Synthesis and Characterization of Oil Lubricant Antioxidant Degradation Products

by

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Abstract

Lubricating oils play a critical role in the reliable operations of machinery. Numerous additives are used to preserve/extend the lifespan of lubricating oils (among other benefits). Among these additives, antioxidants are added to lubricating oils as a sacrificial substance, that extends the lifespan by preferentially being oxidized over the lubricating oil. GasTops Ltd. is a world leader in condition monitoring of rotating machinery and is interested in developing in-line sensors to accurately predict the remaining useful life of a lubricating oil by monitoring the quantity of antioxidant degradation products. One of the antioxidants of interest is the commonly used $N$-phenyl-1-aminonaphthalene (PAN). Three major oxidation products of PAN have been identified and herein synthesized and isolated in pure form: C–C coupled PAN dimer, C–N coupled PAN dimer, and naphthyl oxidized PAN (Fremy’s PAN). Other products include N–O radical PAN, as well as phenyl oxidized PAN (phenol PAN). Attempts to independently synthesize samples of these PAN derivatives resulted in the unexpected syntheses of other known PAN derivatives. Preparation of C–C coupled PAN dimer resulted in the additional synthesis of Fremy’s PAN as a side product. Synthesis of C–N coupled PAN dimer also resulted in the synthesis of the other two major PAN oxidation products: C–C coupled PAN and Fremy’s PAN. The synthesis of N–O radical PAN also resulted in the unexpected production of C-C coupled PAN dimer, as well as Fremy’s PAN.

![Chemical structures](image)

Figure 1. PAN (1), nitroxyl radical PAN derivative (2), carbon-carbon coupled PAN dimer (3), naphthyl oxidized PAN (4), carbon-nitrogen coupled PAN dimer (5), phenyl oxidized PAN (6).
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List of Abbreviations

API: American Petroleum Institute
BHT: butylated hydroxytoluene
BIPY: 2,2’-bipyridine
FCC: flash column chromatography
NMR: nuclear magnetic resonance
OIT: oxidation induction time
PAN: N-phenyl-1-aminonaphthalene/N-phenyl-1-naphthylamine
PAO: Poly(α-olefin)
RT: room temperature
TAN: total acid number
TLC: thin-layer chromatography
TMS: tetramethylsilane
VI: viscosity index

List of NMR Abbreviations

s: singlet
d: doublet
t: triplet
q: quartet
m: multiplet
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Chapter 1: Introduction

1.1 Lubricants

Lubricants are, *inter alia*, key to the reliable operation of large industrial equipment such as generators, gas turbines, and engines. They can be defined as a substance or mixture that has the ability to reduce the friction between two surfaces rubbing against each other.¹ The use of lubricants can be found as early as 1400 BCE, where grease made up of calcium salts and fats used to lubricate chariot wheels was found in Egyptian tombs.² Art decorations were also discovered in the tomb of Tehuti-Hetep in Egypt, depicting the use of olive oil on wooden planks to facilitate sliding large stones, statues and other building materials.¹

Initially, the lubricants used were natural oils isolated from olives, rape seed, and castor plant seeds.² The onset of the industrial age in 1769 with the development of the steam engine by James Watt began the demand for improved lubricants, however it wasn’t until the mid to late 1800’s that the technique of vacuum distillation of crude petroleum arrived to refine lubricants and began to satisfy that demand.² This would give the sought-after improvements that came with the demand of industrial revolution. By 1877, the first synthetic hydrocarbon oils were produced by Charles Friedel and James Mason Crafts,¹ known for developing the Friedel-Crafts alkylation and acylation reactions.³

There was no significant motivation for further improvement of synthetic lubricants until the demands of World War II increased the criteria for functional lubricants.¹ With the expansion of applications such as jet engines as well as new conditions such as having to perform in extreme environmental conditions, the use of traditional mineral oil based lubricants was no longer applicable.
There are many physical properties that need to be considered when selecting a lubricant. The lubricant must have a wide operating temperature range to be able to function in different conditions. It needs to have a high viscosity index (VI), which is a unitless property. VI measures the rate of the viscosity change due to a change in temperature. Lubricants must also have a low pour point (the threshold where the temperature under this point will cause the lubricant’s inability to be poured), as well as low viscosity at lower temperatures, which make it appealing for use in cold-climate applications.\(^1\) The lubricant must also have low volatility to reduce the amount lost to evaporation.

Other properties that make for a good oil lubricant include resistance to hydrolytic degradation (which can lead to acidic products which in turn promote corrosion).\(^1\) In addition to having a high temperature operating range, the lubricant must also be able to be thermally stable at these temperatures. High oxidative stability is also an important property as some applications may result in the contact with air, which can result in oxidative degradation, and therefore loss of function. Metal catalysts (usually from contact with the surface being lubricated) may also become incorporated into the lubricant,\(^4\) and resistance to reacting with these metals is beneficial. Other external drivers for chemical change includes elevated pressure and shearing (mechanical bond dissociation). Latent electrons from rubbing two surfaces together, which have low energy to promote a chemical reaction can produce radical intermediates that can then undergo a chemical reaction.\(^5\)
1.1.1.1 Applications

As stated previously, lubricants are defined as a substance that reduces the friction between two surfaces.\(^1\) Other purposes of lubricating oils include acting as a coolant and as a sealant.\(^6\) Because of these benefits, the array of applications is vast, ranging from everyday vehicle usage to large scale industrial uses such as wind turbines or power plant generators. Lubricants can be classified by their main function. These classifications include: anti-wear additives, extreme pressure additives, friction modifiers, corrosion inhibitors, and viscosity index improvers.

