Abbreviations

%N percentage nitrogen by mass

2-NDPA 2-Nitrodiphenylamine

AO atomic orbital

a.u. atomic units

B3LYP Becke, 3-parameter, Lee-Yang-Parr hybrid functional

BCP bonding critical point

CH$_3$CH$_3$ NC repeat unit with two $-$OCH$_3$ capping groups

CH$_3$OH NC repeat unit with $-$OCH$_3$ capping group on ring 1 and $-$OH group on ring 2

CCP cage critical point

CP critical point

DFT density functional theory

DSC differential scanning calorimetry

DOS degree of substitution

DPA diphenylamine

ELF electron localisation function

EM energetic materials

EN ethyl nitrate

ESP	electrostatic potential
G09	Gaussian 09 revision D.01
GM	genetically modified
GTO	Gaussian type orbitals
GView	Gauss View 5.0.8
HF	Hartree Fock
HMF	hydroxymethylfurfural
HOMO	highest occupied molecular orbital
IR	infra-red spectroscopy
LOL	localized orbital locator
MD	molecular dynamics
MEP	minimum energy path
MM	molecular mechanics
MMFF94	Merck molecular force field 94
MO	molecular orbital
MP2	Møller–Plesset perturbation theory with second order correction
MW	molecular weight
NC	nitrocellulose
NCP	nuclear critical point
NG	nitroglycerine
NMR	nuclear magnetic resonance spectroscopy
OHCH$_3$	NC repeat unit with $-$OH capping group on ring 1 and $-$OCH$_3$ group on ring 2

PCM	polarisable continuum model
PES	potential energy surface
PETN	pentaerythritol tetranitrate
PETRIN	pentaerythritol trinitrate
QM	quantum mechanics
QTAIM	quantum theory of atoms in molecules
RCP	ring critical point
SB59	1,4-bis(ethylamino)-9,10-anthraquinone dye
SCF	self-consistent field
SEM	scanning electron microscopy
SMD	solvation model based on density
S_N2	bi-molecular nucleophilic substitution reaction
STO	Slater type orbitals
TG	thermogravitmetric analysis
TS	transition state
UFF	universal force field
UV	ultraviolet
UVvis	ultraviolet–visible spectroscopy
ωB97X-D	ωB97X-D long-range corrected hybrid functional
ZPE	zero-point energy

Chapter 1

Introduction

1.1 A brief history of Nitrocellulose

NC, cellulose nitrate, or "guncotton" is a nitrated cellulose derivative (figure 1.1) that has been widely utilised in the manufacture of plastics, inks, propellant formulations and thin films since its discovery in 1833 by Henri Braconnot [1].
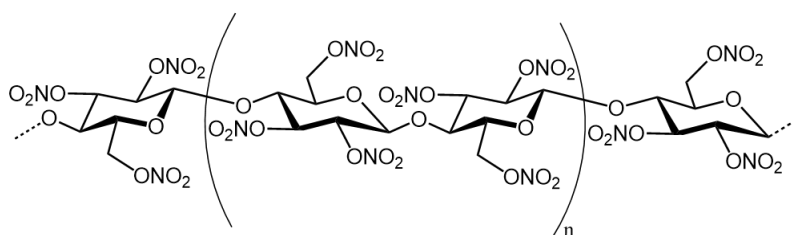

Figure 1.1: The structure of Nitrocellulose.

Cellulose is the primary component of plant cell walls and the most abundant polymer in nature [2, 3]. An example is cotton, which is almost entirely comprised of cellulose [4]. It can be considered an almost inexhaustible ingredient in manufacturing. As environmental concerns drive the shift towards renewable raw materials and carbon neutral industrial processes, interest and innovation in the use of bio-materials has also skyrocketed [5, 6, 7, 8, 9]. Bio-plastic products utilising thin films made of cellulose derivatives, such as Natureflex™ [10], have emerged in the consumer market offering attractive replacements to traditional crude-oil plastics (figure 1.2). These alternatives provide biodegradable food packing films, 3D printing elements, wound dressings and film-blown plastics, spanning almost the full range of current applications. Whilst the durability of cellulose-based products may not yet meet that of their plastic counterparts, they come with the key advantage of compostability. This facilitates their secondary use as an organic feedstock, such as in fertiliser for

Figure 1.2: Comparison of degradation times for Natureflex™ bioplastic against conventional plastic packaging, from The Mindful Chef blog [8].

agricultural applications, fostering a circular carbon economy [11].

It was found by Braconnot that when fibres of cellulose in the form of sawdust, cotton, linen and paper were treated with nitric acid, the product burned rapidly and in the absence of the thick black smoke that was characteristic of gunpowder of the era [12]. He named this material xyloidine [13]. In his Berlin laboratory in 1845, Dr. Schönbein serendipitously discovered that acid treated cotton wool burned violently, and was the first to obtain a stable product using a mixture of nitric and sulfuric acids [14]. He was granted a U.S. patent the following year, and variations of his techique are currently still used in the commercial manufacture of nitrocellulose (NC) [15, 16].

Subsequent progress in the synthesis of stable NC products followed this discovery:

1855 - George Audemars pulls a NC filament from solution of ether and alcohol [15].

1864 - Baron Lenk patents a method for producing "improved guncotton" [17].

1866 - British chemist Frederick Abel patents another method for manufacturing NC, this time removing impurities and generating a more stable product, establishing its commercial importance [18].

1868 - John Wesley Hyatt combines NC with camphor to produce one of the first plastics, celluloid. This is later used to make billiard balls, which were previously made from ivory [15].

1883 - Whilst working on an early version of the lightbulb, Joseph Swan develops a method of extruding nitrocellulose into filaments [15].

1884 - Paul Vielle invents the first NC-based smokeless gunpowder [13].

1.1.1 Applications

NC is commonly found in adhesives, paints and lacquer coatings [19, 20]. Since Schönbein's day, NC has seen applications in dynamite, artificial silks and printing inks. Reels of historical cinematographic film made from NC were notoriously flammable, banned on public transport, and permitted storage and use only within fire-proof projection boxes [21, 22, 23, 24]. Conservation efforts attempted to preserve these materials *via* cold storage or duplication onto more stable cellulose triacetate or polyester films. For heavily deteriorated film, destruction was recommended due to fire and safety hazards [25, 21]. Today, the information on NC films is preserved by digitisation [26].

