO$_x$-abatement behaviour. The attenuated total reflectance (ATR) produced the IR spectra of the recycled PE, and a carbon-hydrogen-nitrogen-sulfur (CHNS) elemental analyser yielded the elemental composition of the material. Further analyses comprised the multi-detector high temperature size exclusion chromatography (HT-SEC), ion (anion) chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP-OES) for determination of molecular mass distributions (MMD), halogens and trace metals, respectively. Supporting Information (Chapter 10) includes details of these analytical techniques. Table 6.1 itemises the molecular characteristics of the PE samples. The FTIR spectrum of the recycled PE, documented in Figure 6.2, indicates no contamination with other plastics, and Table 6.2 reveals the combined amount of metals and halogens, mostly Fe, Ca and Cl, of less than 1 %. The recycled PE contains no sulfur, nitrogen, fluorine and bromine-containing contaminants, confirming presence of no brominated flame retardants in the sample.
Table 6.1. HT-SEC parameters of neat and recycled PE samples: Peak-average, number-average and weight-average molar masses ($M_p$, $M_n$ and $M_w$), as well as intrinsic viscosity $[\eta]$, radius of gyration ($R_g$ based on the root-mean-square average distance of the components of the molecule from the centre of gravity) and polydispersity index $I_p$ in TCB solution.

<table>
<thead>
<tr>
<th></th>
<th>$M_p$ (kg/mol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w$ (kg/mol)</th>
<th>$[\eta]$ (dL/g)</th>
<th>$R_g$ (nm)</th>
<th>$I_p = M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PE</td>
<td>59.5</td>
<td>14.2</td>
<td>144</td>
<td>1.1</td>
<td>31.6</td>
<td>10.1</td>
</tr>
<tr>
<td>Recycled PE</td>
<td>77.1</td>
<td>24.4</td>
<td>105</td>
<td>1.9</td>
<td>34.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Table 6.2. Elemental characterisation of the recycled polymer; basic elements from a CHNS analyser, halogens from IC and trace metals from ICP-OES. Error margin for CHNS analysis is 0.3 %.

<table>
<thead>
<tr>
<th>Ultimate elements and halogens (wt. %)</th>
</tr>
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<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>86.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Average trace metals (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>0.10</td>
</tr>
</tbody>
</table>
6.2.2. Experimental methods

Figure 6.3 illustrates the complete schematics of the three arrangements of the experimental apparatus. A carefully calibrated (by melting point standards) PerkinElmer STA 8000 system facilitated all thermogravimetric analyses (TGA), with the quantitation of the gases performed by infrared spectroscopy (TGA-FTIR, PerkinElmer Frontier) and chemiluminescence (TGA-NOx, Thermo Scientific model 42i-HL). All TGA experiments involved three replicable runs (Figure S6.4) of 5.2 ± 0.2 mg samples, placed in alumina crucible, subjected to the nominal heating rates of 5, 10, 15, and 20 K/min, bracketing temperatures between 25 °C to 600 °C in argon, synthetic air and NOx (610 ± 5 ppm NO and 18 ± 3 ppm NO2 with balance of dry helium gas) atmosphere. The continuous flow rate of the purge gases amounted to 80 mL/min, as measured under the standard temperature and pressure (STP). Blank runs completed under identical conditions to the production experiments yielded the thermal buoyancy corrections.
We have achieved excellent reproducibility of the TGA results (Figure S6.3 of Supporting Information).

**Figure 6.3.** Schematics of adopted experimental configurations. A standalone thermogravimetry apparatus (TGA, top) eliminates any unwanted experimental artefacts that could be carried over into the subsequent kinetic evaluations. Hyphenated TGA–FTIR (middle) and TGA–NO$_x$ analyser (bottom) enabled identification and quantitation of evolved gases.
The TGA-FTIR and TGA-NO\textsubscript{x} measurements required larger sample sizes of 10.2 ± 0.2 mg to improve the detection and quantitation of gaseous species. The FTIR spectrometer averaged two accumulated scans per spectrum at 1 cm\textsuperscript{-1} resolution. This resulted in a temporal resolution of 30 s, which we found sufficient even for the fastest temperature TGA ramp of 20 K/min. The TGA-FTIR set-up incorporated an electrically heated transfer line (PerkinElmer TL 8500) linking the TGA system to 100 mm path-length online gas sampling cell placed inside the FTIR compartment. Both the sample line and the sampling cell operated at 220 °C, to avoid the condensation of product volatiles prior and during the analysis. An externally controlled vacuum pump maintained a balanced flow throughout the system. The lag time between the TGA and FTIR corresponded to 10 s, requiring a time-delay correction for comparison of the mass-loss and the evolved gas-composition signals.

### 6.3. Results and Discussion

#### 6.3.1. Thermal decomposition of PE in NO\textsubscript{x} atmosphere and evolved gas analysis

Figure 6.4 presents the characteristic thermogravimetric measurements of neat and recycled PE, as the samples decompose under Ar, He-NO\textsubscript{x} and air atmospheres. In agreement with previous studies, in inert argon purge, the pyrolysis proceeds in an apparent single-step process that commences at around 446 °C (extrapolated onset temperature), attains a maximum at around 477 °C, and then rapidly slows down owing to depletion of the material, to cease by 490 °C (extrapolated offset temperature). The residual char and ash constitutes about 0.8 % for neat and 2 % for the recycled PE, respectively. Furthermore, the presence of oxygen
triggers multi-step, low-temperature, peroxy-channelled reactions, because of O\textsubscript{2} addition to radical sites in the polymer chains.\textsuperscript{51}

**Figure 6.4.** TGA curves for the thermal decomposition of neat (a) and recycled (b) PE in different purge atmospheres at a nominal heating rate of 10 K/min. Inset plots magnify the respective normalised derivatives of the thermal events. NO\textsubscript{x} denotes a mixture of 610 ppm NO and 18 ppm NO\textsubscript{2} in balance of dry helium.
Under an inert shield gas, PE decomposes into a series of lower molecular weight hydrocarbons, mostly linear \( n \)-alkanes and \( n \)-alkenes\(^{48,50,52} \) and this can be monitored by the series of CH\(_2\) bands, most easily at 2922 cm\(^{-1}\) that corresponds to CH\(_2\) asymmetric stretch; see Figure 6.5. Other evolved functional group characteristics include CH\(_3\) asymmetric and symmetric stretches, C–H out-of-plane bend, CH\(_2\) rocking vibration and symmetric stretch, as well as CH\(_3\) asymmetric bend. These species emerge within the temporal range, corresponding to ca 400 °C – 500 °C, correlating well with the thermal decomposition period of the samples shown in Figure 6.4.
Figure 6.5. IR monitoring of hydrocarbon bands evolved during thermal decomposition of PE samples (10 mg) in two purge atmospheres at nominal heating rate of 20 K/min. The four inset plots represent the maximum evolution events with respect to absorbance values, at different time t. List of observed absorbance peaks (cm\(^{-1}\)) - 2922: CH\(_2\) asymmetric stretch; 2850: CH\(_2\) symmetric stretch; CH\(_3\) asymmetric bend; 915/990: out-of-plane C–H bend; 723: CH\(_2\) rocking vibration. CH\(_2\) bands overlap with the CH\(_3\) asymmetric stretch at 2962 and the symmetric stretch at 2873.

The presence of NO\(_x\), delivered in helium bath gas, accelerates the thermal decomposition of PE, resulting in the maximum rate of pyrolysis shifting from 477 °C (or 479 °C in the case of recycled PE) to 471 °C and 474 °C, for neat and recycled PE, in that order. This acceleration occurs due to the oxidative nature of NO\(_x\). The onset and completion temperatures, under He-NO\(_x\) purge, correspond to 433 and 483 °C as well as 444 and 486 °C, for neat and recycled PE, respectively. The observed delay in the thermal events of recycled PE suggests different
molecular branching structures\textsuperscript{53} (Figure S6.1 of Supporting Information) as well as possible confining activity of the constituent inorganic residues. Inorganic residues can form micro-glassy layers that may become impenetrable to volatiles, hence inhibit the thermal breakdown of the underlying organic matrices.\textsuperscript{54}

As shown in Figure 6.6,\textsuperscript{55} below the decomposition temperature, the barrierless exothermic addition of NO and NO\textsubscript{2} follows the formation of radical sites in condensed-phase PE. This process results in formation of C-nitroso and nitro species, respectively, and leads to internal tautomerisation or concerted elimination of nitroxy (HNO) and nitrous acid (HNO\textsubscript{2}). This set of reactions can disrupt the C–C bonding configurations, and in turn lower the overall enthalpic requirements for the homolysis of the C–C bond and unzipping of the polymer in the successive $\beta$-scission reactions.\textsuperscript{56}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{reaction_networks}
\caption{Reaction networks for interactions between condensed-phase PE and aggressive NO\textsubscript{x} species. Bolded values represent reaction enthalpies and values in italic correspond to the activation enthalpies. All values (in kJ/mol) relate to respective reactants at 298.15 K.\textsuperscript{55}}
\end{figure}
The peak value of 2922 cm\(^{-1}\) (Figure 6.5) reduces substantially when similar amount (10 mg) of PE decomposes under NO\(_x\) atmosphere, signifying decrease in concentration of CH\(_i\) fragments and hence, gas-phase reactions between the PE pyrolysates and the NO\(_x\) gases. This interaction involves several chain steps that can be globalised as\(^{4,40}\):

\[
\sum C_iH_j + NO \rightarrow HCN + ...
\]

In excess NO\(_x\), the HCN decays through series of intermediates, and ultimately reaches N\(_2\) via the reverse Zeldovich reaction, Equation (6.5):

\[
\begin{align*}
HCN + O & \rightarrow NCO + H \\
NCO + H & \rightarrow NH + CO \\
NH + H & \rightarrow N + H_2 \\
N + NO & \rightarrow N_2 + O
\end{align*}
\]

In the absence of fuel-N in PE, the other NH\(_3\) pathways remain dormant. The detection limit of the employed gas cell (100 mm path-length and 11.3 cm\(^3\) volume) restrains the online elucidation of nitrogenous species. However, the chemiluminescence analyser monitors the NO/NO\(_x\) profile ensuing under the dynamic thermal conditions. As illustrated in Figure 6.7 (as well as Figures S6.11 and S6.12 in Supporting Information), within the decomposition regime of the polymer, the experimental measurements show significant reduction of NO\(_x\) up to 80 %. The heating ramp affects the reaction via the Arrhenius term in the rate expression,\(^{57}\) dictating the composition of the volatile species.\(^{48,50,58}\) Even though the moderate heating rates alter the NO\(_x\) conversion profile in Figure S12, the maximum conversion efficiency remains
approximately the same (Figure 6.7b). As explained earlier, although the recycled PE displays a delay in the evolution of volatile fragments, the maximum NO\textsubscript{x} reduction efficiency remains the same when compared to that of neat PE samples.

![Graph showing NO\textsubscript{x} conversion history and maximum possible conversion efficiency as function of heating rate.]

**Figure 6.7.** Typical NO\textsubscript{x} conversion history during the thermal decomposition of PE samples (10 mg) in NO\textsubscript{x} atmosphere under a nominal heating rate of 20 K/min (a), and a comparison of maximum possible conversion efficiency as function of the dynamic temperature ramp (b).

The overall weighted mean for NO\textsubscript{x} conversion corresponds to 81 %. Online NO\textsubscript{x} data treatment involves response analysis (time-lag corrections), but it does not account for the spatial dispersion in the system.
6.3.2. Degradation kinetics

As expected, the decomposition of PE exhibits strong dependency on the heating rate (Figures 6.4 and S6.4). This allows the application of the isoconversional principle,\textsuperscript{57} to obtain the activation energy as function of the conversion $\alpha$. As illustrated in Supporting Information, the calculations rely on the advanced isoconversional method of Vyazovkin\textsuperscript{57,59} (Equation 6.6) that provides an accurate estimation of activation energy values from the temperature integral, as compared to Lyon,\textsuperscript{60} Kissinger-Akahira-Sunose,\textsuperscript{61} and Starink’s\textsuperscript{62} approximate approaches. For a series of runs performed at different heating rates, the appropriate activation energy value minimises the following function:

\[
\varphi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{I(E_{\alpha},T_{\alpha,i})\beta_{j}}{I(E_{\alpha},T_{\alpha,j})\beta_{i}} \quad (6.6)
\]

The subscripts $i$ and $j$ represent integer numbers of different experiments performed under varying heating programs, i.e., $i$ equals 1 – 3 for replicates, and $j$ corresponds to 1 – 4 for heating rates, and $I(E,T)$ denotes the Arrhenius temperature integral. Furthermore, the so-called compensation effect permits the determination of the pre-exponential factor $A$ by the substitution of integral form of various reaction models $g(\alpha)$ into numerical approximation of Equation 6.\textsuperscript{57,63} Although this method relies on the assumption that the thermal process obeys single-step kinetics, it can also provide a reasonable estimation\textsuperscript{64} of $A_{\alpha}$ dependency on $\alpha$, provided that the processes underlying this dependency follow a general model of $f(\alpha) = (1-\alpha)^n$. Figure S6.6 indicates that, the thermal decomposition of PE remains consistent with the
Mampel first order model of \( f(\alpha) = (1-\alpha) \) over the range of measured activation energies, satisfying this requirement. Supporting Information provides detailed discussion of the adopted method to determine the pre-exponential factor \( A \).