Anti-wear additives work by forming a protective layer between the surfaces. The lubricant can separate the face of the two surfaces and substitute the friction between the two faces with the friction between each face and the lubricant independently.\(^7\) These include lubrication of joints\(^8\), as well as the moving parts of a motor.\(^6\) Extreme pressure additives form a coating on the surface and this helps protect the components from seizure (the halt of motion due to friction).\(^9\) Applications would include gearboxes and cutting fluids used for the machining of metals.\(^10\) Friction modifiers, typically made of very fine solid particles such as graphite or molybdenum disulfide, work to control friction. Corrosion inhibitors protect the surface by creating a corrosion resistant layer to protect the surface from effects such as oxidation via atmospheric oxygen. Viscosity index improvers minimize or prevent the decrease of said viscosity index of the lubricant at higher temperatures.

1.1.1.2 Chemical Structures

The crude petroleum that is eventually converted into lubricating oil contains a very complex mixture of hydrocarbons. The mixture can range from the most simplistic methane
molecules to asphalt-like resins that have yet to have their structures elucidated. Some other elements, such as nitrogen and sulfur are also present. Crude petroleum can also contain even heavier elements such as vanadium and iron, but they are usually removed through the refining process. Crude petroleum may also contain phospholipids, free sterols and sterol esters, tocols, triterpene alcohols, and fat-soluble vitamins.

Some of the classifications of structures found in mineral oil based lubricants include isoparaffins, cycloalkanes (also known as naphthenes), aromatics, multiring aromatics, organosulfur and organonitrogen compounds, and normal (i.e. linear or \( n \)-) paraffins. The first three are desirable and are what make it to the final composition of the lubricating oil while the last four are removed during the refining process.

![Figure 2](image-url)

Figure 2. Three different classifications of desirable mineral oil-based lubrication and four different classifications of undesired lubricant molecules.

Organonitrogen compounds are able to promote oxidation and cause the formation of unwanted sludge. Although sulfur compounds have the ability to naturally inhibit oxidation, they are removed in the same step as organonitrogen compounds and later replaced with additives that exhibit better oxidation inhibition. Normal paraffins, otherwise known as linear chain hydrocarbons have a low operating temperature range due to their
linear structure\(^2\) and thus are unwanted. Multiring aromatic compounds, while having good solubility, have many unwanted properties, such as poor VI, poor pour point, and very high toxicity.\(^2\)

Poly(\(\alpha\)-olefins) (PAOs) are one of the most popular versions of synthetic oils, as they have very appealing properties such as a wide operational temperature range; a high viscosity index; high oxidative, hydrolytic and shear stability; low corrosivity and compatibility with other mineral oils.\(^1\) They have also have extremely low pour points, which make them a good choice for applications in cold climates. They are generally manufactured in a two-step reaction sequence. The first step involves the synthesis of linear \(\alpha\)-olefins derived from ethylene. The second step involves the use of a catalyst (primarily a Lewis acid catalyst such as BF\(_3\) or AlCl\(_3\))\(^12\) and a protic cocatalyst (water or alcohol) to produce an array of oligomers, which can be isolated via distillation.\(^1\)

![Diagram of PAOs](image)

**Figure 3. The different classes of PAOs, usually characterized by the amount of monomer used in its synthesis.**\(^13\)

Similar to PAOs, plant-based lubricants possess many properties that would make them viable for many lubricant applications such as high chemical stability, high VI, low volatility and good lubricity because of the ester bonds present.\(^14\) Bio-lubricants are also beneficial because of their renewable source and low to negligible aquatic toxicity;
however, their laborious isolation and purification, as well as limited supply restricts their wide adoption.

![Diagram of ricinoleic acid and tetraester biolubricant](image)

**Figure 4. Example scheme of bio-lubricants derived from ricinoleic acid.**

### 1.1.1.3 Sources

Crude petroleum is the major raw material used for manufacturing mineral-based stocks and other petroleum products.\(^2\) By using gas-to-liquid processes, natural gas can be converted into liquid petroleum hydrocarbons. Conventional processes involve separation by distillation and then solvent extraction. Afterwards, additional steps can be done to improve the base stock quality.

As the demand for more stable, more robust oils began to rise in the 1990s,\(^1^5\) the use of conventional oil lubricants (i.e. mineral oil-based lubricants) failed to satisfy the performance needs of modern applications. Higher quality base stocks can be catalytically synthesized from gaseous hydrocarbons in multi-step catalytic processes. Instead of extracting existing lubricant molecules present in crude petroleum, a catalyst is used instead to change the molecular structure of low molecular weight compounds into the desired product. This is helpful because the process allows lower value compounds to be converted into more desirable ones using high pressure hydrogen and isomerization.
catalysts. Compared to more conventional techniques, the new method provides higher yields at a lower cost.²

1.1.1.3.1 Petrochemicals

The American Petroleum Institute (API) developed a classification for lubricant base stocks (or also known as base oil).² This system has been used to categorize and guide the proper selection of base stock needed for the specific lubrication product. Of the five groups of base oils, the first three are made from the separation of crude petroleum by distillation. The fourth group of base oils are synthetically made oils, while the fifth group acts as a ‘catch-all’ for any oils not included in the first four categories.²

The first group are products found from traditional solvent refining techniques. Group I base stocks usually contain higher counts of sulfur and lower counts of paraffin. Compounds in this group are not typically present in signification concentrations. Undesired aromatics are first removed using polar solvents such as furfural, N-methylpyrrolidone or phenol. What is left is then recovered through the addition of ketones at lower temperature, which can then be recovered through filtration. The final step, which can improve colour and stability, is done through hydrofinishing. This involves use of a steady supply of hydrogen that comes into contact with the crude petroleum, reacting with and removing any remaining heteroatom and polar compounds.¹⁶ Group I stocks are usually used for their solubility and natural long-term oxidation control.²

Group II and Group III base oils are produced by hydroprocessing and catalytic dewaxing. Hydroprocessing is a general term that denotes the processes needed to refine the crude oil into high-quality lubricants. These reactions include aromatic ring saturation, napthenic ring opening, olefin saturation, and cracking of paraffins.¹⁶ Once
hydroprocessing is finished, catalytic dewaxing is done to convert straight chain waxy paraffins to isoparaffins.² Both groups have lower sulfur and high paraffin counts. But what sets the distinction between Group II and Group III is the VI range. The VI range of Group II base stocks is similar to that of Group I (between 80 and 120) whereas Group III base stocks have a VI range of greater than 120.