Collodin, a solution of 6% NC in 70% ether and 24% ethanol [27], is used both in surgical dressings and in theatrical make-up. To create special effects, a non-flexible variety of colloidin is applied to skin, which puckers as the solvent evaporates, effectively creating the appearance of scarred tissue. NC thin films also perform an essential role in research. Tonkinson and Stillman produced a review on the merits of NC film in blotting practices, utilised as a microporous membranes in genomic experiments for decades [28, 29]. Finding that it could bind DNA-RNA duplexes in solution, the first application of NC in molecular biology was as a molecular sieve to separate DNA duplexes from free RNA. Later work exploited this property to study protein-DNA interactions [**?**].

Varieties of high percentage nitrogen by mass (%N) are used for their energetic properties, such as in rocket fuel and gun propellants. NC of above 12.5 %N is considered explosive (figure 1.3). The theoretical maximum level of nitration is 14.14 %N. This corresponds to a degree of substitution (DOS) of three, where each of the three free hydroxyl groups has been replaced by a nitrate ester (equation 1.1, figure 1.3). In practice, only a maximum of 13.6 - 13.8 %N (DOS=2.9) is routinely achieved [30, 31], though higher, unstable levels of nitration have been obtained at high temperatures [13].

$$\text{Degree of substitution (DOS)} = \frac{3.6 \times \text{nitrogen content (\%)}}{31.13 - \text{nitrogen content (\%)}} \qquad (1.1)$$

DOS values do not directly correlate to the exact level of nitration at each monomeric site due to the imprecision during the nitration reaction; the approximate %N corresponding to each level of nitration is given in table 1.1. A non-integer value for DOS indicates non-uniform nitration on individual glucopyranose rings throughout the polymer structure.
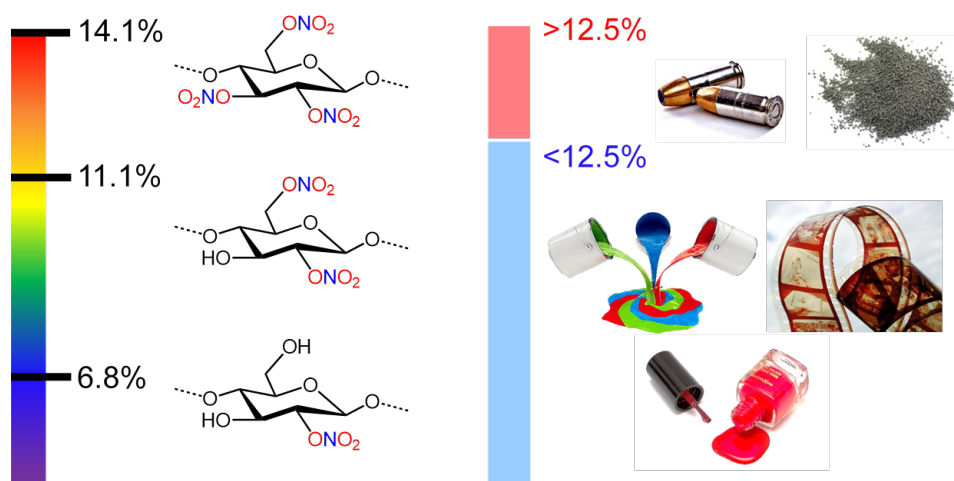
When NC is the only energetic component in an explosive mixture, it is termed a

Table 1.1: Degree of substitution (DOS) in NC and the corresponding percentage nitrogen by mass (%N).

DOS	%N	Description
1	6.76	Cellulose mononitrate
2	11.11	Cellulose dinitrate
3	14.14	Cellulose trinitrate

single-base propellant. NC mixtures with one or more energetic materials (EM) such as nitroglycerine (NG), where NG also acts as a plasticiser, are classed as double or triple-base propellants. Due to the degradation of NC over time, stabilisers are necessary to neutralise the decomposition products that facilitate further reactions.

The behaviour and ageing of NC within product formulations depends on the structure and degree of nitration of the material itself, in addition to the environmental and storage conditions, and interactions with any plasticisers and stabilisers in the product mixture.

Figure 1.3: Left: The percentage nitrogen by mass (%N) of NC corresponding to each degree of substitution (DOS).
Right: NC with lower levels of nitration play a role in the manufacture of paints and lacquer coatings, whilst >12.5%N is used in the production of explosives and propellants.

1.2   Synthesis and structure

Nitrocellulose is derived from the nitration of cellulose. Biological variation in cellulose has implications on the quality and properties of the NC produced. During synthesis, the backbone of cellulose is largely preserved [32, 33]. Wood pulp and cotton linters are two major sources of starting material for NC production; though more expensive, cotton linters are preferred for their uniformity. Cotton sources are usually reserved for the production

of military and industrial grade propellants, with pulps from softwoods used for manufacture of explosives used in blasting and mining operations [34]. A polysaccharide cellulose chain is comprised of glucose units linked via β-1,4-glycosidic bonds, resulting in the alternating orientation of individual monomers. This is then reflected in the synthesised NC structure (figure 1.4). A single strand of cellulose is estimated to contain between 100 - 200 glucose units, representing a molecular weight (MW) of 20,000-40,000 daltons [15]. Each monomeric repeat unit in the chain has three hydroxyl groups that form hydrogen bonds between groups on neighbouring strands. In ordered regions of the cellulose matrix, these hydrogen bonds allow the chains to arrange in a sheet or fibril structure.
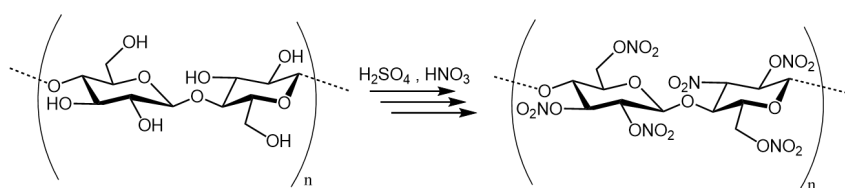

Figure 1.4: Cellulose is converted to NC by a mixture of nitric and sulfuric acids.

For the conversion of cellulose to NC, a common nitrating mixture of nitric and sulfuric acids is used to generate the nitronium ion (equation 1.2). The nitronium ion is attacked by the lone pair on the oxygen of the hydroxyl group on cellulose, leading to the formation of a nitrate ester (equation 1.3 and figure 1.5).