Previous investigators obtained the kinetic parameters for the pyrolysis of neat PE. \(^{51}\) Their reported isoconversional activation energies (150 – 240 kJ/mol) match with our estimated values of 160 – 255 kJ/mol. The illustrated growth in \( E_\alpha \) (Figure 6.8b) is a result of change in reaction mechanism. The initial low value relates to the initiation process occurring at the defect sites in the polymer chain. \( E_\alpha \) varies as the limiting step of the degradation process shifts towards other mechanisms, such as unzipping, backbiting, random scission and branching.\(^{48,51,65,66}\) As shown in Figure 6.8, the presence of ca 600 ppm of NO\(_x\) lowers the \( E_\alpha \) values for the decomposition of neat PE by 13 – 18 %. Returning to Figure 6.4, both the neat and recycled PE experience acceleration of degradation (shift to lower temperature) under NO\(_x\) atmosphere. However, the effect manifests itself differently in the kinetics. For neat PE, the drop in \( E_\alpha \) (Figure 6.8a) represents a lower energy barrier in the presence of NO\(_x\), hence reaction is faster. On the contrary, \( E_\alpha \) increases in the case of recycled PE, but Figure 6.4 depicts accelerating reaction. This means that, the mechanism of acceleration for recycled PE differs from that of neat PE. The observed acceleration during decomposition of recycled PE under He-NO\(_x\) relates to a higher pre-exponential \( A \) factor. This factor depends on MMD, in particular on higher number-average molar mass (\( M_n \) in Table 6.1) for recycled PE. The recycled PE comprises longer linear chains (as also evident from the higher value of intrinsic viscosity [\( \eta \)] for recycled polymer in Table 6.1). The longer the chain that breaks during the reaction with NO\(_x\), the higher entropy change, and larger the pre-exponential \( A \) factor.
Figure 6.8. Kinetic parameters accompanying the thermal decomposition of neat (a) and recycled (b) PE in argon and He-NO$_x$ baths. The grey trend-shades depict accuracy thresholds of the evaluated parameters.

The isoconversional kinetic parameters (plotted in Figure 6.8 and assembled in Tables S6.4 and S6.5 in Supporting Information) substituted in Equation 6.7$^{67}$ provide a means to estimate the time ($t_\alpha$) needed to achieve a target conversion $\alpha$ under isothermal condition ($T_0$):
\[ t_\alpha = \frac{1}{E_\alpha} \int_0^{T_\alpha} \exp\left( -\frac{E_\alpha}{RT} \right) \, dT \exp\left( -\frac{E_\alpha}{RT_0} \right) \]  

(6.7)

Figure 6.9 provides validation of the kinetic evaluations. At moderate temperatures, our calculated \( E_\alpha \) values predict well (according to Equation 6.7) the conversion-time required to reach a target conversion during the isothermal operation.

**Figure 6.8.** Isothermal decomposition of neat (a) and recycled (b) PE under the He-NO\(_x\) atmosphere at three moderate temperatures. Continuous lines represent experimental results, and dotted points denote the corresponding theoretical predictions (up to \( \alpha = 0.95 \)) as evaluated from Equation 6.7.

In practical applications, strict isothermal processing of PE would not be possible, as heating and cooling do not occur at infinite rate. In such situations, for process design under non-isothermal conditions, one can rely on the isoconversional data presented in Tables S6.4 and S6.5. The fundamental kinetic and conversion measurements revealed in the current
contribution make it possible to optimise practical systems for removal of NO$_x$ by pyrolysates from neat and recycled PE.

6.4. Conclusions

In conclusion, the pyrolysates of PE reduced NO$_x$ content by about 80 % with PE decomposing under the nonisothermal heating conditions. The maximum NO$_x$ reduction efficiency of recycled PE remains approximately the same relatively to that of neat samples. The injection of waste PE into a reburning zone of combustors may significantly reduce the emission of NO$_x$. Reburning of NO$_x$ in practical combustors usually occurs in a temperature window between 1000 °C and 1200 °C. Therefore, a change of the reaction mechanism may occur at those high temperatures. A subsequent study should address the high-temperature isothermal and flash-particle heating conditions in drop-tube experiments. This will reveal possible effects of the presence of oxygen and mass transfer on the reaction of NO$_x$ with PE pyrolysates under realistic reburning temperatures (i.e., 1000 – 1200 °C).

The Supporting Information is included in Chapter 10 (Appendix I) of the thesis. It comprises the assessments of calibration and repeatability of TGA experiments, thermal characterisation of recycled PE, derivation of cited equations, as well as analysis of the compensation effect, complete isoconversional kinetic data, enlarged time-resolved FTIR spectra, and complete NO$_x$ reduction trends.
6.5. References


25. Folsom, D. B. A.; Sommer, T. M.; Payne, D. R., Demonstration of combined NOx and SO2 emission control technologies involving gas reburning. **1991**.


The chapter demonstrates the effect of emitted NO$_x$ on ignition of biomass residues. It elucidates the low-temperature interaction of NO$_x$ with biomass, establishing the necessary bases for N-conversion at high temperatures as later describe in Chapter 8...
7.0. Abstract

This chapter presents an experimental study on a relative effect of nitrogen oxides (NO\textsubscript{x}) on ignition temperature of morpholine, an important surrogate of biomass, to reveal the sensitising role of NO\textsubscript{x} in combustion of biomass fuels and to gain mechanistic insights into this behaviour. The experiments employed a flow-through tubular reactor, operated at constant pressure and residence time of 1.01 bar and 1.0 s, respectively, and coupled with a Fourier-transform infrared spectroscopy. For a representative fuel-rich condition (\(\Phi = 1.25\)), the concentration of NO\textsubscript{x} as small as 0.06 \% lowers the ignition temperature of morpholine by 150 °C, i.e., from approximately 500 °C to 350 °C. The density functional theory (DFT) calculations performed with the CBS-QB3 composite method, that comprises a complete basis set, characterised the dynamics and energies of the elementary nitration reactions. We related the observed reduction in ignition temperature to the formation of unstable nitrite and nitrate adducts, as the result of addition of NO\textsubscript{x} species to morphyl and peroxyl radicals. Furthermore, the reaction of NO\textsubscript{x} with low-temperature hydroperoxyl radical leads to the formation of active OH species that also propagate the ignition process. The present findings quantify the ignition behaviour of biomass residues under NO\textsubscript{x}–doped atmospheres, the result that is of great importance in practical applications.
7.1. Introduction

Thermal interaction of biomass with oxides of nitrogen (NOx, mainly NO and NO2) has important practical implications. While such interaction serves the intended industrial purposes in low-emission combustion technologies,1-3 it has an unintended consequence of degrading the safety of organic dust-producing plants. One reason for this is the particular way in which NOx reacts with hydrocarbons, by accelerating their oxidation process.4,5 In other words, NOx enhances the ignition of combustible materials, and this effect is generally referred to as sensitisation via nitration reactions.6-10 The addition of NO and/or NO2, to fuel-oxygen systems, significantly alters the overall kinetics by turning the usual low-temperature chain-terminating steps of formation of peroxy (RO2) radicals into a chain-propagating step.5

Premature ignition of biomass particles, as a result of the sensitising effect of NOx gases, can lead to unexpected fires and dust explosions. The latter occur upon direct exposure of combustible dust clouds (dispersed in air at concentrations above the flammability limit) to an ignition source, such as electrical or electrostatic sparks, overheated powder particles, hot surfaces, etc., within a certain degree of confinement.11-14 Wood dusts in the timber industry display the same potential to explode as coal powders in underground mining operations.15,16 Minor quantities of NOx (e.g., from diesel engines) promote the primary ignition of small wood particles. These enflamed particles prompt the formation of dust clouds creating conditions for secondary deflagration or detonation. In fact, the industrial safety literature presents numerous examples of explosions and fire accidents in wood-processing plants, for example, sawmills.11,17-19 Biomass dusts form during harvesting, sizing, transportation, preparation, storage, as well as through usage in combustion plants. Fire hazard arises when the dust sediments (and suspensions) accumulate on hot surfaces of electrical, and mechanical devices,
such as conveyers, dryers, hot bearings and other machineries.\textsuperscript{20} Although, the storage conditions in silos aggravate the propensity for low temperature ignition,\textsuperscript{21-23} local conditions, such as NO\textsubscript{x} presence from plant equipment, constitutes a contributing factor. Examples of biomass-related fire incidents involved storage facilities and power plants.\textsuperscript{24}

The complex nature of biomass necessitates the use of representative model compounds to gain an understanding of the ignition, combustion and pyrolysis of biomass-derived fuels. These model compounds include hetero-element species, also known as surrogates, embodying the well-defined N- and O-functionalities within their structures.\textsuperscript{25-27} Morpholine (C\textsubscript{4}H\textsubscript{9}NO, 1-oxa-4-aza-cyclohexane) represents an excellent surrogate species for an oxygen and nitrogen-containing biofuel, due to its unique heterocyclic structure, well-characterised and studied behaviour, and a wide range of industrial applications. Its N-, C-, and O-content correspond to that revealed by ultimate analysis of typical biomass feedstocks. Furthermore, morpholine is widely used as an impregnating agent for fruit, cardboard, and paper, and as a fuel additive. The molecule also bears structural resemblance to ethanol, dimethyl ether, ethyl amine, and dimethyl amine.\textsuperscript{26} Several investigations have described its decomposition, combustion, ignition and flame characteristics.\textsuperscript{26,28-33}

Accordingly, the present work focuses on experimental and theoretical aspects of initiation of thermal decomposition of morpholine, as a model for oxygen and nitrogen-containing compounds present in real biomass fuel, exposed to NO\textsubscript{x}-laden atmosphere. Our results offer insights into the low-temperature nitration reactions that govern the interaction of biomass with NO\textsubscript{x}. The conclusions drawn from the present work apply equally to herbaceous, woody and/or chaff biomass.
7.2. Applied Methodologies

7.2.1. Materials and experimental setup

Figure 7.1 provides a schematic representation of the experimental setup in which a digital syringe pump delivered the reactant fuel (morpholine; TCI, purity > 99.0 %, 2.6 – 1.4 μL/min) into the preheated combined stream of helium, NO\textsubscript{x} and oxygen gases flowing through the system at combined rates of between 730 and 390 mL/min (at STP). The concentration of morpholine in the diluted stream amounted to 1000 ppm on molar basis. An electrically heated three-zone horizontal split furnace accommodated the quartz reactor tube, and ensured a well-defined isothermal reaction zone (cf. Figure 7.1). The current experimental rig represents a typical bench-scale flow-through tubular-reactor system employed in similar gas-phase kinetic studies\textsuperscript{34-38}. The reactor operated at nominal Reynolds numbers of 7.8 (at 300 °C) – 2.8 (at 800 °C), indicating a laminar flow regime with an average hydrodynamic entry length of approximately 0.9 % of the total reaction zone (300 mm). We maintained NO\textsubscript{x} concentration at 620 ppm (600 ppm of NO and 20 ppm of NO\textsubscript{2}), adjusting the flow rate of O\textsubscript{2} to maintain the fuel-oxygen equivalence ratio $\Phi$ of 1.25 (i.e., moderately fuel rich condition, also corresponds to oxygen-fuel equivalent ratio $\lambda = 0.8$) as per the following stoichiometric reaction:

$$C_4H_9NO + 5.75O_2 = 4CO_2 + 4.5H_2O + 0.5N_2$$  \hspace{1cm} (7.1)

We maintained a constant residence time of 1.0 s in the reaction zone, at ambient pressure of 1.01 bar, by regulating the flowrate. Charles’ temperature-volume relationship served to adjust the gas flow rates metered by the mass flow controllers (MFC, operated at the room
temperature) but preheated just before the reactor entry. Similarly, we employed a mass balance to convert the flow rate of the fuel needed for the predefined concentration at isothermal reaction temperature, into the corresponding set-values at room temperature. The relatively small volume of the annual space of zones 1 and 3 (Figure 7.1) makes a minor contribution to the overall reaction in the system. The volume of the preheating and cooling-down zones amounts to 4% of the reaction zone.