Group IV base stocks (commonly PAOs) have the unique combination of high-temperature viscosity retention, low volatility, very low pour point and a higher degree of oxidation resistance. Their VI can range from 125 to more than 200. These characteristics are due to the wax-free combination of relatively unbranched molecules of predetermined chain length.²

Group V base oils are made from crude naphthalene products. The refining process is similar to the Group I base oils except for the fact that the naphthenic crude contains no paraffins. These base stocks have a number of specialized applications such as metalworking, process oils, refrigeration compressor oils and automatic transmission oils.²

1.1.1.3.2 Plant-based Renewables

Due to the increasing demand in oil for multiple applications (lubrication being one of them), the need for different and renewable sources of oil has increased. Additionally, the use of traditional oils are associated with producing hazardous waste and dangerous exhaust.¹⁷ Furthermore, the toxic properties can be incompatible with applications that are required to be bio friendly, such as applications that require what is called a ‘total-loss lubricant’, where the lubricant is lost to the environment over time (e.g. two-stroke engine oils, and chainsaw oils)¹⁸. Renewable lubricants can be sourced from vegetable oils (not to be confused with vegetable oil in context of the food industry) such as palm oil,¹⁴
rapeseed, jojoba oil, castor oil, sunflower, ricinoleic acid, and even waste cooking oil. These renewable lubricants can be synthesized from native oils via several methods such as transesterification, selective hydrogenation and epoxidation.

In addition to being renewable, vegetable oils come with an array of extra benefits such as being biodegradable, less toxic compared to their mineral oil counterparts, and can sometimes be low-cost alternatives to their synthetic fluids. Not only are some vegetable oils cheaper and less toxic, they can sometimes match or even surpass the desired properties of their petrochemical counterparts. These properties include having a lower volatility due to their higher molecular weight (e.g. triacylglycerols), a narrow range of viscosity change from varying temperatures, ester linkages can aid in lubricity, as well as having a higher solubilizing capacity for contaminants and additives. Jojoba oil has been used to improve viscosity, anti-corrosion and anti-foaming properties. Castor oil comes from the castor bean plant, one of the oldest crops used for vegetable oil production, and its hydroxy fatty acids provide superior viscosity, density, thermal conductivity and pour point values.

Unfortunately, along with the preceding advantages can certainly come some disadvantages to using renewable sources for oil lubricant. The unsaturated fatty acids (oleic, linoleic, and linolenic acids) found in plant oils are used to maintain fluidity in cell membranes, but the bis allylic protons found in polyunsaturated oils make these oils susceptible to oxidation. Since the protons are between double bonds, the resulting radical from proton abstraction can delocalize over a larger five-atom π system, resulting in a lower bond dissociation energy when compared to the three-atom π system associated with a mono allylic proton, such as those in oleic acid. Due to this, they follow the same free
radical oxidation mechanism (see Section 1.1.4.1) that mineral oil-based lubricants undergo, but at a faster rate.\textsuperscript{14}

![Chemical structures of oleic, linoleic and linolenic acids. Highlighted in red are the bis allylic protons that are prone to oxidation.]

1.1.1.3.3 Synthetic Oils

When mineral oil-based lubricants fail to satisfy the needs of the application, synthetic oils are used as they can be manufactured to meet said needs. Upwards of 10\% of the total global production of oils are synthetic lubricants. What separates them from mineral oil-based lubricants is the source of the raw material. While mineral oil-based lubricants are derived from petroleum, synthetic lubricants are synthesized from other hydrocarbon intermediates.\textsuperscript{15} One such example of synthetic oils are ester oils, which have chemical structures similar to natural triglycerides. They are of great demand, especially in applications such as metal working and hydraulic fluids.\textsuperscript{24}

![Figure 6. The chemical structure of a triglyceride made up of palmitic acid (left) compared to the diester structure of diisoctyl sebacate (right).\textsuperscript{25}]

24
Other classes of synthetic oils include those with a carbonate functional group. Most known methods for producing dialkyl carbonates include cheap and available materials such as phosgene, dimethyl carbonate, ethylene carbonate and urea with ethylene oxide or zeolite as a catalyst. Phosgene is a reactive donor of a carbonate group due to the carbonyl carbon becoming polarized by induction because of the electronegative chlorines present. This increases the reactivity which can then undergo nucleophilic substitution using alcohol.

![Figure 7. General synthesis of dialkyl carbonates using alcohol, phosgene and base.](image)

1.1.1.4 Lubricant Oxidation

Over time, the oil lubricant will degrade, due to multiple reasons such as elevated pressure, heat, mechanical shearing, catalysis via the lubricated surface, or oxidation. Studies have shown that as the quality of the oil lubricant starts to decline, so does its performance. As the oil lubricant degrades, it causes a change in viscosity which reduces the frictional stress and ultimately raises the contact fatigue, increasing the likelihood of failure cracks and other damage. Degradation via oxidation causes the lubricant to be less mobile and increases the likelihood to form a rigid emulsion. Without a high quality lubricant, the performance and efficiency of the application will diminish.