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^+ + H_2O \qquad (1.2)$$

$$R-OH + NO_2^+ + H_2O \longrightarrow R-ONO_2 + H_3O^+ \qquad (1.3)$$

Where R = Cellulosic backbone

Primary nitrates are those with one non-hydrogen moiety on the carbon, (additional to the nitrate linkage) with the remaining two bonds linked to hydrogens. Secondary nitrates are those where the nitrate carbon possess one bonded hydrogen atom, and two further non-
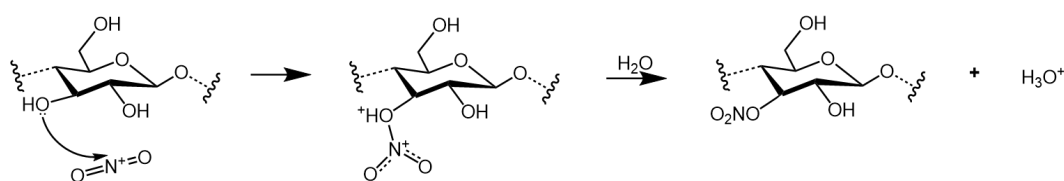

Figure 1.5: Nitration of cellulose by the nitronium ion.

hydrogen moieties. Carbon centres of tertiary nitrates possess no attached hydrogen, and are usually sterically hindered but as a result strongly stabilise the formation of carbocations, favouring mononucleic mechanistic pathways. When counting from the oxygen of the ring, fully nitrated NC posses a primary nitrate ester at carbon 6. Secondary nitrate esters are joined to the ring at carbon positions 2 and 3.

The IR and ^{13}C nuclear magnetic resonance spectroscopy (NMR) studies coupled with roentgenographs of the NC structure at different levels of nitration showed that the cellulose backbone becomes more ordered with accumulating levels of nitrogen [35]. Globular structures in bulk NC with 8 %N are converted to fibrils as the nitrogen content increased. A relatively high degree of ordering within the bulk is observed at 13%N, facilitating significant interaction between chains, contributing to increased hydrogen bonding. In the disordered regions of the structure the hydroxyl groups may be free or only weakly bonded, without a long-range hydrogen bonding network. Water may also more easily interact with these hydroxyl groups in the disordered region, introducing an increased susceptibility to hydrolysis within the chain. The oxygen in the glycosidic linkage between monomer units allows for rotation, introducing flexibility in the polymer chain via twisting and bending motions.

As in the case of its parent molecule cellulose, NC is largely insoluble in water, though recent studies have successfully synthesised a "high solubility" variety using unconventional cellulose feedstocks [36]. Due to the insolubility of cellulose esters in general, the addition of plasticisers are necessary to encourage malleability for processing [37]. The properties of a NC formulation therefore depend on extent of nitration, the molar mass, and crucially, the plasticiser level [38].

In addition to molecular and microstructural properties leading to variation in the decomposition of NC, it was shown by Wei *et al.* that the macroscopic bulk preparation of NC as soft fibres or as chips also changed the reactivity [39]. The soft fibre structure was found to be more easily ignited, possibly due to the less compact preparation leading to increased surface exposure to oxygen, higher porosity to reactants and easier penetration of the environmental effects, such as increased rate of heating due to lower density. This emphasises the holistic perspective that must be taken when evaluating the spectrum of factors and properties responsible for the decomposition behaviour of any given sample of NC.

1.3 Nitrocellulose degradation

Even under optimal storage conditions, NC undergoes slow decomposition over time. A detailed understanding of these mechanisms is imperative in the design of efficient and economical processes for NC disposal. Whilst many studies in the past century have shed light on the various decomposition schemes, a review of the literature reveals conflicting opinion on the general mechanisms of degradation. Most notably, a distinct lack of mechanistic detail hinders improvement of processing and storage treatments, or effective redirection of degradation products to more useful substances, such as plant fertiliser [40, 41].

Understanding of the mechanism is also crucial for control of the harmful materials released into the atmosphere as part of disposal or the ageing process. Traditional methods of disposal usually include incineration of waste NC (figure 1.6) [42]. In order to limit safety risks, propellants are often burned as an aqueous suspension. Specialised equipment (figure 1.7) allows sequential evaporation of water, drying, followed by ignition of the propellant within a controlled manner. Combustion gases are then scrubbed with water before release into the environment [43].

Due to regulation on incineration as a waste disposal method, experimentation with treatments such as alkaline hydrolysis, acidic hydrolysis, photochemical, biodegradation, mechanical, or combined methods have also been studied as an alternative techniques for removal.
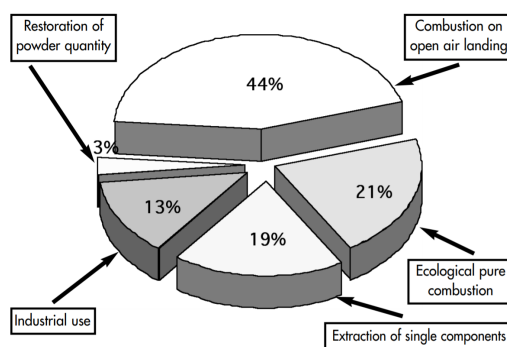

Figure 1.6: The fate of waste NC powders discarded from military stocks. The majority undergoes a form of combustion. From the work of Ganev *et al.* [44].