Fourier transform infrared (FTIR) spectroscopy facilitated online monitoring of product species exiting the tubular reactor. The setup incorporated an electrically heated transfer line (3.175 mm ID × 300 mm) linking the reactor to a small volume (100 mL) 2.4 m path-length online gas sampling cell (Pike) placed inside the FTIR compartment. The spectrometer averaged 64 accumulated scans per spectrum at 1 cm⁻¹ resolution. Both the sample line and the sampling cell operated at 140 °C, to avoid the condensation of volatile products prior and during the analysis.

Figure 7.1. Schematic representation of experiment rig. Symbol “T” denotes thermocouples.
7.2.2. **Computational methods**

Gaussian 09 suite of programs\(^{39}\) served to study the structures of reacting species, transition states, reaction products, as well as the dynamics and energetics of the nitration reactions themselves. The complete-basis-set CBS-QB3\(^{40}\) composite method afforded all structural optimisations, reaction enthalpies, as well as vibrational frequencies, using the tight convergence criteria and rigid-rotor/harmonic-oscillator approximations. In agreement with previous studies,\(^{30,33}\) the adopted computational method offers an accurate evaluation of thermochemical properties of all species studied herein. The accuracy limit of the computational basis set (CBS-QB3) usually settles within the mean absolute deviation of 6 kJ/mol from experimental values of gas-phase enthalpy.\(^{41-45}\) To confirm this, we have computed the absolute mean error to be 4.5 kJ/mol for bond dissociation enthalpies (BDH) of selected nitrogenated heterocyclic compounds (Table 7.1). Furthermore, the reported exothermicity of O\(_2\) addition to \(o\)-morphyl (152 kJ/mol) and, \(m\)-morphyl (136 kJ/mol) concur with the literature values of 148 and 136 kJ/mol, respectively.\(^{32}\)
Table 7.1. Comparison of the calculated CBS-QB3 BDH with the literature values for selected heterocyclic hydrocarbons. Bracketed values in italics correspond to the results an alternative high-level composite G4 method. The second last column assembles the experimental estimates obtained from photoacoustic calorimetry (PAC), acidity–oxidation potential measurements (AOP) and shock tube (ST) techniques, as well as one computational value calculated at the G2(MP2) level of theory.

<table>
<thead>
<tr>
<th>Heterocyclic species</th>
<th>Homolytic BDH reaction</th>
<th>Calculated CBS-QB3 and G4 BDH (kJ/mol)</th>
<th>Experimental and theoretical BDH (kJ/mol)</th>
<th>Absolute error (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morpholine</td>
<td></td>
<td>393.8 (386.6)</td>
<td>393.3 (46,47) PAC</td>
<td>0.5 (6.7)</td>
</tr>
<tr>
<td>Piperidine</td>
<td></td>
<td>377.1 (371.0)</td>
<td>384.9±8.4 PAC</td>
<td>7.8 (13.9)</td>
</tr>
<tr>
<td>Pyrrolidine</td>
<td></td>
<td>381.9 (376.0)</td>
<td>385.0±10.0 PAC</td>
<td>3.1 (9.0)</td>
</tr>
<tr>
<td>Pyrrole</td>
<td></td>
<td>451.1 (444.3)</td>
<td>N/A (48) N/A</td>
<td>8.9 (0.9)</td>
</tr>
</tbody>
</table>

Mean absolute error

4.5 (5.6)
7.3. Results and Discussion

7.3.1. Effect of NO\textsubscript{x} on ignition temperature of morpholine

As illustrated in Figure 7.2, the IR spectrum of vaporised morpholine (e.g. at 300 °C) contains CH\textsubscript{2} stretches (2840 – 2955 cm\textsuperscript{-1}), CH\textsubscript{2} scissors (1455 cm\textsuperscript{-1}), CH\textsubscript{2} wagging (1321 cm\textsuperscript{-1}), and oxazines signatures of C-O-C symmetric stretches (1237 cm\textsuperscript{-1}, 1062 cm\textsuperscript{-1}), asymmetric C-N-C stretching (1320 cm\textsuperscript{-1}) and aromatic N-H wag (712 cm\textsuperscript{-1}). Previous studies on thermal decomposition of morpholine\textsuperscript{28-33} have demonstrated the vulnerability of the heterocyclic ring that readily opens up into linear adducts via homolytic cleavages and/or β-scissions at elevated temperatures. Hence, we selected one of the aromatic group frequencies at 1132 cm\textsuperscript{-1} to compute the fuel conversion, as indicated in Equation 7.2:

\[
X = \left[ \frac{Abs_{i} - Abs_{T}}{Abs_{i}} \right] \times 100 \% \tag{7.2}
\]

where \(Abs_{i}\) denotes the initial concentration (proportional to absorbance value at 1132 cm\textsuperscript{-1}) at the reactor inlet, and \(Abs_{T}\) stands for the concentration of the fuel at the reactor outlet. This band represents a characteristic vibration of morpholine that does not appear in any of the product species.
Figure 7.2. IR spectrum of vaporised morpholine. I: CH$_2$ stretches (2840 – 2955 cm$^{-1}$), II: CH$_2$ scissors (1455 cm$^{-1}$), III: CH$_2$ wagging (1321 cm$^{-1}$), IV: oxazines signatures of C-O-C symmetric stretches (1237 cm$^{-1}$, 1062 cm$^{-1}$), V: asymmetric C-N-C stretches (1320 cm$^{-1}$), VI: aromatic N-H wag (712 cm$^{-1}$), and VII: selected group frequency (1132 cm$^{-1}$).

Figures 7.3a, 7.3b, 7.3c, and 7.3d depict the IR profiles in He, He-NO$_x$, He-O$_2$, and He-O$_2$-NO$_x$, respectively. The additional low-temperature peaks (1755 – 1960 cm$^{-1}$) appearing in experiments for He-NO$_x$ and He-O$_2$-NO$_x$ bath gases correspond to NO. The figures elucidate the structural identities of the products exiting the reactor. At relatively low temperatures (denoted by black-coloured spectra), the fuel remains unchanged, i.e., no detectable chemical addition, decomposition, or isomerisation reactions occur. However, as the operating temperature increases, morpholine converts into acetylene (C$_2$H$_2$), ethylene (C$_2$H$_4$), formaldehyde (CH$_2$O), methane (CH$_4$), carbon monoxide (CO), carbon dioxide (CO$_2$), hydrogen cyanide (HCN) and ammonia NH$_3$, depending on the composition of the inlet gas mixture (indicated in red in Fig. 7.3). NO$_x$ concentration of 620 ppm, selected for experiments, represents that of untreated diesel engine exhausts.
Figure 7.3. IR profile of morpholine decomposition at different temperatures, in He (a), He-NO\textsubscript{x} (b), He-O\textsubscript{2} (c) and He-O\textsubscript{2}-NO\textsubscript{x} (d) atmospheres. Black coloured spectra correspond to morpholine, with functional identities as described in the text of the chapter. Red coloured spectra indicate obvious conversion to product species.

Figure 7.4 plots the fuel conversion, as well as the extrapolated onset ignition temperatures for all experiments. The presence of NO\textsubscript{x} inhibits the decomposition of morpholine under pyrolytic conditions. Under oxidative environment (i.e., in presence of O\textsubscript{2}), NO\textsubscript{x} reduces the ignition temperature by 150 °C, i.e., from 500 °C to 350 °C. The trend is similar to that experienced in other types of fuels\textsuperscript{4,5,7-10,34-36}. For instance, Bendtsen et al.\textsuperscript{4} reported that the presence of NO or NO\textsubscript{2} lowered the onset temperature for oxidation of methane (CH\textsubscript{4}) by 250 °C, at shorter residence time of 200 ms. This implies that, with an adequate heat/ignition source, NO\textsubscript{x} can initiate premature atmospheric combustion of biomass residues. The present measurements indicate that, safe operation of wood-working plants requires avoiding trace concentration of NO\textsubscript{x} within the vicinity of dust-prone areas. This can be facilitated by proper (and separate) venting of engine exhausts.
7.3.2. Initial steps in nitration of morpholine

The initial reaction of NO/NO₂ with biomass produces nitro and nitro species (Equations 7.3 and 7.4) which then decompose to generate two new radical species RO· and NO₂/NO₃. The latter, chain-branching reactions, underpin the sensitising effect of NO/NO₂. Equation 7.5 expresses the biomolecular O-abstraction.⁷

\[
\begin{align*}
R· + NO & \rightarrow RNO \\
R· + NO₂ & \rightarrow RNO₂ \\
R· + NO₂ & \rightarrow RO· + NO
\end{align*}
\]
Oxidative environments allow the biomolecular H-abstraction by triplet oxygen to form HO$_2$ radicals (see Figure 7.5a), opening channels for the formation of peroxyl adducts (Reaction 7.6), an important combustion intermediates.$^{50-54}$ Reactions 7.7 and 7.8 describe the subsequent interaction of oxides of nitrogen with the peroxyl radicals.

$$R^* + O_2 \rightarrow ROO^*$$  \hspace{1cm} (7.6)

$$ROO^* + NO \rightarrow RO^* + NO_2$$  \hspace{1cm} (7.7)

$$ROO^* + NO_2 \Leftrightarrow ROONO_2$$  \hspace{1cm} (7.8)

The thermal stability of peroxynitrate (RO$_2$NO$_2$) depends on the chemical nature of the R backbone.$^{55,56}$ It can dissociate back into peroxyl adduct, or preferably form alkoxy radical via Reaction 7.9.$^{57}$

$$ROONO_2 \rightarrow RO^* + NO_3$$  \hspace{1cm} (7.9)

Previous studies$^{35,38}$ described the importance of low temperature chemistry in understanding the sensitisation effect of NO$_x$ during oxidation and ignition of hydrocarbons. In fact, these calculations confirmed that, modelled results remain incomplete, as well as insensitive (to the effect of NO$_x$) without the inclusion of the low-temperature initiation in the overall mechanism. Work is underway in our laboratory to produce a kinetic mechanism describing the initiation reaction responsible for the enhanced ignition of morpholine by NO/NO$_x$.

In the present context, initial decomposition of morpholine involves abstraction and direct dissociation (under pyrolytic condition) of H atom and formation of three morphyl radicals, namely, $o$-morphyl, $m$-morphyl and $p$-morphyl, depending on the relative position of the
radical site to the oxazine O atom. Figure 7.5 illustrates the enthalpies ($\Delta_r H^o_{298}$) of these reactions, and of the barrierless addition of molecular (triplet) oxygen.

**Figure 7.5.** Radical initiation of morpholine decomposition by H-abstraction (a) and H-dissociation (b) and formation of peroxy adducts. Reaction enthalpies ($\Delta_r H^o_{298}$) and Gibbs energies ($\Delta_r G^o_{298}$, in bold and italic) are reported in kJ/mol at 298.15 K (25 °C).

HO$_2$ radical remains highly stable at low temperatures. However, NO reacts with HO$_2$ according to Reactions 7.10,\textsuperscript{58-60} generating OH, an active propagating radical sustaining the oxidation process. Reactions 7.11 \textsuperscript{61,62} and 7.12 \textsuperscript{63,64} illustrate the interaction of NO$_2$ with HO$_2$. The nitrous acid (HNO$_2$) also dissociates and/or reacts with H/O radicals to form OH species.

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 & k(T) = 3.5 \times 10^{-12} \text{ [cm}^3\text{/molecule s] } \exp(250/T) \\
\text{HO}_2 + \text{NO}_2 & \rightarrow \text{HO}_2\text{NO}_2 & k(T) = 2.1 \times 10^{-31} \text{ [cm}^6\text{/molecule}^2\text{s] } (T/298\text{ K})^{-3.1} \\
\text{HO}_2 + \text{NO}_2 & \rightarrow \text{HNO}_2 + \text{O}_2 & k(296\text{ K}) = 5.0 \times 10^{-16} \text{ [cm}^3\text{/molecule s]}
\end{align*}
\]
The appearance of radical sites (Figure 7.5) enables subsequent addition reactions. Figure 7.6 depicts the addition of NO/NO$_2$ to morphyl radicals under inert atmosphere, such as that of He-NO$_x$. These reactions proceed without a barrier, and lead to formation of C-nitroso and nitro species, respectively. The nitro products convert into more thermodynamically stable tautomers (i.e., aci forms) by migration of $\alpha$-H atom (i.e., from the ipso carbon atom) to the nitro group. The nitroso and nitro compounds, except for nitromethane, are highly stable,$^{65,66}$ and this explains why we observe no reduction to the onset temperature of decomposition of morpholine under the He-NO$_x$ atmosphere. Along the same line of inquiry, Venkatesh et al. $^{67}$ also reported higher inert decomposition temperatures for 2- and 4-nitroimidazoles, relatively to that of imidazole. The authors have demonstrated that, the underlying Arrhenius constants remain relatively large for the nitro compounds.