There are multiple ways that the oil lubricant can degrade but the major route is through oxidation. Exposure of the hydrocarbons in the oil lubricant to oxygen and heat will accelerate the oxidation process. In addition, the equipment’s metal parts often
contain large amounts of Earth-abundant metals, such as copper and iron, which can be oxidized and also act as oxidation catalysts.\textsuperscript{28} Maintaining the integrity of oil lubricants is very important in retaining the performance of the application for which the lubricant is used. A major portion of the annual market for lubricants is dedicated to simply replacing oil lubricants.\textsuperscript{29} Some of the common indicators of lubricant performance include the serviceable lifetime,\textsuperscript{30} or number of miles a car can drive before the oil has to be changed.\textsuperscript{30} Tests have been developed to measure relative performance or the remaining operating life of a lubricant. Some of these tests include oxidation induction time (OIT) and total acid number (TAN) determination.\textsuperscript{27} Oxidation induction time is the time needed for the onset of oxidation when exposed to an oxidizing gas (oxygen in the context of lubricants).\textsuperscript{31} The TAN is defined as the amount of potassium hydroxide needed to neutralize the organic acid that forms in the lubricant as it deteriorates.\textsuperscript{32} These tests provide a good measure of performance by measuring the quality of the lubricant but don’t give much insight on the physical mechanism of lubricant failure (e.g. erosive wear, fatigue).

Hydrocarbon oxidation is a widely known process because it can be used to obtain intermediate petrochemical products, such as methyl ethyl ketone, cyclohexanone, phenol, acetic, adipic and terephthalic acids, vinyl acetate, propylene oxide and cumene hydroperoxide.\textsuperscript{33}
Figure 8. Intermediate petrochemical products that can be obtained through hydrocarbon oxidation.

1.1.1.4.1 Free Radical Oxidation

Scheme 1. The general reaction scheme summarizing the steps that occur in the free radical oxidation that oxidizes the lubricant (R-H) into the many different oxidation products.30,27
The performance of the oil lubricant is driven by the changes in the molecular structure. As the structure changes (mainly through oxidation), so do the properties. The exact mechanism of these reactions can be extremely complex with many reactions taking place. However a general set of mechanisms have been determined.

The first step occurs with the penetration of oxygen into the oil chains (known as the initiation step). The initiating molecule reacts with oxygen, breaking the C–H bond and creating a peroxyl radical. The structure of the oil lubricant dictates which C–H bond is most readily broken. Tertiary hydrogens and hydrogens alpha to a carbon-carbon double bond are most reactive. From here the initiating molecule can react with other molecules and propagate the radical.

\[
R_1-H + O_2 \rightarrow R_1^\cdot + HO-O^\cdot
\]

Scheme 2. The Initiation Step. Oxygen abstracts a hydrogen atom from the lubricant molecule.

This free radical continues to be propagated from one molecule to another until a second oxygen molecule is encountered and a hydroperoxide is formed. This step is known as chain growth or chain propagation step. It is named the chain propagation step because the products (RO₂^•) can interact with more oil molecules to produce a hydroperoxide and another alkyl radical, which both can react in turn with additional oil molecules. The formation of these alkyl radical intermediates and hydroperoxides can occur at any temperature but sufficient heat is required for the reactions to continue. The accumulation of these peroxyl radicals is the rate limiting step as well as a key step when it comes to oil oxidation, as it is a product of early stages of oxidation.
Scheme 3. The alkyl radical reacts with yet another oxygen molecule to yield a peroxyl radical which can propagate the radical to other lube molecules.

The next step (known as chain branching) is the thermal decomposition of the hydroperoxides, which can occur unimolecularly to yield an alkoxy radical (RO•) and hydroxy radical (HO•). If temperatures are insufficient, this decomposition doesn’t occur and the oxidation reactions stop here, and an accumulation of hydroperoxides occur, until the temperature is sufficient to progress the reactions.

Scheme 4. The Branching Step. The peroxide molecule can thermodynamically decompose into an alkoxy radical and a hydroxide radical. Both molecules can reenter the oxidation cycle and further propagate their radicals.

Even though it proceeds slowly, an alternative route for the hydroperoxide molecule includes reacting with an oil molecule, producing one alkyl radical and one oxygen radical and the formation of water. Experiments have reported the presence of water in some early stages of oxidation. At sufficiently high temperatures, isomerization and decomposition reactions can occur, which can lead to the formation of CO₂ and CO.
Scheme 5. Alternate routes for the peroxide molecule can result in reacting with a lubricant molecule to yield an alkoxide and alkyl radical as well as decomposing into CO₂, CO and water.

Once alkoxy radicals (RO•) and hydroxy radicals (HO•) are formed, they are able to react with yet another oil molecule, producing an alkyl radical that can return back to the beginning of the oxidation mechanism and continue propagating oxidation, as well as an alcohol. If the hydroxyl radical reacts, water is formed.

Scheme 6. The alkoxide and hydroxyl radicals can interact with yet another alkane molecule to yield an alcohol or water as well as another alkyl radical.

Secondary and tertiary alkoxy radicals will react with other oil molecules to form aldehydes and ketones respectively as well as more alkyl radicals to continue the oxidation cycle.

Scheme 7. Depending on the nature of the alcohol, they can form ketones or aldehydes which are the necessary molecules needed for acid formation.
Under low temperature conditions, the products formed during free radical oxidation include peroxides, alcohols, aldehydes, ketones and water. Only under higher temperatures will acids form by reacting an aldehyde with a peroxyl radical to form a carbonyl radical. This radical can then react with another molecule of oxygen and subsequently an oil molecule to form a peroxy acid. Two peroxy acids can react to form two carboxylic acids and a molecule of oxygen.