1.3.1 Hydrolysis degradation methods

The alkaline hydrolysis reactions of NC have undergone thorough study due to their central role in large-scale NC disposal from manufacturing waste streams. It was realised early on by Kenyon and Gray that the action of alkalis on NC did not just yield cellulose and the cor-
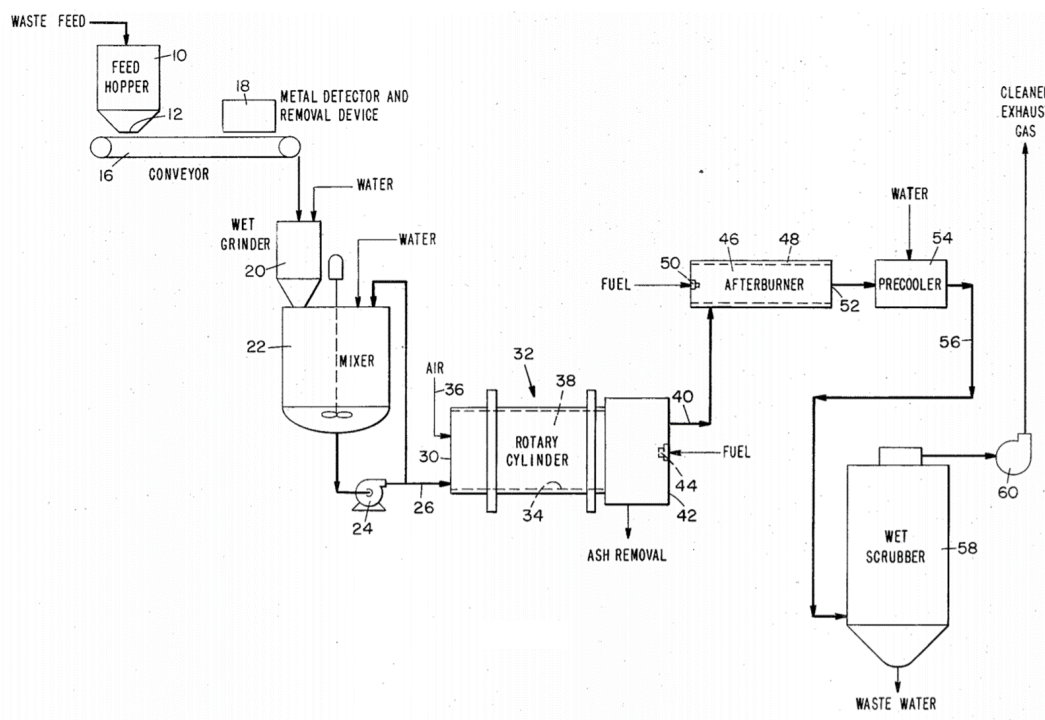
Figure 1.7: Schematic of an incinerator designed for the destruction of waste explosives, patented by Bolejack *et al.* [43].

responding metal nitrate salt, but a whole mixture of highly variable organic and inorganic products [45]. Miles observed that whilst acid and alkaline hydrolysis both produced similar products, the rate of the latter reaction was much greater [46]. Baker and Easty stated that alkaline hydrolysis was on the order of 480 times faster than acid hydrolysis [47]. Typically, NC is treated with concentrated sodium hydroxide and heated. Though other alkalis maybe used, such as barium hydroxide, calcium hydroxide or sodium carbonate, these alternative alkalis require longer contact and heating times in addition to a larger measure of alkali to dissolve the NC [48]. In 1976, Wendt and Kaplan reported that a sodium hydroxide solution of 3 % by weight at 95°C was able to effectively degrade NC of 12.6-13.4 %N to completion, in only 30 minutes. Su and Christodoulatos observe a similar rate, with 90 % of digestion occurring within 35 minutes, in 2 % sodium hydroxide at 70°C for NC of 12.2 %N [49].

Though less studied than alkaline hydrolysis and deemed a slower process, the acid hydrolysis mechanism is extremely important for the understanding of decomposition and ageing processes of NC. "Spent" or residual acids always remain in the system from incomplete washing following synthesis. Products liberated *via* other breakdown routes also

go on to form acidic species within the local environment, and contribute to more extensive decomposition via secondary reactions and autocatalysis [50]. Assary stated that acid catalysed decomposition of sugars in aqueous medium were initiated by protonation at hydroxyl groups [51]. This was later observed computationally by Feng *et al.*, where intramolecular hydrogen transfers, dehydration reactions, and ring-opening processes resulted from protonation of hydroxyl groups at specific sites on various sugars [52].

The study of Kim *et al.* explored the possibility of combining acid hydrolysis with biodegradation on an industrial scale [53]. Feasibility of the hydrolysis reaction using hydrochloric acid with heat, was thoroughly investigated. Kim achieved denitration by treatment with acid more dilute than that initially used to synthesise the NC sample. The study assumed that the nitrate group of C6 reacted the fastest, reasoning that groups on C2 and C3 experience more steric hindrance. A lower concentration of acid promoted shift of the equilibrium towards denitration. In addition, acid catalysed side reactions may introduce complications. Though glucose was the major product of the monitored denitration process, it was stated that the rate of denitration was more rapid than the peeling-off reaction. In theory, it should be possible to regenerate strands of cellulose under the appropriate conditions. However, these results only focussed on the retrieval of end-stage hydrolysis products such as glucose, nitrates, nitrites and ammonia.

1.3.2 Biological degradation methods

Multiple studies demonstrate that microbial biodegradation is an effective method of degrading NC [54]. Wendt and Kaplan's study presented a bench-scale continuous treatment process involving initial degradation by alkaline hydrolysis followed by biological digestion using naturally occurring microbes in raw wastewater, for which they acquired a patent a year earlier [55]. It was noted by Fan *et al.* that highly substituted cellulose derivatives were resistant to direct biodegradation and require pre-treatment. Work on the enzymatic hydrolysis of cellulose revealed that increasing the crystallinity of the substrate reduced its digestibility [56, 57, 58, 59]. This is reinforced in the study by Mittal *et al.* involving alkaline and liquid-ammonia treatments on crystalline cellulose [60]. Substitution of hydroxyl groups to increase solubility of cellulose derivatives lead to increased enzymatic hydrolysis, up to complete solubilisation. After this point, susceptibility to biodegradation slowly decreased. As solubility was no longer the limiting property, further increase in substitution began to inhibit enzymatic digestion. It may be that as the levels of substitution
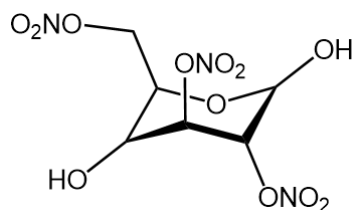
Figure 1.8: The work of Shukla *et al.* employed 2,3,6-trinitro-beta-glucopyranose as a monomer
for NC [61, 62, 63].

increase, polymer geometries become less suited to the active sites of enzymes involved in
degradation.