**Figure 7.6.** Pyrolytic nitration of morpholine with NO$_x$. Reaction enthalpies ($\Delta_r H^{\circ}_{298}$) and Gibbs energies ($\Delta_r G^{\circ}_{298}$, in bold and italic) are reported in kJ/mol at 298.15 K (25 °C). The reversibility signs indicate the preferred reaction direction based on thermodynamic stabilities.
Figure 7.7. Oxidative nitration of morpholine with NO$_x$. Reaction enthalpies ($\Delta H^\circ_{298}$) and Gibbs energies ($\Delta G^\circ_{298}$, in bold and italic) are reported in kJ/mol at 298.15 K (25 °C).

Bracketed digit implies corresponding trans conformation.

In presence of O$_2$, hydrocarbons degrade along the peroxy (ROO-) corridor$^{50,51,68}$ into oxidation products, such as aldehydes, epoxides, oxetanes, ketones and hydroxyl, with the first step often involving the isomerisation (ROO- → ·R’OOH). However, under NO$_x$-containing atmosphere (e.g. He-O$_2$-NO$_x$), as shown in Figure 7.7, NO/NO$_2$ attaches to the outer oxygen atom of peroxy species, leading to formation of unstable organic peroxynitrites and peroxynitrates, respectively. The addition channels release considerable amount of energy. The heat feedback from the exothermicity of these reactions compensates the endothermicity of reactions of Figure 7.4, sustaining the ignition process. Analogous reactions constitute the major sink for ROO- in urban areas with high levels of NO$_x$ concentration.$^{69-71}$ From a kinetic viewpoint, considering the typical rate parameters for the addition of NO/NO$_2$ to peroxy species,$^{72,73}$ and the representative NO$_x$ level (i.e., ca 620 ppm), the bimolecular addition reactions predominate over unimolecular isomerisation of ROO- adducts.
7.4. Conclusions

This chapter presented new results from experimental measurements and theoretical calculations on the ignition of a representative biomass surrogate, due to sensitising effect of NO$_x$. Approximately 620 ppm of NO$_x$ reduces the ignition temperature of morpholine by 150 °C under a characteristic fuel-rich condition. The formation of organic nitrites and nitrates plays an important role in decreasing the ignition temperature of fuel in NO$_x$-laden oxidative environments, but has negligible contributions in pyrolytic decompositions. The addition reactions exhibit significant exothermicity. Further studies at varying fuel-oxygen equivalence ratio, and NO$_x$ concentrations will help elucidate the limit of the sensitising effect. Measurements of the ignition induction time involving actual biomass should provide further insights into this behaviour. We recommend other experimental parameters for assessing the risk of biomass ignition, e.g., thermogravimetrically-derived apparent activation energy ($E_a$) and the temperature of maximum rate of weight loss ($T_{MWL}$).$^{20,22,23,74}$ The thermochemical parameters of low-temperature intermediates identified herein will facilitate the development of an improved reaction mechanism.

7.5. References


CHAPTER 7 — Enhanced Ignition of Biomass in Presence of NOx


CHAPTER 8

Paper VI: Experimental Study on Thermal Reaction of Modelled Biofuel (Morpholine) with NO\textsubscript{x}

Oluwoye, I.; Dlugogorski, B. Z.; Gore, J.; Altarawneh, M. Manuscript in preparation as an extension of Chapter 7.

The chapter inspects the thermal interaction of NO\textsubscript{x} with biomass fuels. It focuses on high-temperature reaction of biofuel surrogate (morpholine) with NO\textsubscript{x}, elucidating the N-conversion profiles, and NO\textsubscript{x}-reduction efficiency as compared to conventional hydrocarbon fuels...
8.0. Abstract

This chapter investigates the thermal reaction of a biomass surrogate (morpholine), with oxides of nitrogen (NO$_x$). At conditions pertinent to industrial applications, we synergistically employed experimental and analytical techniques to explore the effect of NO$_x$ on the pyrolytic and oxidative thermal decomposition of morpholine. A laboratory-scale tubular laminar-flow reactor enabled a flexible optimisation of reaction parameters within the temperature range of 300 °C to 1100 °C at different helium/oxygen/NO$_x$ reactive mixtures. Fourier transform infrared (FTIR) spectroscopy, NO$_x$ chemiluminescence analysis and gas chromatography (μGC) supported the assessment of major gas products as well as the N-conversion profiles. The results indicate that, the presence of NO$_x$ lowers the ignition temperature of the fuel via nitration processes. Furthermore, at high temperature, above 800 °C, the fuel effectively convert NO$_x$ (ca 80 %) via HCN/NH$_3$ oxidation channel, depending on the abundance of O$_2$ in the system. These findings shed light on biomass-NO$_x$ interactions occurring in various industrial processes, such as interaction of reactive nitrogen species with biomass residues during thermal firing of solid fuels, and particularly, in fuel stagging technology utilising biomass as the major reburn fuel.
8.1. Introduction

Practical interaction of biofuel and nitrogen oxides (NO\textsubscript{x}, mainly NO and NO\textsubscript{2}) occurs in several industrial thermal processes. For instance, a broad assessment of biomass co-firing and combustion framework reveals various NO\textsubscript{x} formation channels, categorically grouped as the fuel, the thermal, and the prompt mechanisms. These channels serve as an active platform for the NO\textsubscript{x} species (and its precursors) to react with volatile hydrocarbons, as well as the parent biofuel. Such reactions can occur homogeneously within the gas-phase entities, and in form of heterogeneous reaction with solid fuel residues.\textsuperscript{1-3}

Furthermore, reburning technology serves in mitigating NO\textsubscript{x} formation during thermal utilisation of solid fuels in combustion plants. The process basically involves the use of secondary fuels (in a reburning zone) to reduce the NO\textsubscript{x} produced in a slightly lean-fuel condition (primary zone) to intermediate nitrogenous species and molecular nitrogen (N\textsubscript{2}).\textsuperscript{4-7} Among other alternatives, it has been proven that the injection of organic-based materials such as wood, straw, rice husk, bio-oil, sewage sludge, and carbonised municipal solid waste effectively supports the reduction of NO\textsubscript{x} formation in this kind of combustion-modification technology.\textsuperscript{8-17} Thus, it is essential to further understand the fundamental parameters underpinning the thermal decomposition of biomass/biofuel in reactive NO\textsubscript{x} atmospheres, in terms of product selectivity and NO\textsubscript{x} conversion efficiency.

The complex nature of biomass necessitates the use of representative model compounds in understanding the conversion of nitrogen species during combustion and pyrolysis of biomass-derived fuels. This includes hetero-element compounds, also known as surrogates, embodying N- and O-functionalities within their structural entities.\textsuperscript{3,18} Morpholine (C\textsubscript{4}H\textsubscript{9}NO, 1-oxa-4-aza-
cyclohexane) has been revealed as an excellent surrogate candidate for an oxygenated and nitrogen-containing biofuel compound due to its unique structure and wide industrial applications.\textsuperscript{18} The molecule bears structural resemblances to ethanol, dimethyl ether, ethyl amine, as well as dimethyl amine, and it is widely used as an impregnating agent for fruit, cardboard, and paper, and as a fuel additive.\textsuperscript{18} Its N-, C-, and O-content correspond to that revealed by ultimate analysis of typical biomass feedstocks. Several studies have described its decomposition, combustion, ignition and flame characteristics.\textsuperscript{18-24}

To this end, the present chapter focuses on experimental aspects of high-temperature decomposition of morpholine, as a model for oxygenated nitrogen-containing compounds present in the real biomass fuel, in different NO\textsubscript{x}-laden atmospheres. As it furnished knowledge to the conversion of fuel-N in excess NO\textsubscript{x} conditions, it also aims to provide insight into the interaction of biomass with NO\textsubscript{x} ensuing during thermal energy recovery from biofuels, and in fuel reburning technology utilising herbaceous, woody and/or chaff biomass as the secondary reburn fuel. In addition, it can also help describe the effect of NO\textsubscript{x}, arising from detonation of ammonium nitrate explosives, on the ignition of lignocellulosic materials in open-cut mines.

8.2. Applied Methodologies

8.2.1. Materials and experimental apparatus

We obtained the morpholine chemical from commercial source (TCI, purity > 99.0\%). Figure 8.1 presents a schematic representation of the experimental apparatus in which a digital syringe
pump delivered the reactant fuel (2.6 – 1.1 μL/min) into the preheated dilute stream of helium/NOx/oxygen running through the reactor at combined rates of between 730 and 305 mL/min, at standard temperature and pressure (STP). The concentration of morpholine in the diluted stream amounted to 1000 ppm on molar basis. An electrically heated three-zone horizontal split furnace accommodated the quartz reactor tube, and ensured a well-defined isothermal regime bracket a temperature range of 300 °C and 1100 °C. The use of helium (99.999 %) as primary dilution gas allowed quantitative measurement of N2 formation. The reactor operated at nominal Reynolds numbers of 7.8 (at 300 °C) – 1.8 (at 1100 °C), indicating a laminar flow regime with an average hydrodynamic entry length of approximately 0.9 % of the total reaction zone (300 mm). The NOx concentration remained constant at 620 ppm (600 ppm of NO and 20 ppm of NO2). During oxidative experimental conditions, we adjusted the O2 concentration to deliver the fuel-oxygen equivalence ratio Φ of 1.25 (i.e., moderately fuel rich condition) as per the following stoichiometric reaction:

\[
\text{C}_4\text{H}_9\text{NO} + 5.75\text{O}_2 = 4\text{CO}_2 + 4.5\text{H}_2\text{O} + 0.5\text{N}_2
\]  

(8.1)

We set a residence time of 1.0 s in the reaction zone at ambient pressure of 1.01 bar. The reaction time corresponds to the average residence time in a practical reburning zone and a typical experimental set-value in study of combustion of cyclic compounds.4,6 Furthermore, we employed Charles’ temperature-volume relationships to adjust the gas flow rates metered by the mass flow controllers (MFC, operated at the room temperature) but preheated just before the reactor. Similarly, we employed a mass balance to convert the flow rate of the fuel needed for the predefined concentration at isothermal reaction temperature, into the corresponding set-values at room temperature. Due to the relatively small volume (4 % of the reaction zone) of the annual preheating space of zone 1 (Figure 8.1), we conclude that the annual volume has
negligible contribution in the system. The products exit into various assemblages designed for appropriate sampling and quantitation.

Figure 8.1. Schematic representation of experiment setup. Symbol “T” denotes thermocouples.

8.2.2. Product sampling and analyses

As illustrated in Figure 8.1, gaseous product analyses involved three parallel stages. Firstly, FTIR spectroscopy (Perkin Elmer) facilitated online monitoring of product species exiting the tubular reactor. The setup incorporated an electrically heated transfer line (3.175 mm ID × 300 mm) linking the reactor to a small volume (100 mL) 2.4 m path-length online gas sampling cell
(Pike) placed inside the FTIR compartment. The spectrometer averaged 64 accumulated scans per spectrum at 1 cm\(^{-1}\) resolution. Both the sample line and the sampling cell operated at 140 °C, to avoid the condensation of product volatiles prior and during the analysis. Furthermore, the chemiluminescence NO\(_x\) analyser (Thermo Scientific model 42i-HL) monitored the concentration of NO and NO\(_2\). Finally, the use of μGC (Agilent 490 micro-gas chromatography, 20 m MolSieve-5A column, heated injection) assisted N\(_2\) quantitation. The train of three impingers consisting of glass units filled with standardised 0.1 M H\(_2\)SO\(_4\), 1 M NaOH, and orange silica gel removed any contaminant species, e.g. ammonia and H\(_2\)O that could damage the GC column.