Scheme 8. At higher temperatures, aldehydes can react with peroxy radicals, oxygen, a lubricant molecule to form a peroxy acid. The peroxy acid can then react with another peroxy acid to yield carboxylic acids, the precursor to sludge formation.

Once acids have formed, they can catalyze the aldol condensation between the aldehydes and ketones present in the oil lubricant. The outcome is the formation of high molecular weight compounds that will increase the viscosity and ultimately lead to sludge and varnish formation.
Scheme 9. Through acid-catalyzed enol condensation, the carbonyl compounds can polymerize, leading to the formation of sludge which is detrimental to the application that the lubricant is used for.

The final step can occur and form non-radical products, which are ultimately the final oxidation products and therefore terminating the oxidation cycle (hence it is called the Termination Step). Two alkyl radicals can react and dimerize, a peroxyl radical and an alkyl radical can give peroxide products, or alternatively two peroxyl radicals can react to give the same peroxide product plus one molecule of oxygen. These reactions have very low activation energy and can occur almost immediately once peroxide decomposition occurs. However, they are limited by the low concentration of these highly reactive species.

Scheme 10. The Termination Step. The reaction with alkyl radicals and peroxyl radicals can result in products that will no longer contribute to the oxidation.
1.1.1.4.2 Metal Catalyzed Oxidation

Metal ions, which arise predominantly from the metal in the engines, are able to act as catalysts for lubricant oxidation. Through a redox mechanism, they are able to lower the activation energy and therefore commence the oxidation reactions at a lower temperature. A metal ion can interact with an oil lubricant molecule and initiate the process in place of oxygen. The reduced ion can interact with oxygen to return to its reactive state and continue the catalytic cycle.

\[
\begin{align*}
M^{(n+1)+} + R_1\rightarrow H & \rightarrow \quad M^{(n)+} + H^+ + R_1^- \\
M^{(n)+} + O_2 & \rightarrow \quad M^{(n+1)+} + O_2^-
\end{align*}
\]

Scheme 11. Metal ions that are present in the lubricant can catalyze the oxidation process but abstracting a proton from the lubricant molecule, resulting in an alkyl radical that can now participate in the free radical mechanism.

The metal ion can also react with hydroperoxides during the propagation step to either yield a peroxyl or alkoxy radical. The use of a metal ion catalyst to produce the peroxyl radical can be done to circumvent the thermal barrier needed for the reaction under uncatalyzed conditions. The alkoxy radical can continue its cycle in the chain branching step.

1.2 Lubricant Additives

Early iterations of oil lubricants didn’t have any additives. But as the technology advanced, and lubricant synthesis became more refined and complex, additives were developed to further improve any aspect of the oil lubricant that was not adequate for its application. The base stock (lubricant without any additives) must be compatible with the additives and finding a perfect balance between improving the deficient characteristics
while maintaining the desired performance in other aspects is typically a difficult process. The composition of an oil lubricant is usually 70-90% base stock while the remainder is additives.\textsuperscript{36}

Some additives add new properties to the base stock, while others enhance some existing properties or reduce the rate at which undesirable effects occur over the lubricant’s lifetime. Some classes of lubricant additives include pour point depressants, VI improvers, defoamants, rust and corrosion inhibitors, and antioxidants.

1.2.1.1 Pour Point Depressants

The pour point is the threshold at which any temperature below this point will render the lubricant unpourable. This is usually caused by wax structures that form when the temperature are low enough (around 50 °C).\textsuperscript{36} These solids can then impede the oil flow and therefore decrease its ability to lubricate. By adding pour point depressants, which are usually high molecular weight polymers, they can inhibit the formation of these wax structures. They don’t physically prevent the formation of wax solids, but instead lower the temperature at which they begin to form. There are two general types of pour point depressants: alkylaromatic polymers and polymethacrylates. They work by either preventing the wax crystals from forming by adsorbing them or by cocrystallizing with the wax to prevent crystal growth.

1.2.1.2 VI Improvers

VI improvers function by increasing the viscosity of the oil lubricant at high temperatures but not as much at low temperatures. The exact mechanism is not known but the working theory is that VI improvers at low temperatures adopt a coiled form so that the
effect on viscosity is minimized, but at high temperatures they straighten out, and the interactions between the long molecules and the lubricant produce a greater thickening effect.\textsuperscript{2} VI improvers are typically used in applications such as engine oils, automatic transmission fluids, and multipurpose tractor fluids.\textsuperscript{37} By using VI improvers, these applications can be used over a much wider temperature when compared to using the base stock without any additives.

1.2.1.3 Defoamants

In many applications, the oil lubricant is agitated enough that foaming can occur. In some cases, even the slightest amount of foaming can be detrimental and could cause catastrophic failure. When foaming occurs, gas (usually air) is trapped between the bubbles that are formed, which prevent the lubricant from cooling.\textsuperscript{36} By adding defoamants, such as silicone polymers in the parts per million range, they can help reduce foaming. These polymers are insoluble in oil, therefore great care is taken to choose the correct polymer size and procedures for blending to avoid these polymers from settling and causing damage rather than imparting beneficial properties.