1.3.3   Computational Studies

A review of published works yields very few NC mechanistic degradation studies involv-
ing computational methods. Due to the nature of the topic, many of the referenced works
above are linked with private or military organisations. Thus, their release may be restricted
until declassified many years later, or completely withheld. The timeline of much of the
material reviewed here ranges from mid to late 1900s, before the widespread use of com-
putational methods in conjunction with experimental chemical research. Consequently, it is
to be expected that more NC computational studies will appear in the near future. Shukla *et
al.* performed a series of mechanistic studies on 2,3,6-trinitro-β-glucopyranose (figure 1.8),
exploring its validity as a monomer model for the NC polymer during alkaline hydrolysis
via the saponification route, whereby the nitrate ester was cleaved to restore the hydroxyl
group and the nitrate salt [61, 62, 63]. If the hydrolysis reaction were to proceed via the
saponification route, in practice it is unlikely that all nitro groups are liberated simultane-
ously.

The work examined the possible sequence for nitrate group removal from a fully ni-
trated NC polymer in the hydrolysis reaction, in addition to whether depolymerisation or
rupture of the ring could instead precede denitration. It was reported that nitrate groups
would undergo an bi-molecular nucleophilic substitution reaction (S_N2) substitution reac-
tion whereby each nitrate ester group is replaced by the incoming hydroxide nucleophile,
liberating a nitrate ion. Calculated enthalpies and free energies indicated a C3 $\rightarrow$ C2 $\rightarrow$
C6 sequence of denitration for the monomeric unit. Their later work involving the dimer
and trimer models suggests a significant change in behaviour when scaling up from the
monomer. Dimer and trimer activation energies proved comparable, but showed an incon-
sistency with the monomer, instead exhibiting a C3 $\rightarrow$ C6 $\rightarrow$ C2 sequence. There is the

problem that the latter sequence for the dimer and trimer was extrapolated only from the energies required to remove the first nitrate group. In contrast, the monomeric sequence was derived from energies calculated at each of the three stages of nitrate removal; the reaction energy was evaluated for sequential cleavage starting with a different nitrate site each time. As there is little disparity between the dimer and trimer energies, but a large difference to the monomer results, it was said that the dimer was the smallest unit able to adequately describe the alkaline hydrolysis behaviour of NC.

Though not a study involving NC, detailed work on the nitrate ester degradation routes in pentaerythritol tetranitrate (PETN) was conducted by Tsyshevsky, Sharia and Kuklja [64]. PETN is an energetic material possessing four nitroester moieties. Similarly to NG, it is used as both an explosive and in medicine [65]. Existing experimental activation energies for decomposition were scattered in the range of 30 to 70 kcal mol^{-1}. The group attributed the dispersion in data to inconsistent procedures and experimental conditions between studies. The most common degradation products recorded were CO, CO_2, NO, N_2O, CH_2O, HCN, and HNCO. Echoing earlier NC and other nitroester thermolysis studies [66], the first degradation step was assumed to be nitrate ester homolytic fission. Activation barriers calculated using PBE, PBE0 and wB97XD were compared, finding that homolytic cleavage of the $O-NO_2$ bond was most favourable due to the fastest rate of reaction. The competing elimination of nitrous acid possessed a lower activation barrier of only approximately 6 kcal mol^{-1} but was slower. However, this second reaction was also exothermic, and through bulk calculations it was determined the secondary reaction would accelerate global processes *via* self-heating. Analyses of the implemented functionals found that PBE consistently underestimated barrier height by 12 to 14 kcal mol^{-1} on average, with respect to the other functionals used, but that all methods give good agreement for the energies of reaction.

1.4 Environmental impact of NC waste products

NC is extremely flammable when dry and so is usually kept in solvent to prevent detonation when under storage [67, 68]. Mixed with at least 25 % of water or alcohol, NC is completely stabilised [53]. This has facilitated the use of aqueous solvents as dispersion and transport mediums in manufacturing processes, leading to small NC fibres, or "fines", in output streams [69]. Demilitarisation activities have resulted in large volumes of NC waste which regulatory action now prevents the disposal of via incineration [40, 70, 71, 72].

A high level of side group substitution relative to cellulose, in addition to its insolubility, contributes to resistance to microbial degradation [73, 74]. As a result, NC exhibits poor mobility and a long lifetime in the environment.

Burning releases a myriad of toxic and harmful products into the atmosphere [44]. N_2O is a potent greenhouse gas but is a known decomposition product. It can be produced via a number of potential mechanistic routes, including oxidation of liberated nitrate species. Knowledge of the key formation pathways would allow manipulation of product formulations and storage conditions to limit N_2O release.

Whilst NC itself is relatively harmless to most mammals, macroinvertebrates, fish and algae [75, 27], this cannot be said for the effluents from NC production and any nitro byproducts. Nitration, bleaching and delignification solvents require treatment before discharge into the environment, due to toxicity to the aquatic environment [76, 77, 78]. In addition, the fibrous nature of small NC fines in wastewater can alter the natural habitat at the bottom of ponds and bodies of water, by covering and thus limiting the oxygen access to benthic organisms [75]. Although NC itself is unstable and degrades gradually over time, its insolubility means that decomposition under natural environmental conditions is slow, as in the case of discarded munitions or explosive residues [79].

1.5   Motivation

Despite its long history, NC is still an essential ingredient in many propellant and lacquer formulations today, with its versatility spanning an extensive range of products and applications. The diversity of its use means that we come into contact with it in some shape or form everyday. Whilst efforts have been made to substitute it with other polymeric binders in attempt to reduce the manufacturing risk it poses due to its volatility, this has only been partly successful [80].

NC, amongst other EM have caused many thermal runaway reactions, leading to accidents and explosions worldwide. Insufficient understanding of the internal processes has lead to unintended explosions during storage and at nitration industrial plants, and in the most severe cases, casualties [3, 39, 81, 82, 83, 84] . It is therefore imperative that we seek to clarify the understanding of the ageing mechanisms to inform the reduction of associated risks, whilst more effectively preserving existing NC stock.

NC disintegration is also of relevance in the preservation of historical artefacts and cinematographic film, where knowledge of the decomposition processes are crucial to the

maintenance of items of historical value [21, 85].