It must be noted that the spectroscopy technique\(^{25-27}\) has proven highly instrumental in the detection and quantitation of the aforementioned gaseous nitrogenous compounds. QASoft database (Infrared Analysis, Inc., Anaheim, CA) enabled semi-quantitation of the species by their characteristic IR bands listed in Table 8.1. The accuracy of the measurements is highly dependent upon the tolerance of the absorption coefficients of the reference spectra. This is estimated to be within ±5 % in the QASoft library.
### Table 8.1. List of gaseous species studied, and their selected unique IR frequencies.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Chemical formula</th>
<th>Analysis frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
<td>3019 – 3011</td>
</tr>
<tr>
<td>Ethyne (acetylene)</td>
<td>C(_2)H(_2)</td>
<td>729 (Q-branch)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C(_2)H(_4)</td>
<td>950 (Q-branch)</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CH(_2)O</td>
<td>1747 – 1743</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>2171 – 2157</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO(_2)</td>
<td>2420 – 2207</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>HCN</td>
<td>712 (Q-branch)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH(_3)</td>
<td>1047 – 1045</td>
</tr>
<tr>
<td>Nitric oxide(^1)</td>
<td>NO</td>
<td>1901 – 1900</td>
</tr>
</tbody>
</table>

\(^1\)Concentration confirmed by chemiluminescence NO\(_x\) analyser.

### 8.3. Results and Discussion

#### 8.3.1. Overview of ignition temperatures

We selected one of the group frequencies of morpholine (at 1132 cm\(^{-1}\)) for quantitative monitoring of the fuel conversion according to Equation 8.2:

\[
\alpha = \left[ \frac{Abs_i - Abs_T}{Abs_i} \right] \times 100 \% \tag{8.2}
\]

where \(Abs_i\) represents the initial concentration (proportional to absorbance value at 1132 cm\(^{-1}\)) before the thermal reaction, and \(Abs_T\) denotes the concentration of the fuel at the outlet of the...
reactor. Figure 8.2 presents the conversion of morpholine under different gas-stream conditions. It is evident that, the presence of NO$_x$ plays a crucial role in the ignition features of the fuel. This can be attributed to the distinct way in which NO$_x$ reacts with hydrocarbons, by accelerating their oxidation process.$^{28,29}$ NO$_x$ enhances the ignition of organic fuels in a process generally referred to as sensitisation via nitration reactions.$^{30-34}$ The addition of NO and/or NO$_2$ to fuel-oxygen systems, significantly alters the overall kinetics by turning the usual chain-terminating steps of formation of peroxyl (RO$_2$) radicals into a chain-propagating step.$^{29}$

![Graph](image_url)

**Figure 8.2.** Conversion of morpholine at the outlet of the reactor, under different reaction atmospheres. The extrapolated onset ignition temperatures amount to 581 °C, 613 °C, 494 °C, and 356 °C for He, He-NO$_x$, He-O$_2$, and He-O$_2$-NO$_x$ conditions, respectively.

As shown in Chapter 7, the sensitisation of morpholine develops within the chain-propagating NO/NO$_2$ cycle.$^{35}$ In the absence of oxygen, addition of NO$_x$ species to morphyl radicals (formed as the result of H abstraction from the ortho, meta and para sites of morpholine) operates via Equations 8.3 and 8.4:
R· + NO → RNO

R· + NO₂ → RNO₂

Furthermore, the presence of O₂ allows the formation of peroxo (ROO⁻) adducts and hydroperoxyl radical (HO₂)₃⁶-⁴⁰ that subsequently interact with NOₓ in following reactions:

R· + O₂ → ROO⁻

ROO⁻ + NO → RO⁻ + NO₂

ROO⁻ + NO₂ ⇌ ROONO₂ → RO⁻ + NO₃

HO₂ + NO → OH + NO₂

HO₂ + NO₂ → HNO₂ + O₂

8.3.2. Quantitative analysis of N-conversion at high temperatures

This section focuses on the formation of N-products, but also describes the consumption of some major hydrocarbons species. As shown in Figure 8.3, the principal reaction products include acetylene (C₂H₂), ethylene (C₂H₄), methane (CH₄), formaldehyde (CH₂O), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen cyanide (HCN), ammonia (NH₃) and nitric oxide (NO), depending on the composition of the inlet gas mixture.
Figure 8.3. Annotated IR spectra of product species during decomposition of morpholine at different temperatures, in He (a), He-NO (b), He-O2 (c) and He-O2-NO (d) atmospheres.

Figure 8.4 plots the measured product species’ profiles over a wide range of temperatures, at different atmospheres. The influence of these variables has been studied by measuring the output concentration of the reaction zone of different nitrogenous species (NO, HCN, NH3), carbonaceous species (in particular CO and CO2), and low molecular weight hydrocarbons (C2H2, C2H4, CH4 and CH2O).
Figure 8.4. Mole-fraction profile of selected product species during decomposition of morpholine at different temperatures, in He (a), He-NO\(_x\) (b), He-O\(_2\) (c) and He-O\(_2\)-NO\(_x\) (d) atmospheres. The initial concentration of morpholine amounted to 1000 ppm; reaction residence time equalled 1 s; and initial concentration of NO in (b) and (d) corresponded to 600 ppm.

Previous studies have describe the pyrolysis and oxidative decomposition of morpholine.\(^{19-24}\) The interaction of NO relies on the action of the hydrocarbon radicals/fragments originated from the decomposition and/or oxidation of the hydrocarbon fuel. Radicals from the morpholine fuel can originate by two important mechanisms: oxidation and/or thermal decomposition. The thermal decomposition (i.e., pyrolysis) of hydrocarbons occurs at high temperatures. However, the presence of oxygen initiates relatively low-temperature
degradation. Hence, CH radicals from the oxidation of hydrocarbons will be responsible for the NO conversion at low temperaturs. Comparing Figures 8.4a and 8.4b, the presence of NO somewhat reduced the concentration of the low molecular weight hydrocarbons. The observed trend of CH2O match that of previous studies on its formation and destruction in exhaust system of gas engines. The characteristic temperature regime for the oxidation (Figures 8.4c and 8.4d) of the morpholine to CO and CO2 at similar reaction times differs appreciably between the stream compositions. In the case of He-O2, the CO forms in relatively lower concentration (at a temperature of approximately 500 °C) and rapidly increases to peak at around 750 °C. Above this temperature, the CO concentration remains approximately constant. He-O2-NO results in higher CO concentration. However, the oxidation of CO to CO2 is generally favoured at higher temperatures.

The concentrations of NH3 and fuel-NOx appear negligible in all the experiments as compared to the concentration of the total reactive nitrogenous species. Figure 8.4 shows that, the interaction of NO with hydrocarbon radical increases HCN concentration. The subsequent role of HCN remain highly dependent of the conditions that exist in the reaction zone. Reaction of HCN with O2 recycled it into NO, while the total NOx (He-NOx + fuel NOx) converts it into molecular nitrogen. The peak concentration of HCN, in oxidative conditions, also appears at around 750 °C, after which it decreases significantly to its valley at higher temperatures. Hence, the presence of oxygen in the reaction zone promotes the conversion of the intermediate nitrogenous species to N2, since it is responsible for an increase of the radical pool.
8.3.3. Comments on NO reduction and formation of N2

Equation 8.10 defines the transient NO conversion in terms of NO concentrations at the inlet of the reactor $[\text{NO}]_{i,\text{inlet}}$, the outlet of the reactor $[\text{NO}]_{i,\text{outlet}}$, and the diminutive NO concentration in the decomposition product of morpholine $[\text{NO}]_{i,\text{fuel}}$. The subscript $i$ denotes the gas composition, i.e., with and without O$_2$.

$$\text{NO conversion} = \frac{[\text{NO}]_{i,\text{inlet}} - ([\text{NO}]_{i,\text{outlet}} - [\text{NO}]_{i,\text{fuel}})}{[\text{NO}]_{i,\text{inlet}}} \times 100 \% \quad (8.10)$$

Figure 8.5a depicts the NO conversion efficiency of morpholine in pyrolytic and oxidative ($\Phi = 1.25$) conditions. The results show that, HCN, formed from fuel-N transformation and as an intermediate, plays crucial role in overall conversion of NO. The oxygen content of morpholine also allowed low temperature NO$_x$ reduction during pyrolytic conditions, in agreement with former experimental study on furan (C$_4$H$_4$O).\textsuperscript{45} The maximum NO conversion amounts to approximately 83 %, at 900 °C, after which it decreases to 80 % due to the activity of the reduction scheme at higher temperatures.\textsuperscript{4,5,44}


**Figure 8.5.** NO\textsubscript{x} conversion efficiency of morpholine (a), and N\textsubscript{2} formation (b) in thermal decomposition the fuel at different experimental conditions. Initial morpholine and NO concentration are 1000 ppm and 600 ppm, respectively.

Likewise, the trend of N\textsubscript{2} formation in Figure 8.5b confirms the overall reduction of NO\textsubscript{x}. The NO\textsubscript{x} reduction efficiency of morpholine show an analogy with literature data. For example, Biomass fuels such as wood, straw, rice husk, bio-oil, sewage sludge, and carbonised municipal solid waste provide effective means of reducing NO\textsubscript{x} formation (50 – 75 %) in combustion systems.\textsuperscript{8-17,46,47} In comparison to other conventional hydrocarbon fuels, morpholine reduction efficiency surpasses that of acetylene, ethylene, ethane, natural gas, methane, and biogas.\textsuperscript{46,48-51} However similar reduction efficiency had been reported for pyrolysate fragments of coal and waste polymers.\textsuperscript{13,52-57}

**8.4. Conclusions**

This chapter provided experimental measurements of thermal reaction of morpholine with NO\textsubscript{x}, showing the ensuing products at different temperatures and gas stream compositions. The reported NO\textsubscript{x} reduction efficiency elucidate morpholine as a good biomass surrogate with
efficiency values similar to that of actual biomass residues. In presence of oxygen, the effectiveness of morpholine as NO reduction reagent compares well to that of C₃H₆. For conventional hydrocarbon fuels, it has been demonstrated that the NO reduction efficiency follows the order of C₂H₂ > C₃H₆ > CH₄.⁴⁸,⁵⁸ Hence, morpholine should be more effective than CH₄, and better preferred to C₂H₂ that usually leads to the formation of NO₂ rather than the more desirable N₂ or HCN. Finally, the O-content of morpholine permits NOₓ reduction at relatively lower temperature, making it an excellent reburning fuel in O₂-deficient environment.

8.5. References


CHAPTER 9

Conclusion and Recommendations

This chapter concludes the entire dissertation, and lays out some significant recommendations for future studies...
9.1. Conclusion

This thesis contributed towards finding sustainable solutions that could alleviate the unprecedented increasing anthropogenic emission of \( \text{NO}_x \), serving to mitigate adverse effects on the environment. \( \text{NO}_x \) discharge surfaces as a result of lack of adequate mitigation techniques in power plants, oxidation of reactive nitrogen species (e.g. \( \text{NH}_3 \) from the Haber-Bosch system) in chemical and agricultural processes, combustion activities involving untreated fossil, bushfires and mining operations, especially large open cut mines that require significant movement of materials (including overburden) by diesel-driven excavators and trucks. To tackle this problem, supplementary-fuel reburning remains a viable technological approach through which an overall decrease in \( \text{NO}_x \) emission of about 50 – 85% can be attained. Therefore, the present research work explored new sustainable technologies for reducing industrially formed \( \text{NO}_x \), based on biomass and recycled plastics, particularly for applications relevant to blasting of mining-grade ammonium nitrate (AN) based high-energy materials.

The thesis reviewed the global \( \text{NO}_x \) formation channels in light of consequential environmental impacts. It quantitates \( \text{NO}_x \) emissions during detonation of ammonium nitrate blasting agents with valid explanation of different underlying mechanisms, and assesses their contributions with respect to the global nitrogen budget. The estimated \( \text{NO}_x \) emission from AN-based explosives amounts to 0.05 Tg (i.e., 5\times10^4 t) N per annum, in comparison to the total rate of \( \text{NO}_x \) of 41.3\times10^6 t N/y, entering the environment from all anthropogenic sources. Although small on a global scale, these emissions involve concentrated discharges characterised by \( \text{NO}_x \) concentration in the order of 500 ppm. With respect to the current World Health Organisation air quality guidelines, the typical concentrations of \( \text{NO}_x \) in post-blast clouds exceeds the safe
limits by around 30 to 3000 times. Furthermore, the chemical reactivity of blasting-related NO$_x$ in the presence of other atmospheric substances, produces secondary pollutants. For instance, the mineral particles and fugitive dusts synchronously present in post-blast fumes can easily facilitate the oxidation of NO$_x$, contributing to atmospheric formation of nitrate aerosols.