1.2.1.4 Rust and Corrosion Inhibitors

The most important type of corrosion that can occur is due to organic acids that are formed when the lubricant itself degrades as well as any contaminants that are picked up and carried by the lubricant. These corrosion inhibitors act by forming a protective film and prevent the corrosive materials from coming into contact with the surface to which the inhibitors are bonded.\textsuperscript{36} By adding highly alkaline polar materials into the lubricant, it will
help neutralize any of the acids that are formed. By having a polar nature they are attracted towards the metal surface and are able to form the protective film.²

1.2.1.5 Antioxidants

Researchers discovered that different oils were able to provide a greater resistance to oxidation compared to others. It was later determined that the difference was due to the presence of naturally occurring antioxidants, which varied depending upon the source of the crude petroleum or the refining technique. The natural antioxidants found in the lubricants were found to have either sulfur or nitrogen containing functional groups. It was later discovered that phenols had similar properties. Certain amines and metals salts of phosphorous or sulfur containing acids were next to be discovered. This led to many classes of antioxidant compounds, which include: sulfur, phosphorus, sulfur-phosphorus, aromatic amine, hindered phenolic, organo-alkaline earth salt, organozinc, organocopper, and organomolybdenum compounds.²⁸ Once these antioxidant additives are consumed, the lubricants are no longer protected from oxidation and begin to degrade.
Figure 9. The different classes of antioxidants used as lubricant additive.

By adding antioxidants into lubricant oil mixtures, they can preserve the integrity of the lubricant by minimizing and delaying the onset of oxidative degradation. By using radical scavengers, peroxide decomposers, and metal deactivators, they can work by trapping catalytic impurities and destroying alkyl radicals, peroxy radicals and hydroperoxides.

Primary antioxidants, otherwise known as radical scavengers, work by readily donating a hydrogen atom to react with alkyl or peroxy radicals and thus effectively stopping the oxidation early in the cycle. Upon losing the hydrogen atom, and reacting, the net result is the formation of a stable radical from the antioxidant, a hydrocarbon and an alkyl peroxide. Hindered phenolic and aromatic amines are two common classes of primary antioxidants. The transfer of hydrogen from the oxygen or nitrogen atom forms quinones or quinoneimines, which do not contribute to the oxidation cycle. Some examples of
primary antioxidants include butylated hydroxytoluene (BHT)\textsuperscript{38} and alkylated diphenylamines.\textsuperscript{28}

Secondary antioxidants are peroxide decomposers. These include compounds that have sulfur or phosphorus present. They work by reducing the peroxyl radicals to alcohols. Some examples of secondary antioxidants include zinc dialkyldithiophosphate, phosphites and thioethers.\textsuperscript{28}

Metal deactivators function in two different ways. They can work as chelating agents and form a stable complex with the metal ion and thus render it unable to react catalytically.\textsuperscript{28} Alternatively, they can function as film-forming agents and coat the metal surface and form a protective film over the surface and physically restrict the metal ions from interacting. An examples of metal deactivators include substituted benzotriazoles.

1.3 \textit{N-Phenyl-1-naphthylamine}

\textit{N-Phenyl-1-naphthylamine}, or also known as \textit{N-phenyl-1-aminonaphthalene} (PAN) (1) is a lipophilic crystalline solid that is commonly used as an antioxidant in lubricating oils; heat, hydraulic, lubrication and bearing oils;\textsuperscript{39} and as protective agent in rubbers and rubber mixtures.\textsuperscript{40} The estimated production levels in Western Europe, China, USA and Japan were approximately 1000-15000 tonnes per year, 10000 tonnes per year, 500 tonnes per year and 3000 tonnes per year, respectively\textsuperscript{39} between 1986 and 1990.\textsuperscript{39} The secondary aromatic amine is thermally stable and exhibits good oxidation protection, especially for synthetic ester based oil lubricants.\textsuperscript{41}
The mechanism of action that 1 undergoes is mainly through interacting with the highly reactive and propagating peroxyl radicals. 1 can lose its N–H hydrogen atom, forming an aminyl radical and an alkyl peroxide molecule. What makes 1 a good antioxidant are its aromatic rings attached to the nitrogen, allowing for the delocalization of the unpaired electron. The aminyl radical can react with a second peroxyl radical, either at the nitrogen or at a carbon on either aromatic ring. Products resulting from the aminyl radical can include dimerization or reacting with another peroxyl on the nitrogen to yield a nitroxyl radical. This nitroxyl radical can further react to with more peroxyl radicals to yield a quinone imine oxide.
1.4 Current Methods of Lubricant Analysis

While current methods of lubricant investigation (TAN, OIT, as well as tests for contamination such as FTIR or elemental analysis)\textsuperscript{43,44} are thorough and can give an understanding of the lubricant’s health. They can be costly and the lubricant samples need to be taken off site to a lab to be performed. This can increase the time between sample acquisition and the delivery of the results.

1.5 GasTops

GasTops is a Canadian company and a world leader in the condition monitoring of rotating machinery. Their goal is to study the physical and chemical mechanisms of the degradation that occurs in lubricants. This proprietary technology can eventually lead to a possible in-line sensor to monitor lubricant ageing/oxidation via fluorescence of antioxidants and their oxidation products. By having a sensor that can monitor the lubricant (more specifically the antioxidant additives in the lubricant and its oxidation products) in real time, it reduces the need for the machine to be taken offline to acquire a lubricant sample, as well as the time needed to transport the sample to the lab and perform the various tests to determine the lubricant health. By monitoring the levels of antioxidants and its oxidation products, the machine will be able to identify the ideal time to change the lubricant (right before the antioxidants are completely spent).

In order to develop such technology, two scientific contributions are required: a method to calibrate the signals produced by the in-line sensor, and an accurate model of the oil degradation process. Once the sensor has been calibrated, it will be able to accurately
identify the types and concentrations of key degradation products and predict the remaining life of the lubricating oil extrapolated from the previously determined model.