Changing policy on the use of genetically modified (GM) crops may impact the NC supply chain. Cotton linters provide the highest grade cellulose for military and industrial grade production. As this feedstock diminishes in availability or quality, alternative sources, such as lower quality softwood pulp, may be substituted. Experimental studies over the past 100 years have shed light on the macroscopic degradation behaviour of bulk NC. However, the fine mechanistic details of degradation have only been alluded to, and are as yet unvalidated. Identifying a clear map of the possible reactions that occur during ageing will promote adaptability against a variable cellulose feedstock, and facilitate better understanding of the possible changes in chemical properties for different batch lines [34].

In this study we will elucidate the dominant degradation schemes in NC with scrutiny of previously proposed decomposition pathways, and present new mechanistic considerations. This will be achieved via the application of computational techniques to give insight where it has been restricted by the limitations of laboratory experimentation in the past.

1.6 Research objectives

In this thesis the dominant degradation reactions that occur in NC are investigated. The objectives of this study are as follows:

1. Determine a representative system for modelling the degradation chemistry of NC.

2. Apply the model in the investigation of primary degradation reactions that occurr in the slow ageing of NC.

3. Map the secondary reactions that occur in NC and shed light on the processes responsible for the autocatalytic rate of degradation.

Bibliography

[1] Henri Braconnot. De la Transformation de plusieurs Substances végétales en un principe nouveau. *Annales de Chimie et de Physique*, 1(52):290–294, 1833.

[2] Dieter Klemm, Brigitte Heublein, Hans Peter Fink, and Andreas Bohn. Cellulose: Fascinating biopolymer and sustainable raw material, may 2005.

[3] B. Zhao. Facts and lessons related to the explosion accident in Tianjin Port, China. *Natural Hazards*, 84(1):707–713, oct 2016.

[4] James Kettering and Carl Conrad. Quantitative Determination of Cellulose in Raw Cotton Fiber. Simple and Rapid Semimicro Method. *Industrial & Engineering Chemistry Analytical Edition*, 14(5):432–434, may 1942.

[5] Moein Ghaderi, Mohammad Mousavi, Hossein Yousefi, and Mohsen Labbafi. All-cellulose nanocomposite film made from bagasse cellulose nanofibers for food packaging application. *Carbohydrate Polymers*, 104(1):59–65, apr 2014.

[6] Material District. Material made from cellulose and chitin could replace flexible plastic packaging - MaterialDistrict.

[7] BioMass Packaging. NatureFlex Clear Bag (5.75x7.75).

[8] Olivia Parker. Natureflex a compostable replacement for plastics, 2018.

[9] A. J. Morfa, T. Rödlmeier, N. Jürgensen, S. Stolz, and G. Hernandez-Sosa. Comparison of biodegradable substrates for printed organic electronic devices. *Cellulose*, 23(6):3809–3817, dec 2016.

[10] Futamura. NATUREFLEX - COMPOSTABLE AND RENEWABLE PACKAGING FILMS, 2019.

[11] Martin W. King, Bhupender S. Gupta, and Robert. Guidoin. *Biotextiles as medical implants*. Woodhead Publishing Limited, 2013.

[12] Edward Chauncey Worden. *Nitrocellulose Industry*, volume 2. D. Van Nostrand Company, 1911.

[13] Maria Ángeles Fernández de la Ossa, María López-López, Mercedes Torre, and Carmen García-Ruiz. Analytical techniques in the study of highly-nitrated nitrocellulose. *TrAC Trends in Analytical Chemistry*, 30(11):1740–1755, dec 2011.

[14] A. S. Greenberg and Simon Broder. Story of Nitrocellulose, The. *Journal of the Patent Office Society*, 8:517–530, 1925.

[15] C. W. Saunders and L. T. Taylor. A review of the synthesis, chemistry and analysis of nitrocellulose. *Journal of Energetic Materials*, 8(3):149–203, sep 1990.

[16] Christian Friedrich Schönbein. US4874 Improvement in Preparation of Cotton-wool and Other substances as Substitutes for Gun-Powder, 1846.

[17] Baron W. Lenk. Improved Gun-Cotton, 1864.

[18] Frederick Augustus Abel. Improvement in the manufacture of Gun-Cotton, 1866.

[19] Hadi Gholamiyan and Asghar Tarmian. Weathering resistance of poplar wood coated by organosilane water soluble nanomaterials. *Drvna Industrija*, 69(4):371–378, 2018.

[20] Y. Shashoua, S.M. M Bradley, and V.D. D Daniels. Degradation of cellulose nitrate adhesive. *Studies in conservation*, 37(2):113–119, 1992.

[21] M. Edge, N.S. Allen, M. Hayes, P.N.K. Riley, C.V. Horie, and J. Luc-Gardette. Mechanisms of deterioration in cellulose nitrate base archival cinematograph film. *European Polymer Journal*, 26(6):623–630, jan 1990.

[22] Kodak. Storage and Handing of Processed Nitrate Film — Motion Picture Film, 2019.

[23] International Federation of Film Archives. Handling, storage and transport of cellulose nitrate film. *UNESCO Digital Library*, 26(Perspectivas: revista trimestral de educación comparada):41–54, 1991.

[24] Konstantina Konstantinidou, Stanislav Strekopytov, Emma Humphreys-Williams, and Mark Kearney. Identification of cellulose nitrate X-ray film for the purpose of conservation: Organic elemental analysis. *Studies in Conservation*, 62(1):24–32, jan 2016.

[25] John M. Calhoun. The Preservation of Motion-Picture Film on JSTOR. *The American Archivist*, 30(3):517–525, 1967.

[26] Krystyna Matusiak and Tamara Johnston. Digitization for preservation and access: Restoring the usefulness of the nitrate negative collections at the American geographical society library. *American Archivist*, 77(1):241–269, apr 2014.

[27] Michael J. Quinn. Wildlife Toxicity Assessment for Nitrocellulose. In *Wildlife Toxicity Assessments for Chemicals of Military Concern*, pages 217–226. Elsevier, 2015.

[28] John L Tonkinson and Brett A Stillman. Nitrocellulose: a tried and true polymer finds utility as a post-genomic substrate., jan 2002.

[29] B.T. Kurien and R.H. Scofield. Electrophoresis Blotting Techniques. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*. Elsevier, 2015.

[30] Dow Wolff Cellulosics. Walsroder® Nitrocellulose Essential for an Extra-Special Finish. Technical report, Dow Wolff Cellulosics, 1998.