The computational studies analysed the primary initiation reactions occurring during aggressive low-temperature oxidation of PE. In the NO$_x$-laden atmosphere, formation of diverse nitrogen-containing species ultimately accompanies the free-radical processes in solid PE. Nitroso and nitroalkyl species appear as a result of respective addition of NO and NO$_2$ molecule to a carbon radical site in PE chain. It has been noted that, the availability of neighbouring chemical functional groups alters the thermodynamic and kinetic properties of the reactions. Concerted elimination of HNO and HONO from nitroso- and nitroadducts, respectively, requires moderate activation energies, compared with unimolecular tautomerisation of the adducts. However, the presence of molecular oxygen induces the formation of peroxy species, that subsequently bond with NO and/or NO$_2$, thereby serving as a potential source of organic nitrites and nitrates. In comparison with previous studies that substantiated the addition of nitrogen oxides to solid polymer resins, the current investigation delivered the concrete thermodynamic evidence of such events, and provides the reaction channels describing the fate of consequential nitrogenous species. On this note, the calculated thermochemical and kinetic parameters offer an improved understanding of the polymer-gas reactions, and present insights into similar reaction sequences in other crystalline polyolefins.

Although fuel reburning constitutes an effective technologies for NO$_x$ reduction, practical applications are sometimes influenced by cost. This study has shown that, recycled plastics offer a relatively effective and cheaper means of reburning. An extensive experimental study
characterised the behaviour of waste polymer pellets under pyrolytic low-temperature (<600 °C) conditions. In particular, TGA-based analyses measured the thermal decomposition pattern of neat and recycled polymer samples under controlled and representative NOx environments, and developed a mechanistic insight explaining the formation of initial product. The limiting initial step of thermal decomposition involved H-dissociation to form an alkyl radical. NOx then acts in the further decomposition steps by adding to the radical sites to form double bonds in the oligomer chain, eliminating HNO or HONO, respectively. The well-established isoconversional method constructed the kinetic parameters showing conversion dependent apparent activation energies of 135 kJ/mol – 226 kJ/mol, and 188 kJ/mol – 268 kJ/mol, for neat and recycled PE, respectively. Also, the so-called compensation effect accounted for the natural logarithmic of the pre-exponential factors ln (A/min^-1 ) ranging between ca 19 – 35 and 28 – 41, in same order., depending on the PE conversion in the experimental interval between 5 and 95 %. The typical NOx reduction efficiency of pyrolysing fragments of waste PE amounted 80 %, hence the injection of waste PE into a reburning zone of combustors may significantly reduce the emission of NOx. The gathered kinetic data on the thermal decomposition of PE in a NOx atmosphere, in the absence of mass transfer limitation will serve to predict the polymer conversion (in NOx atmosphere) at elevated temperatures, to plan the practical vertically-entrained drop-tube experiments.

In agreement with principles of green chemistry and engineering, thermal reduction of NOx by recycled polyethylene assigns value to minimisation of solid wastes by providing an ecofriendly exit route for excess plastic wastes in our society. Moreover, its application to NOx formation in combustion plants promotes the growth of innocuous degradation products, thereby enhancing low-emission technologies and effective energy recovery from polymeric waste materials. Furthermore, the scientific approach can be optimised to deploy waste
polyethylene in bulk ammonium nitrate/fuel oil (ANFO)/emulsions explosive mixtures, so as to mitigate the NO\textsubscript{x} formation during detonation of nitrate-based explosives, for example, in mining operations. Application of waste PE in reducing NO\textsubscript{x} emissions from detonation of AN explosives relies strongly on the heating condition. Since explosions are generally characterised with flash heating rates of the order of 10,000 K/s, defragmentation of PE at such conditions results in relatively low molecular weight hydrocarbon, which are expected to further enhance the reduction efficiency of the system.

The second wing of this dissertation investigated the thermal interaction of biomass with NO\textsubscript{x}. In which, low-temperature tubular reactor experiments gauged the sensitising role of NO\textsubscript{x} on biomass ignition/combustion. We concluded that, this has an unintended consequence of degrading the safety of organic dust-producing plants. For a representative fuel-rich condition (\( \Phi = 1.25 \)), the concentration of NO\textsubscript{x} as small as 0.06 % lowers the ignition temperature of morpholine by 150 °C, i.e., from approximately 500 °C to 350 °C. The formation of organic nitrites and nitrates, as the result of addition of NO\textsubscript{x} species to morphyl and peroxyl radicals, plays an important role in decreasing the ignition temperature of biomass fuel in NO\textsubscript{x}-laden oxidative environments, but has negligible contributions in pyrolytic decompositions. Other contributing factor includes the reaction of NO\textsubscript{x} with low-temperature hydroperoxyl radical leading to the formation of active OH species that also propagate the ignition process. The present measurements indicate that, safe operation of wood-working plants requires avoiding trace concentration of NO\textsubscript{x} within the vicinity of dust-prone areas. This can be facilitated by proper (and separate) venting of engine exhausts.

Furthermore, our high temperature tubular reactor arrangements elucidated morpholine as a good biomass surrogate with NO\textsubscript{x} reduction efficiency values similar to that of actual biomass
residues at conditions pertinent to industrial applications. The principal reaction products include acetylene ($C_2H_2$), ethylene ($C_2H_4$), methane ($CH_4$), formaldehyde ($CH_2O$), carbon monoxide ($CO$), carbon dioxide ($CO_2$), hydrogen cyanide ($HCN$), ammonia ($NH_3$) and nitric oxide ($NO$), depending on the composition of the reaction mixture. In presence of oxygen, the effectiveness of morpholine as NO reduction reagent compares well to that of propene ($C_3H_6$). For conventional hydrocarbon fuels, it has been demonstrated that the NO reduction efficiency follows the order of $C_2H_2 > C_3H_6 > CH_4$. Hence, morpholine should be more effective than $CH_4$, and better preferred to $C_2H_2$ that usually leads to the formation of $NO_2$ rather than the more desirable $N_2$ or HCN intermediate. Finally, the O-content of morpholine permits NO$_x$ reduction at relatively lower temperature, making it an excellent reburning fuel in O$_2$-deficient environment. These findings shed light on biomass-NO$_x$ interactions occurring in various industrial processes, such as interaction of reactive nitrogen species with biomass residues during thermal firing of solid fuels, and particularly, in fuel staging technology utilising biomass as the major reburn fuel. In addition, it also help describe the effect of NO$_x$, arising from detonation of ammonium nitrate explosives, on the ignition of lignocellulosic materials in open-cut mines.

**9.2. Recommendations**

The scientific studies embodied in this dissertation had led to a number of intriguing research questions. The following paragraphs discuss some suggestion for potential future work.

We have identified the possibility of the formation of secondary pollutants (nitrate aerosols) as a result of atmospheric nitration of the mineral particles and fugitive dusts synchronously
present in post-blast fumes. Therefore, development of new sampling methodologies should include the environmental monitoring of such species from blasting activities. Lightweight remote-controlled drone-sampling instrumentation, as well as surface sampling, could facilitate the measurements of nitrate aerosols, as well as other pollutants including supplementary Nr species (e.g. HNO₃, NH₃, and N₂O), hydrocarbons, nitrogenated analogues of dioxins and secondary contaminants such as peroxyacyl nitrates (PAN). Understanding the mechanism of the formation and the survival of these pollutants in detonation of heavy AN explosives is crucial to achieve sustainable mining activities, as are further testing of OW emulsions and bulking agents, and generating new knowledge on the exact mechanism of deflagration that involves the surface burning of AN particles.

The low-temperature non-isothermal measurements in Chapter 6 gathered the kinetic data on the thermal decomposition of PE in a NOₓ atmosphere, in the absence of mass transfer limitation, serving to predict the polymer conversion (in NOₓ atmosphere) at elevated temperatures. The preliminary quantitative NOₓ reduction efficiency concluded that, the injection of waste PE into a reburning zone of combustors may significantly reduce the emission of NOₓ. Reburning of NOₓ in practical combustors usually occurs in a temperature window between 1000 °C and 1200 °C. Therefore, a change of the reaction mechanism may occur at those high temperatures. Hence, we recommend a subsequent study to address the high-temperature isothermal and flash-particle heating conditions in drop-tube experiments, with valid economic analysis. This will reveal possible effects of the presence of oxygen and mass transfer on the reaction of NOₓ with PE pyrolysates under realistic reburning temperatures (i.e., 1000 – 1200 °C). Along the same line of interest, the suitability of other complex-chain polymer should be investigated, with respective to their NOₓ reduction efficiencies, and most importantly, the likelihood of the formation of ecotoxic nitrogenated analogue dioxins, such as
diphenylamine (DPA), carbazole, phenoxazine, and phenazine. Figure 9.1 illustrates a proposed laboratory-scale vertically-entrained drop-tube experimental setup for high-temperature studies.

**Figure 9.1.** Proposed laboratory-scaled drop tube furnace reactor, equipped with variable speed DC motor that allows the adjustment of feeding rate of pulverised polymer sample, being carried downstream by inert (helium) gas. The symbol “T” refers to thermocouples.

Finally, regarding the sensitising role of NO\textsubscript{x} in biomass ignition, further studies at varying fuel-oxygen equivalence ratio, and NO\textsubscript{x} concentrations would help elucidate the limit of the sensitising effect. Measurements of the ignition induction time involving actual biomass should provide further insights into this behaviour. We recommend other experimental parameters for assessing the risk of biomass ignition, e.g., thermogravimetrically-derived apparent activation energy (\(E_a\)) and the temperature of maximum rate of weight loss (\(T_{MWL}\)).
Finally, confirmation of interactions between fuel-N and NO\textsubscript{x}, (e.g., by experiments involving isotopically labelled $^{15}$NO\textsubscript{x}), and quantitative measurements of nitro- and nitroso-adducts (e.g., by employing Tenax cartridge in thermal desorption unit, coupled with gas chromatography/mass spectrometry setup) would constitute a significant advance in our understanding of N-selectivity in high-temperature thermal reaction of morpholine with NO\textsubscript{x}. Future work should assemble a complete reaction mechanism, validated by the experimental conversion profile of morpholine, and the quantitative data on the formation of product species.
CHAPTER 10

Supplementary Document

This section provides the necessary supporting information for some of the chapters included in this thesis...
Appendix I: Supporting Information for Chapter 6

S6.1. Characterisation Techniques

- Fourier transform infrared (FTIR) spectroscopy: This method elucidated the major functional groups present in the polymer samples. We applied Agilent Cary 670 equipped with attenuated total reflectance (ATR) accessory. Prior to analyses, samples were cryogenically pulverised to achieve reproducible measurements. The FTIR recorded the spectra at 4 cm\(^{-1}\) resolution, with accumulation of 32 scans per spectrum. The bands at 2916 cm\(^{-1}\), 2848 cm\(^{-1}\), 1470 cm\(^{-1}\) and 718 cm\(^{-1}\) correspond to CH\(_2\) asymmetric stretch, CH\(_2\) symmetric stretch, CH\(_2\) scissors and CH\(_2\) rock modes, respectively.

- Carbon-hydrogen-nitrogen-sulfur (CHNS) analysis: CHNS elemental analyser provided a means for rapid determination of carbon, hydrogen, nitrogen and sulfur in the organic polymer matrices. Pulverised samples were fed into the pre-calibrated instrument (EuroVector EA3000) under dry helium and O\(_2\) purge, and the combustion furnace operated at approximately 1100 °C. The reactor functioned in a dynamic flash combustion mode, and contained both the oxidation zone represented by tungsten oxide and copper wired reduction zone. Two repeated runs resulted in 86.24 and 86.10 wt. % for C, 14.25 and 14.20 wt. % for H, 0.00 and 0.00 wt. % for N as well as 0.00 and 0.00 wt. % for S.

- Ion chromatography: Dissolved sample was injected into DX-120 anion chromatograph. The result showed no trace of halogens, except for Cl present at < 0.1 %.
• Inductively coupled plasma emission spectroscopy (ICP-OES): Varian 715-ES ICP OES (University of Newcastle, Australia) served to measure the metal concentration in the sample. About 140 mg of the recycled PE were digested in microwave, and then transferred via Varian SPS 3 sample preparation system for analyses. High-purity ICP multi-element standard solution containing different metal cations in 2.0 % HNO₃ facilitated the necessary calibration.

• High temperature size exclusion chromatography (HT-SEC) in TCB: We performed HT-SEC analyses using a Viscotek system (from Malvern Instruments) equipped with three columns (Polefin 300 mm × 8 mm I. D. from Polymer Standards Service, porosity of 1000 Å, 100 000 Å and 1 000 000 Å). Sample solutions 200 µL in volume, with a concentration of 5 mg/mL, were eluted in 1,2,4-trichlorobenzene (1,2,4 TCB) with a flow rate of 1 mL/min at 150 °C. The mobile phase was stabilised with 2,6-di(tert-butyl)-4-methylphenol (200 mg/L). Online detection was performed with a differential refractive index detector and a dual light scattering detector (LALS and RALS) for absolute molar mass measurement. The OmniSEC 5.02 software facilitated the calculation of the SEC parameters.
Figure S6.1. High temperature size exclusion chromatogram of neat (a) and recycled (b) PE, and estimated molecular parameters. Symbols are explained in the caption to Table 6.1 in the main manuscript. Ret. Vol. denotes the corresponding peak retention volume.