To be able to calibrate the signals produced by the in-line sensor, a library of characterized degradation products is required in order to be able to compare the signals to that produced by the in-line sensor. The goal of this thesis is to synthesize known and/or hypothesized oxidation products arising from 1 in order to be used for the calibration and modeling processes.
Chapter 2: Results and Discussion

2.1 Oxidation of N-phenyl-1-naphthylamine

2.1.1 Rationale for Selecting Certain Compounds

The exact mechanism of lubricant degradation is complex, and instead of trying to elucidate the degradation mechanism of the oil lubricant and attempting to synthesize degradation products of the oil lubricant itself, it was thought to characterize the antioxidant oxidation products instead. By understanding what the oxidation products of the antioxidants are, monitoring them in practical scenarios would offer a good indicator of when the lubricant is approaching the end of its serviceable lifetime. The rationale for this is that once these antioxidants have served their purpose as sacrificial antioxidants (i.e., there is no more antioxidant remaining), the lubricant is left to be oxidized and therefore needs to be changed.

![Chemical structures](attachment:chemical_structures.png)

Figure 10. PAN (1), nitroxyl radical PAN derivative (2), carbon-carbon coupled PAN dimer (3), naphthyl oxidized PAN (4), carbon-nitrogen coupled PAN dimer (5), phenyl oxidized PAN (6).

Ideally, the exact mechanism of the oxidation of 1 would be completely characterized. Each intermediate and endpoint in the oxidation process would be identified and the characterization of these compounds would be done. The end goal would be a library of compounds that can be used to help calibrate any instruments that GasTops Ltd. would require. However, this isn’t the case, and in practice, the exact mechanism is unknown and there are many intermediates that 1 oxidation may produce and some of them
will have limited lifetimes. Additionally, during the development phase of the sensor, oil samples will be obtained from discarded oils rather than live, real-time data acquisition in a running system. Therefore, there will be a lag between the acquisition of the oil sample and the sample being analyzed. Therefore, certain compounds were selected and prioritized based on their relative stability. Not all compounds that were hypothesized to be formed were synthesized if their relative stability was known or hypothesized to be less than the time it would take for an oil sample to be obtained and analyzed. The rationale was that it would simply further degrade into other compounds (in many cases the ones we would be synthesizing) and therefore would not be observed in the analysis. Furthermore, such reactive compounds would likely not be found in high concentrations, as the barrier to their further reaction is low. One such compound (mentioned in Section 2.1.3) is 2, the nitroxyl radical derivative of 1 (Figure 10). It was picked first due to the ease of its synthesis, as reported in the literature, but other compounds were quickly prioritized due to its unstable nature. If it had degraded into other compounds by the time it was characterized, the time was better spent focusing on synthesizing these endpoint products.

2.1.2 \textit{N-Phenyl-1-naphthylamine} (PAN) 1

Unpurified, 1 directly from the manufacturer consists of large pink crystals. Due to previous literature reporting that 1 is an off-white powder, its ability to oxidize easily and its expected behavior to degrade photochemically in air,\textsuperscript{39} the first step was to purify 1 by removing the contaminants that may have accumulated during the manufacturing, packaging, and shipping process. After some optimization, a sequence of dissolution using hot ethanol, multiple rounds of decolourizing charcoal, filtration and finally crystallization
by addition of cold water was deemed the best procedure to reproducibly yield the desired white crystals (Figure 11).

![Unpurified 1 from the manufacturer’s bottle (left) and 1 recrystallized (right).](image)

During the recrystallization optimization, it was noted that the colour of the solution would gradually get clearer after each subsequent use of decolourizing charcoal and the proceeding filtration. After multiple filtrations, adding cold distilled water to the almost colourless ethanol solution would cause the 1 to precipitate, resulting in a turbid white suspension. However, through visual inspection, it was observed that while the majority of the coloured contaminants were removed, there were still some present, as some red-pink material would co-precipitate (as seen in Figure 12). If the solution was left undisturbed, this coloured precipitate would always collect at the bottom of the solution, and form a hard solid that can easily be removed during the filtration by decanting the solution carefully. The NMR spectra of the coloured contaminant only showed peaks characteristic of 1. Additionally, the HPLC chromatogram of both crude and purified 1 showed that there was no major change. The conclusion was that it there wasn’t enough of the coloured contaminant to be visible via NMR and HPLC (as seen in Figure 13 and 14).
Storing the purified 1 in the fridge is enough to keep it stable for about a week. Over time the white powder was observed to develop the similar pink colour, suggesting that the degraded material is beginning to accumulate.

Figure 12. Coprecipitation of 1 degradation products (red) during the purification of 1.

Figure 13. NMR spectra comparing unpurified PAN (top) and purified PAN (bottom)
2.1.3 Nitroxyl Radical Derivative 2

Scheme 13. The reaction scheme for the synthesis of the nitroxyl radical derivative using silver oxide.

Due to the ease of the reaction, and availability of various chemicals in the lab, the nitroxyl radical (2) was the first PAN oxidation product that was investigated. Compound 1 was stirred with silver oxide (which is readily available because of the easy reaction between silver nitrate and aqueous hydroxide base). After stirring at room temperature for 30 minutes, the solvent was removed to yield a brown oil.
It was quickly apparent that characterizing 2 via NMR was going to be challenging, due to the only molecular difference between the starting material and the product being a change from an N–H group to an N–O• group. Monitoring the N–H peak via NMR was an option, but it was thought to not be a reliable method due to other facts that may affect the integration and chemical shift of the N–H such as concentration and solvent effects. Therefore, the absence of the N–H peak may or may not be solely due to the consumption of the starting material.

The NMR spectrum of the crude mixture showed unexpected results. In addition to the expected peaks that are similar to the starting material, extra peaks are present, indicating that one or more molecular changes occurred in addition to the intended one.
Figure 16. NMR spectra comparison between freshly prepared 2 crude mixture (bottom), the same mixture after 1 week (middle), and starting material (top).