[31] Elodie Alinat, Nathalie Delaunay, Christine Costanza, Xavier Archer, and Pierre Gareil. Determination of the nitrogen content of nitrocellulose by capillary electrophoresis after alkaline denitration. *Talanta*, 125:174–80, jul 2014.

[32] H J Prask, C S Choi, R Strecker, and E Turngren. Woodpulp Crystal Structure and Its Effect on Nitrocellulose Physical Properties. Technical report, US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND, sep 1980.

[33] H J Prask and C S Choi. The Correlation of Nitrocellulose Properties and Cellulose Feedstock Crystal Structure. Technical report, AA(Army Armament Research and Development Command, Dover, NJ.), AB(Army Armament Research and Development Command, Dover, NJ.), Dover, NJ, 1982.

[34] Wolfgang J F Schimansky. The origin and type of cellulose utilized in the manufacture of Nitrocellulose over the last thirty years. *5th International Nitrocellulose Symposium*, 1(November 1971):1–12, 2012.

[35] N. V. Baranova, L. A. Pashina, S. A. Bogdanova, and A. V. Kostochko. Energy and acid-base characteristics of cellulose nitrate surface with various substitution degree. *Russian Journal of Applied Chemistry*, 84(12):2141–2145, dec 2011.

[36] Yulia A. Gismatulina, Vera V. Budaeva, and Gennady V. Sakovich. Nitrocellulose Synthesis from Miscanthus Cellulose. *Propellants, Explosives, Pyrotechnics*, 43(1):96–100, jan 2018.

[37] A. E. Golubev, A. N. Neshitova, P. V. Singin, S. A. Kuvshinova, V. A. Burmistrov, and O. I. Koifman. Plasticization of Cellulose Nitrate by 4-Nitrophtalic Acid Esters. *Russian Journal of General Chemistry*, 87(12):3086–3092, dec 2017.

[38] Marianne Gilbert. Cellulose Plastics. In *Brydson's Plastics Materials: Eighth Edition*, pages 617–630. Butterworth-Heinemann, jan 2016.

[39] Ruichao Wei, Yaping He, Jiahao Liu, Yu He, Wenzhong Mi, Richard Yuen, and Jian Wang. Experimental Study on the Fire Properties of Nitrocellulose with Different Structures. *Materials*, 10(3):316, mar 2017.

[40] Josh Wilkinson and Duncan Watt. Review of Demilitarisation and Disposal Techniques for Munitions and Related Materials. Technical Report 2, Munitions Saftely Informatoin Analysis Centre, 2006.

[41] Frank H. Bissett and Leonard A. Levasseur. Chemical Conversion of Nitrocellulose for Fertilizer. Technical report, United States Army Natick Research and Development Command, 1976.

[42] Morbidity and mortality weekly MMWR. Recommended guidelines for disposing of nitrocellulose membranes. *MMWR. Morbidity and mortality weekly report*, 34(42):653–655, 1985.

[43] James William Bolejack Jr., Truman Knox Daniel Jr., and Darrell Edward Rolison. United States Patent:, 1973.

[44] Radi Ganev. Utilisation of waste nitrocellulose powders and environmental pollution in their destruction. *Waste Management and Research*, 19(6):533–538, dec 2001.

[45] W. O. Kenyon and H. LeB. Gray. The Alkaline Decomposition of Cellulose Nitrate. I. Quantitative Studies 1. *Journal of the American Chemical Society*, 58(8):1422–1427, aug 1936.

[46] Frank Douglas Miles. Cellulose nitrate: The Physical Chemistry of Nitrocellulose, its Formation and Use. XVIII(90):422, 1955.

[47] John W. Baker and D. M. Easty. Hydrolytic decomposition of esters of nitric acid. Part I. General experimental techniques. Alkaline hydrolysis and neutral solvolysis of methyl, ethyl, isopropyl, and tert.-butyl nitrates in aqueous alcohol. *Journal of the Chemical Society (Resumed)*, 1952(0):1193–1207, 1952.

[48] T.M. Wendt and A.M. Kaplan. A Chemical-Biological Treatment Process for Cellulose Nitrate Disposal. *Water Environment Research*, 48(4):660–668, 1976.

[49] Tsan-Liang Su and Christos Christodoulatos. Destruction of Nitrocellulose Using Alkaline Hydrolysis. Technical report, Defense Technical Information Center, 1996.

[50] T. B. Brill and P. E. Gongwer. Thermal Decomposition of Energetic Materials 69. Analysis of the kinetics of nitrocellulose at 50 C-500 C. *Propellants, Explosives, Pyrotechnics*, 22(1):38–44, feb 1997.

[51] Rajeev S. Assary, Taejin Kim, John J. Low, Jeff Greeley, and Larry A. Curtiss. Glucose and fructose to platform chemicals: Understanding the thermodynamic landscapes of acid-catalysed reactions using high-level ab initio methods. *Physical Chemistry Chemical Physics*, 14(48):16603–16611, nov 2012.

[52] Shuting Feng, Christina Bagia, and Giannis Mpourmpakis. Determination of proton affinities and acidity constants of sugars. *Journal of Physical Chemistry A*, 117(24):5211–5219, jun 2013.

[53] Byung J. Kim, Hsin-Neng Hsieh, and Fong-Jung Tai. Anaerobic Digestion and Acid Hydrolysis of Nitrocellulose. Technical report, US Army Corps of Engineers, 1999.

[54] Aaron L. Bluhm. Chemical Characterization of Nitrocellulose Degradation Products. Technical report, 1977.

[55] Theodore M. Wendt and Arthur M. Kaplan. Process for treating waste water containing cellulose nitrate particles, 1975.

[56] L. T. Fan, Yong-Hyun Lee, and David H. Beardmore. Mechanism of the enzymatic hydrolysis of cellulose: Effects of major structural features of cellulose on enzymatic hydrolysis. *Biotechnology and Bioengineering*, 22(1):177–199, jan 1980.

[57] L. T. Fan, Y. H Lee, and D. R. Beardmore. The influence of major structural features of cellulose on rate of enzymatic hydrolysis, 1981.

[58] M. M. Gharpuray, YongHyun H Lee, and L. T. Fan. Structural modification of lignocellulosics by pretreatments to enhance enzymatic hydrolysis. *Biotechnology and Bioengineering*, 25(1):157–172, 1983.