During recycling processes, the polymer chains of the recycled PE break, with chains of higher molar mass displaying more probability of breaking. Therefore, the molecular mass distributions (MMD) of the recycled PE reveals lower dispersity $I_p$ values. Other contributions to MMD include:

(a) Melting point: Our DSC result (Figure S6.2) showed that, the recycled PE displays a higher melting point (123 °C) with broader peak, compared to the neat sample (116 °C). Higher melting point suggests larger-molecular-mass, i.e., a higher $M_p$ value. However, when $M_p$ varies only by around 18 kg/mol (our case here), there are no effects on melting temperature.\(^1\)\(^2\) Rather, the structure of the PE samples induces this behaviour. The intrinsic viscosity of the recycled PE (1.9 dL/g) exceeds that of the neat PE (1.1 dL/g).
This means that, the neat PE is more branched (short-chain branched LDPE) than the recycled PE. More branches imply lower melting point and lower intrinsic viscosity.³

(b) Delayed decomposition of recycled PE: As shown in Figure S6.3, the relative decomposition of the recycled PE is somewhat delayed due to the presence of more linear chain. Neat PE is more branched, hence, its decomposition occurs earlier at the relatively more sensitive branching-carbon sites. The alpha and beta scission mechanisms around such carbons, during thermal degradation, have been well explained by Haney et al.⁴

S6.2. Assessments of Calibration and Repeatability of TGA Experiments

Prior to experiments, we carefully calibrated the instrument. The reference standards for the mass and temperature calibration were selected according to the desired experimental range. Table S6.1 lists the measured values as compared to the expected correspondence. The table also provides the calculated percent error.

<table>
<thead>
<tr>
<th>Weight (mg)</th>
<th>Expected</th>
<th>Measured¹</th>
<th>Measured²</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified mass</td>
<td>54.37</td>
<td>54.59</td>
<td>54.36</td>
<td>7.36 × 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Expected</th>
<th>Measured¹</th>
<th>Measured²</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>156.60</td>
<td>156.21</td>
<td>156.45</td>
<td>9.58 × 10⁻²</td>
</tr>
<tr>
<td>Zinc</td>
<td>419.47</td>
<td>417.12</td>
<td>419.20</td>
<td>6.44 × 10⁻²</td>
</tr>
<tr>
<td>Aluminium</td>
<td>660.10</td>
<td>662.67</td>
<td>660.30</td>
<td>3.03 × 10⁻²</td>
</tr>
</tbody>
</table>
During the entire duration of the study, we acquired replicate runs randomly at different dates in order to check for the instrumental drift and reproducibility of experimental data. Figure S6.2 shows a typical result of the thermal analysis, and Figure S6.3 depicts the selective reproducibility of three experimental runs under different conditions (Table S6.2).

**Table S6.2.** Experimental conditions for the thermogravimetry analyses

<table>
<thead>
<tr>
<th>Runs</th>
<th>Sample</th>
<th>Treatment</th>
<th>Scan condition</th>
<th>Purge rate</th>
<th>Crucible</th>
<th>Sample mass ((m))</th>
<th>Buoyancy effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td>Neat</td>
<td>Sliced</td>
<td>25 – 620 °C</td>
<td>80 mL/min</td>
<td>Alumina; uncovered</td>
<td>5≤(m)≤5.4 mg</td>
<td>Corrected</td>
</tr>
<tr>
<td></td>
<td>PE</td>
<td>(-400 μm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>Recycled</td>
<td>Sliced</td>
<td>25 – 620 °C</td>
<td>80 mL/min</td>
<td>Alumina; uncovered</td>
<td>5≤(m)≤5.4 mg</td>
<td>Corrected</td>
</tr>
<tr>
<td></td>
<td>PE</td>
<td>(-400 μm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The recycled PE melts over a broader temperature range at 123 °C, a value corresponding to neither low density nor high density polyethylene. This suggests a mixture of different PE types in the recycled polymers.

Also, the presence of elemental residues delays the thermal decomposition events.

As compared to the relative neat sample, the variation in the DSC plot (especially after the decomposition regime) can be attributed to the mixed heat capacity ($C_p$) contribution of the residual metals.

The empirical content of neat PE in the recycled sample can be estimated as:

$$\%_{\text{neat}} = \frac{G(\%) \text{of recycled PE}}{G(\%) \text{ of neat PE}}$$

Thus, the recycled PE sample contains ≈ 98.32 % of pure PE content.

**Figure S6.2.** Thermal characterisation of recycled PE sample at nominal heating rate of 10 K/min under inert (argon) purge. The DSC signal of the simultaneous thermal analysers (STA) cannot facilitate accurate quantitative analysis of thermodynamic properties. The recycled PE sample dissolved completely in toluene (at 80 °C), indicating the absence of cross-linked polymer.
Figure S6.3. Reproducibility of TGA results.
S6.3. Monotonic Behaviour of Heated PE Samples

Under non-isothermal conditions, in which a sample heats at a constant rate, the decomposition pattern often relies on the applied heating rate. The conversion of the tested PE samples exhibits an increasing monotonic behaviour with increasing temperature. This means that, NOx is not incorporated permanently in the reacting solid, consistently with the mechanism of Figure 6.5, included in the body of the article. Figure S6.4 portrays the dependence of $\alpha$ on temperature. Herein, $\alpha$ refers to the fractional conversion of polymer sample, and it represents the normalised form of mass loss data from the thermogravimetry analysis:

$$\alpha = \frac{m_i - m_t}{m_i - m_f}$$

(S6.1)

in terms of initial mass before the thermal analysis $m_i$, instantaneous mass at any temperature/time $m_t$, and the final mass after the entire decomposition process $m_f$. 


Figure S6.4. The monotonic behaviour of samples studied in different purge atmospheres.

S6.4. Derivation of Cited Equations and the Compensation Effect

S6.4.1. Isoconversional method

In solid-state reactions, the rate can be described in terms of three main variables: the temperature \( T \), the conversion \( \alpha \) (already defined), and the pressure \( P \), according to the following equation:
\[ \frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad (S6.2) \]

Ignoring the pressure dependence \( h(P) \), the process rate hinges solely on the temperature function \( k(T) \) and the conversion parameter \( f(\alpha) \), otherwise termed as the reaction model. Model-free or isoconversional methods rely on the assumption that, at constant conversion, the reaction rate remains function of temperature only. Furthermore, Arrhenius equation expresses the temperature dependence:

\[ k(T) = A \exp \left( -\frac{E}{RT} \right) \quad (S6.3) \]

where the kinetic parameters \( A \) and \( E \) respectively represent the pre-exponential factor and the activation energy, while \( R \) denotes the universal gas constant. In a non-isothermal experiment, when temperature changes linearly with time, the heating rate \( \beta \) can be expressed as:

\[ \beta = \frac{dT}{dt} = \text{const} \quad (S6.4) \]

Combination of equations (S6.2), (S6.3) and (S6.4) yields:

\[ \frac{\beta d\alpha}{dT} = A \exp \left( -\frac{E}{RT} \right) f(\alpha) \quad (S6.5) \]

Rearranging, and integrating, one obtains:
\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} \exp\left(-\frac{E}{RT}\right) dT = \frac{A}{\beta} I(E,T) \tag{S6.6}
\]

where \( g(\alpha) \) is the integral form of the reaction model, and the corresponding limits of integration, \( \alpha \) and \( T_\alpha \) follow from Figure S6.3. The integration of Equation (S6.6) eliminates the need for a priori knowledge of the reaction model. However, the temperature integral \( I(E,T) \) has no analytical solution. Consequently, according to Vyazovkin approach,\(^5,6\) for a series of runs conducted at different heating rates, the \( E_\alpha \) can be determined by minimisation of the following function:

\[
\phi(E_\alpha) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \tag{S6.7}
\]

In this work, we experimented with four temperature ramps (5, 10, 15 and 20 K/min), repeating each run three times. The activation energy can be estimated at any particular value of \( \alpha \), by finding \( E_\alpha \) for which the function attains a global minimum. The subscripts \( i \) and \( j \) represent integer numbers of different experiments performed under varying heating programs, i.e., \( i \) equals 1 – 3 for replicates, and \( j \) corresponds to 1 – 4 for heating rates. The temperature integral, also known as the Arrhenius integral, corresponds to:

\[
I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(-\frac{E}{RT}\right) dT \tag{S6.8}
\]

The presence of systematic errors (as a result of the integral approximation) can be eliminated by performing the integration over a small segment of temperature:
\[ I(E_\alpha, T_\alpha) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left( -\frac{E}{RT} \right) dT \]  
\[ \text{(S6.9)} \]

In which \( \alpha \) varies from \( 2\Delta\alpha \) to \( 1-\Delta\alpha \), with a step of \( \Delta\alpha = (m+1)^{-1} \), and \( m \) defines the number of equidistant values of \( \alpha \) selected for the analysis. We applied the fourth order Senum and Yang approximation\(^7\) for the integral function, and minimised Equation S6.7 by employing the solver tool in Microsoft excel. The minimisation task has been repeated for each value of \( \alpha \) to obtain the dependency of \( E_\alpha \) on \( \alpha \).

Alternatively, owing to other forms of numerical approximation of \( I(E,T) \), there have been various standard integral isoconversional methods, in the form:

\[ \ln \left( \frac{\beta_i}{T^{B}_{\alpha,i}} \right) = \text{Const} - C \left( \frac{E_\alpha}{RT_{\alpha,i}} \right) \]  
\[ \text{(S6.10)} \]

The subscript \( i \) represents an integer number for the four heating ramps; i.e., \( i = 1 \) to 4. According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC),\(^6\) the use of \( B = 2 \) and \( C = 1 \) (as in the Kissinger-Akahira-Sunose method; KAS\(^8\)) offers a significant improvement in the accuracy of activation energy values. Also, setting \( B = 1.92 \) and \( C = 1.0008 \) (as proposed in Starink’s approach\(^9\)) provides further improvement in accuracy. Thus, at constant \( \alpha \), the plot of \( \ln \beta_i / T^{B}_{\alpha,i} \) against \( 1/T_{\alpha,i} \) yields a straight line whose slope (Figure S6.4) can conveniently be used to evaluate \( E_\alpha \) values.

Another accurate integral method was proposed by Lyon\(^{10}\).
\[ E_{\alpha,i} = -R \left( \frac{d \ln \beta}{d(1/T_{\alpha,i})} + 2T_{\alpha,i} \right) \]  

(S6.11)

with the differential term representing the slope of \( \ln \beta \) versus reciprocal temperature \( 1/T_{\alpha} \) (Figure S6.5)

In order to estimate the errors in the activation energies, we applied combinations of different replicates of the heating rates. The resulting values (at a specific conversion) then served to compute the standard errors.
Figure S6.5. Parametric plots of $\ln \beta_i/T_{\alpha,i}^\beta$ against $1/T_{\alpha,i}$ for the thermal decomposition of PE samples in He-NO$_x$. 
S6.4.2 Compensation effect

The compensation effect relies on the determination of several kinetic triplets, namely, $E_i$, $A_i$ and $f_i(\alpha)$ or $g_i(\alpha)$ over a wide range of reaction models$^6$. This can easily be achieved by employing the integral analogue of equation (S6.5), i.e., Coats-Redfern equation$^{11}$

$$\ln \left[ \frac{g_i(\alpha)}{T_i^2} \right] = \ln \left( \frac{A_i R}{\beta E_i} \right) - \frac{E_i}{RT_i}$$  \hspace{1cm} (S6.12)

For a constant heating rate, the slope and y-intercept of the plot of $\ln g(\alpha)/T_i^2$ against $1/T_i$ enable the evaluation of $E_i$ and $A_i$. Table S6.3 lists the appropriate $g(\alpha)$ function for different models.