[59] Liang-tseng Fan, Mahendra Moreshwar Gharpuray, and Yong-Hyun Lee. Design and Economic Evaluation of Cellulose Hydrolysis Processes. In *Cellulose Hydrolysis*, chapter Design and, pages 149–187. Springer Berlin Heidelberg, 1987.

[60] Ashutosh Mittal, Rui Katahira, Michael E Himmel, and David K Johnson. Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: Changes in crystalline structure and effects on enzymatic digestibility. *Biotechnology for Biofuels*, 4(1):41, 2011.

[61] Manoj K. Shukla and Frances Hill. Theoretical investigation of reaction mechanisms of alkaline hydrolysis of 2,3,6-trinitro-β-d-glucopyranose as a monomer of nitrocellulose. *Structural Chemistry*, 23(6):1905–1920, apr 2012.

[62] Manoj K Shukla and Frances Hill. Computational elucidation of mechanisms of alkaline hydrolysis of nitrocellulose: dimer and trimer models with comparison to the corresponding monomer. *The journal of physical chemistry. A*, 116(29):7746–55, 2012.

[63] Manoj K Shukla and Frances Hill. Can an α -Anomer of the Trinitro Form of D -Glucopyranose Be More Easily Hydrolyzed in Alkaline Environment than the β - Anomer ? A Detailed Theoretical Analysis. *The Journal of Physical Chemistry A*, pages 4909–4921, 2012.

[64] Roman V. Tsyshevsky, Onise Sharia, and Maija M. Kuklja. Thermal Decomposition Mechanisms of Nitroesters: Ab Initio Modeling of Pentaerythritol Tetranitrate. *The Journal of Physical Chemistry C*, 117(35):18144–18153, sep 2013.

[65] Louis J Ignarro. After 130 years, the molecular mechanism of action of nitroglycerin is revealed. *Proceedings of the National Academy of Sciences of the United States of America*, 99(12):7816–7, jun 2002.

[66] Brian D Roos and Thomas B Brill. Thermal decomposition of energetic materials 82. Correlations of gaseous products with the composition of aliphatic nitrate esters. *Combustion and Flame*, 128:181–190, jan 2002.

[67] Frank Douglas Miles and Maurice Milbourn. The structure of nitrated cellulose. I the swelling and disintegration of ramie cellulose in nitrating acids. *Journal of Physical Chemistry*, 34(11):2598–2606, jan 1930.

[68] Frank E. Wolf. Alkaline Hydrolyis Conversion of Nitrocellulose Fines. Technical Report October, Badger Army Ammunition Plant, oct 1997.

[69] D. Grasso, J. C. Carrington, P. Chheda, and B. Kim. Nitrocellulose particle stability: Coagulation thermodynamics. *Water Research*, 29(1):49–59, 1995.

[70] James E. Alleman, Byung J. Kim, David M. Quivey, and Lucina O. Equihua. AL-KALINE HYDROLYSIS OF MUNITIONS-GRADE NITROCELLULOSE. *Water Science and Technology*, 30(3):63–72, 1994.

[71] Nadja Auer, John N. Hedger, and Christine S. Evans. Degradation of nitrocellulose by fungi. *Biodegradation*, 16(3):229–236, jun 2005.

[72] Byung J Kim, James K Park, and Lee W Clapp. Characterization of Nitrocellulose Fines in Wasterwater and Development of Pollution Prevention Strategy. Technical report, US Army Corps of Engineers, 1997.

[73] Bruce W. Brodman and Michael P. Devine. Microbial attack of nitrocellulose. *Journal of Applied Polymer Science*, 26(3):997–1000, mar 1981.

[74] M. Duran, B.J. Kim, and R.E. Speece. Anaerobic biotransformation of nitrocellulose. *Waste Management*, 14(6):481–487, 1994.

[75] Michael G Ryon. Water Quality Criteria for Nitrocellulose. Technical report, OAK RIDGE NATIONAL LAB TN, OAK RIDGE, 1986.

[76] Elvira E. Ziganshina, Emil M. Ibragimov, Olga N. Ilinskaya, and Ayrat M. Ziganshin. Bacterial communities inhabiting toxic industrial wastewater generated during nitrocellulose production. *Biologia*, 71(1):70–78, 2016.

[77] Elaine N. Ribeiro, Flávio T. Da Silva, and Teresa Cristina B. De Paiva. Ecotoxicological evaluation of waste water from nitrocellulose production. *Journal of Environmental Science and Health, Part A*, 48(2):197–204, jan 2013.

[78] G El-Diwani, N N El-Ibiari, and S I Hawash. Treatment of hazardous wastewater contaminated by nitrocellulose. *Journal of hazardous materials*, 167(1-3):830–4, aug 2009.

[79] A.B. Crockett, H.D. Craig, T.F. Jenkins, and W.E. Sisk. Field sampling and selecting on-site analytical methods for explosives in soil. Technical report, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID, dec 1996.

[80] Manfred A. Bohn. NC-based energetic materials - stability, decomposition and ageing. In *Nitrocelluose - Supply, Ageing and Characterisation*, page 129, Aldermaston, 2007.

[81] Miaomiao Jin, Nan Luo, Guoping Li, and Yunjun Luo. The thermal decomposition mechanism of nitrocellulose aerogel. *Journal of Thermal Analysis and Calorimetry*, 121(2):901–908, mar 2015.

[82] Yu He, Yaping He, Jiahao Liu, Pan Li, Mingyi Chen, Ruichao Wei, and Jian Wang. Experimental study on the thermal decomposition and combustion characteristics of nitrocellulose with different alcoHehol humectants. *Journal of Hazardous Materials*, 340:202–212, oct 2017.

[83] Hua Chai, Qiangling Duan, Lin Jiang, Liang Gong, Haodong Chen, and Jinhua Sun. Theoretical and experimental study on the effect of nitrogen content on the thermal characteristics of nitrocellulose under low heating rates. *Cellulose*, 26(2):763–776, jan 2019.

[84] Kai Wang, Dabin Liu, Sen Xu, and Gaowen Cai. Research on the thermal history's influence on the thermal stability of EHN and NC. *Thermochimica Acta*, 610:23–28, jun 2015.

[85] Julie A. Reilly. Celluloid objects: Their chemistry and preservation. *Journal of the American Institute for Conservation*, 30(2):145–162, jan 1991.