Table S6.3. Set of kinetic models used in describing thermal decomposition of solids

<table>
<thead>
<tr>
<th>$i$</th>
<th>Reaction model</th>
<th>Code</th>
<th>$f(\alpha)$</th>
<th>$g(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power law</td>
<td>P4</td>
<td>$4\alpha^{1/4}$</td>
<td>$\alpha^{1/4}$</td>
</tr>
<tr>
<td>2</td>
<td>Power law</td>
<td>P3</td>
<td>$3\alpha^{2/3}$</td>
<td>$\alpha^{1/3}$</td>
</tr>
<tr>
<td>3</td>
<td>Power law</td>
<td>P2</td>
<td>$2\alpha^{1/2}$</td>
<td>$\alpha^{1/2}$</td>
</tr>
<tr>
<td>4</td>
<td>Power law</td>
<td>P2/3</td>
<td>$2/3\alpha^{1/2}$</td>
<td>$\alpha^{3/2}$</td>
</tr>
<tr>
<td>5</td>
<td>One-dimensional diffusion</td>
<td>D1</td>
<td>$1/2\alpha^{1}$</td>
<td>$\alpha^{2}$</td>
</tr>
<tr>
<td>6</td>
<td>Mampel (first order)</td>
<td>F1</td>
<td>$1-\alpha$</td>
<td>$-\ln(1-\alpha)$</td>
</tr>
<tr>
<td>7</td>
<td>Avrami-Erofeev</td>
<td>A4</td>
<td>$4(1-\alpha)[-\ln(1-\alpha)]^{1/4}$</td>
<td>$[-\ln(1-\alpha)]^{1/4}$</td>
</tr>
<tr>
<td>8</td>
<td>Avrami-Erofeev</td>
<td>A3</td>
<td>$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$</td>
<td>$[-\ln(1-\alpha)]^{2/3}$</td>
</tr>
<tr>
<td>9</td>
<td>Avrami-Erofeev</td>
<td>A2</td>
<td>$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
</tr>
<tr>
<td>10</td>
<td>Three-dimensional diffusion</td>
<td>D3</td>
<td>$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$</td>
<td>$[1-(1-\alpha)^{1/3}]^2$</td>
</tr>
<tr>
<td>11</td>
<td>Contracting sphere</td>
<td>R3</td>
<td>$3(1-\alpha)^{2/3}$</td>
<td>$1-(1-\alpha)^{1/3}$</td>
</tr>
<tr>
<td>12</td>
<td>Contracting cylinder</td>
<td>R2</td>
<td>$2(1-\alpha)^{1/2}$</td>
<td>$1-(1-\alpha)^{1/2}$</td>
</tr>
<tr>
<td>13</td>
<td>Two-dimensional diffusion</td>
<td>D2</td>
<td>$[-\ln(1-\alpha)]^{-1}$</td>
<td>$(1-\alpha)[\ln(1-\alpha)+\alpha$</td>
</tr>
<tr>
<td>14</td>
<td>Second order</td>
<td>F2</td>
<td>$(1-\alpha)^2$</td>
<td>$(1-\alpha)^{-1}$</td>
</tr>
</tbody>
</table>
For kinetic parameter associated with the models in Table S6.3, the plot of ln $A_i$ versus $E_i$ will also yield a straight line (see Figure S6.6), with slope $a$, and y-intercept $b$.

$$\ln A_\alpha = aE_\alpha + b$$  \hspace{1cm} (S6.13)

The substitution of isoconversional values of $E_\alpha$ allows the estimation of the dependence of ln $A_\alpha$ over the entire conversion $\alpha$. We stress that, theoretically, the compensation effect is not affected by heating rates. Thus, we have repeated the evaluation steps for two different heating rates (10 and 20 K/min), and confirmed similar values of the rate constant.
Figure S6.6. The compensation effect during thermal decomposition of PE samples in He-NO\textsubscript{x}. Each point and each boxed number on the graph correspond to the $i$th kinetic parameters, i.e., $\ln A_i$ and $E_i$ derived for different reaction models in Table S6.3. Shaded regions depict the range of experimental data. Models 6, 11 and 12 fall within the window of the experimental results. As our approach to determine $A$ is valid only for models described by a general formula of $f(\alpha) = (1-\alpha)^n$, the thermal decomposition of PE conforms with model 6 (Mampel, first order). Indeed, this model falls in the middle of both shaded regions.

S6.5. Complete Isoconversional Kinetic Data
Table S6.4. Kinetic constants for decomposition of neat PE sample in NO\textsubscript{x} according to isoconversional methods

| \(\alpha\) | \(E_\alpha\) isoconversional methods (kJ/mol) | Reported parameters |
|---|---|---|---|---|---|---|
|  | Numerical minimisation | KAS\textsuperscript{1} | Starink\textsuperscript{1} | Lyon\textsuperscript{1} | \(E_\alpha\)\textsuperscript{2} (kJ/mol) | Standard error | In (A/min\textsuperscript{-1}) | Standard error |
| 0.05 | 134.9 | 135.8 | 136.1 | 135.8 | 135.9 | ± 2.1 | 19.9 | ± 0.2 |
| 0.10 | 149.4 | 149.6 | 150.0 | 149.6 | 149.7 | ± 2.7 | 22.1 | ± 0.3 |
| 0.15 | 158.5 | 158.2 | 158.5 | 158.1 | 158.3 | ± 3.0 | 23.5 | ± 0.3 |
| 0.20 | 165.0 | 164.4 | 164.7 | 164.4 | 164.5 | ± 3.2 | 24.5 | ± 0.3 |
| 0.25 | 170.9 | 170.7 | 171.0 | 170.6 | 170.8 | ± 3.2 | 25.5 | ± 0.3 |
| 0.30 | 177.5 | 176.4 | 176.7 | 176.4 | 176.5 | ± 3.4 | 26.5 | ± 0.4 |
| 0.35 | 184.8 | 182.9 | 183.3 | 182.9 | 183.0 | ± 3.5 | 27.5 | ± 0.4 |
| 0.40 | 190.5 | 188.8 | 189.1 | 188.7 | 188.9 | ± 3.5 | 28.5 | ± 0.4 |
| 0.45 | 197.2 | 194.2 | 194.5 | 194.1 | 194.3 | ± 3.5 | 29.4 | ± 0.4 |
| 0.50 | 201.5 | 199.3 | 199.6 | 199.2 | 199.4 | ± 3.5 | 30.2 | ± 0.4 |
| 0.55 | 206.4 | 204.0 | 204.3 | 204.0 | 204.1 | ± 3.5 | 31.0 | ± 0.4 |
| 0.60 | 211.9 | 208.4 | 208.7 | 208.4 | 208.5 | ± 3.4 | 31.7 | ± 0.4 |
| 0.65 | 214.7 | 212.3 | 212.7 | 212.3 | 212.4 | ± 3.3 | 32.3 | ± 0.3 |
| 0.70 | 218.6 | 216.1 | 216.5 | 216.1 | 216.2 | ± 3.2 | 32.9 | ± 0.3 |
| 0.75 | 222.0 | 219.5 | 219.8 | 219.4 | 219.5 | ± 3.1 | 33.5 | ± 0.3 |
| 0.80 | 226.0 | 222.2 | 222.6 | 222.2 | 222.3 | ± 3.1 | 33.9 | ± 0.3 |
| 0.85 | 226.2 | 224.4 | 224.7 | 224.4 | 224.5 | ± 3.0 | 34.3 | ± 0.3 |
| 0.90 | 228.6 | 226.0 | 226.3 | 225.9 | 226.0 | ± 2.6 | 34.5 | ± 0.3 |
| 0.95 | 228.6 | 226.2 | 226.6 | 226.2 | 226.3 | ± 2.0 | 34.6 | ± 0.2 |

\textsuperscript{1} Average of three values, estimated from the results of three repeatable experimental runs at four heating rates.

\textsuperscript{2} Average of the four models; standard error based on the standard deviation from the population mean.
Table S6.5. Kinetic constants for decomposition of recycled PE sample in NOx according to isoconversional methods

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$E_{a,1}$ isoconversional methods (kJ/mol)</th>
<th>Reported parameters</th>
<th>$\log K$</th>
<th>Standard error</th>
<th>In (A/min)</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
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<td>188.1</td>
<td>188.1</td>
<td>188.4</td>
<td>188.0</td>
<td>188.1</td>
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<tr>
<td>0.10</td>
<td>Starink$^1$</td>
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<td>220.0</td>
<td>220.3</td>
<td>220.0</td>
<td>220.1</td>
</tr>
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<td>Lyon$^1$</td>
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<td>231.9</td>
<td>231.6</td>
<td>231.7</td>
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<td>238.1</td>
<td>238.4</td>
<td>238.1</td>
<td>238.2</td>
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<tr>
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<td>243.6</td>
<td>243.3</td>
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<tr>
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<td>272.6</td>
<td>272.3</td>
<td>272.4</td>
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<tr>
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<td>271.0</td>
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<td>270.7</td>
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<td>267.6</td>
<td>267.9</td>
<td>267.6</td>
<td>267.7</td>
</tr>
</tbody>
</table>

$^1$ Average of three values, estimated from the results of three repeatable experimental runs at four heating rates.

$^2$ Average of the four models; standard error based on the standard deviation from the population mean.
S6.6. Enlarged Time-Resolved FTIR Spectra

Figure S6.7. Time-resolved FTIR spectra acquired during thermal decomposition of neat PE in argon.

Figure S6.8. Time-resolved FTIR spectra acquired during thermal decomposition of neat PE in NOx.
Figure S6.9. Time-resolved FTIR spectra acquired during thermal decomposition of recycled PE in argon.

Figure S6.10. Time-resolved FTIR spectra acquired during thermal decomposition of recycled PE in NO$_x$. 
S6.7. Complete NO\textsubscript{x} Conversion Profile

The NO\textsubscript{x} analyser was pre-calibrated within the experimental range as shown below:

Table S6.6. Calibration of NO\textsubscript{x} analyser.

<table>
<thead>
<tr>
<th>Precision NO (ppm)</th>
<th>Precision NO\textsubscript{x} (ppm)</th>
<th>Measured NO (ppm)</th>
<th>Measured NO\textsubscript{x} (ppm)</th>
<th>Error (% FS)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
</tr>
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<td>2080</td>
<td>2030</td>
<td>2080</td>
<td>0.0</td>
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<tr>
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<td>1030</td>
<td>998</td>
<td>1030</td>
<td>-0.1</td>
</tr>
<tr>
<td>500</td>
<td>516</td>
<td>496</td>
<td>516</td>
<td>-0.2</td>
</tr>
<tr>
<td>250</td>
<td>258</td>
<td>244</td>
<td>258</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

Figure S6.11 depicts the concentration trend of NO and NO\textsubscript{x} (NO + NO\textsubscript{2}), and Figure S6.12 shows the instantaneous NO\textsubscript{x} conversion according to Equation S6.14.

\[
X = \frac{F_{\text{NO}_{\text{in}}}}{F_{\text{NO}_{\text{in}}}} \times 100 \% \quad (S6.14)
\]

\[
F_{\text{NO}_{\text{in}}} = [NO_{x_{\text{in}}}] \cdot Q_{\text{in}} \quad (S6.15)
\]

\[
F_{\text{NO}_{\text{x}_{\text{out}}}} = [NO_{x_{\text{out}}}] \cdot (Q_{\text{in}} + Q_{\text{volatile}}) \quad (S6.16)
\]

\(F_{\text{NO}_{\text{x}_{\text{in}}}}\) and \(F_{\text{NO}_{\text{x}_{\text{out}}}}\) represent the molar flows in terms of the NO\textsubscript{x} concentrations and gas flow rates entering \((Q_{\text{in}} = 80 \text{ mL/min at STP})\) and leaving the furnace, respectively. On the other hand, \(Q_{\text{volatile}}\) corresponds to the estimated dilution term due to generation of volatile products (from pyrolysing PE) in the furnace. Equation S6.17 yields the volumetric rate (in mL/min) of volatile formation.
\[
Q_{volatile} = \frac{\dot{m}}{\rho} = \frac{\dot{m}}{M_{ethylene}} \cdot \frac{RT}{P} \tag{S6.17}
\]

\(\rho\) denotes the average density of volatile species, taken as the density of ethylene for simplicity sake, while \(\dot{m}\) signifies the decomposition rate of PE (in mg/min) as obtained from derivative thermogravimetry data of neat (and recycled) PE decomposition in He-NO\(_x\). According to Equation S6.17, the maximum volumetric rate of volatile product of PE (at 10 K/min) amounts to 1.9 mL/min, i.e. approximately 2.4 % of the \(Q_{in}\).

**Figure S6.11.** Continuous NO\(_x\) concentration profile during thermal of PE samples in NO\(_x\) atmosphere.
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Figure S6.12. Percent NO₅ conversion during thermal of PE samples in NO₅ atmosphere.

S6.8. References


Appendix II: Supporting Information for Chapter 7 and 8

S7.1. Extrapolated Onset Ignition Temperatures

Figure S7.1. Conversion of morpholine at the outlet of the reactor, under different reaction atmospheres. The extrapolated onset ignition temperatures amount to 581 °C, 613 °C, 494 °C, and 356 °C for He, He-NO_x, He-O_2, and He-O_2-NO_x conditions, respectively.