The NMR spectra of the same crude mixture after a week showed that the unexpected peaks were becoming more prominent in comparison to the expected PAN structure peaks. This shows that the contaminants have increased during the time between each of the NMR spectra. TLC data confirms that indeed multiple products have been formed, and that is what is being seen in the NMR spectrum. The identity of these unexpected compounds will be discussed later (see Section 2.2).
Figure 17. TLC plate of 2 after one week. Starting material (left lane), and crude mixture (right lane). The presence of many different spots indicates the formation of many different products.

One piece of evidence that suggests that 2 was formed is the comparison of the NMR spectrum of 1 and that of the crude mixture (seen below in Figure 18). Previously reported literature\textsuperscript{46} has used the peak broadening phenomenon due to the presence of radicals in solution to show that a reaction would undergo a di-radical pathway. When comparing the NMR spectra, the peaks from the nitroxyl radical crude mixture can be seen as more broad when compared to the starting material, which could indeed suggest the presence of 2.
Figure 18. The NMR spectrum of 1 (top) compared to the broad peaks of the spectrum of 2 (bottom).

The broadening is thought to be due to the radicals present in solution. The first couple of attempts at synthesizing 2 were done with exposure to the atmosphere, therefore oxygen was able to potentially react with any product being made, which could be the reason of the unexpected products being formed. The reaction was repeated however this time using anhydrous benzene and under an inert atmosphere. The goal was to limit the amount of oxygen present in order to try and retain as much 2 as possible.
Figure 19. NMR spectrum of nitroxyl radical PAN 2 mixture synthesized under atmospheric conditions (top) versus the same mixture but prepared in inert atmosphere (bottom).

By performing the reaction under an inert atmosphere, the result was the opposite of what was expected. The number of other peaks increased, which suggest that there are even more products being produced when compared to performing the reaction when exposed to the atmosphere. A possible reason could be because the reaction mixture does not have continued access to the oxygen in the atmosphere, and therefore the radical intermediate is allowed to react in other ways to yield different products.

After reading previous literature\cite{footnote} that suggests 2 is a fundamental intermediate during the antioxidant mechanism of 1 and can in turn further degrade into other products, the investigation of 2 was not pursued further. The rationale was that by the time testing (either offline or online) was to occur, any 2 would already have degraded into other compounds. Without any further knowledge on the other PAN degradation products, it would be futile trying to identify what these exact products were.
2.1.4 Carbon-Carbon Coupled Dimer 3

Scheme 14. The reaction scheme for the synthesis of carbon-carbon coupled PAN dimer using FeCl₃ and K₂CO₃.

One of the first PAN degradation products synthesized was the dimerization product between two PAN molecules at the C3 position of the naphthyl group (also known as CC PAN (3)). Using FeCl₃ as the primary reagent, and a mild base (K₂CO₃), the reaction was able to proceed in an hour at room temperature. After addition of triethylamine to presumably complex as much of the iron as possible, purification via flash-column chromatography (FCC) was not difficult because the product had a much lower Rf value than the starting material. The resulting product was a grey powder, which sometimes will have slight yellow-brown discolouration. The NMR spectra showed no apparent difference between the grey and coloured products, which suggests that it could be remaining iron that wasn’t removed.
Figure 20. The coloured fractions obtained after performing FCC on the CC PAN crude mixture (left). The final purified CC PAN product (right) isolated from fraction 2nd to 4th fractions in the top row.

It was noted that between the NMR spectrum between different batches of 3, some would result in the same general spectrum, but with much broader peaks. One hypothesis could be the presence of FeCl₃ that was not removed in the filtration process. It was noted that the final product had a slight brown colouration, which was most likely due to the mentioned FeCl₃ contaminant. Fe(III) possess 5 electrons, which can possibly lead to line broadening, similar to how the presence of the radical PAN derivative 2 could lead to line broadening in NMR.

The ¹H NMR spectrum of 3 yielded peaks at 8.15, 7.46, 6.93 and 6.25 ppm. Each peak integrated for 2H, 8H, 6H, 4H, 2H and 2H, respectively. These match the previously reported ¹H NMR peaks,⁴⁸ with similar integrations. The ¹³C NMR spectra were also compared and also had similar shifts.
Figure 21. NMR spectrum of two different preparations of 3. One resulted in defined peaks in the NMR spectrum (top) while the other resulted in wide peaks (bottom).
2.1.5 Naphthyl Oxidation Using Fremy’s Reagent

![Chemical reaction scheme](image)

Scheme 15. The reaction scheme for the synthesis of 4 using Fremy’s Reagent.

First reported in 1845, Fremy’s reagent (see Scheme 15) is the oldest known stable radical.\(^{49}\) Previous literature has reported success in using it to oxidize the naphthyl ring to produce Fremy’s PAN (4). By abstracting the N–H hydrogen atom, the resulting aminyl can undergo resonance. Further reaction with another molecule of Fremy’s reagent leads to the final product 4.\(^{50}\)

Fremy’s reagent is an orange powder that when dissolved in water, forms a deep purple colour. If left exposed to the moisture in the atmosphere and at room temperature for long periods of time, it may decompose into the disulfate hydroxylamine, \(\text{N}_2\text{O}\) and sulfate ion. Reactions were performed using a bottle of Fremy’s reagent of unknown provenance, but no product was obtained, presumably due to the age of the reagent. Due to the high cost of the reagent, preparing it in the lab was deemed a better alternative. Fremy’s reagent was prepared by preparing disulfate hydroxylamine using sodium bisulfite and sodium nitrate. Potassium permanganate was then used to oxidize to the radical and then precipitate it in its potassium salt state. Many attempts at preparing Fremy’s reagent were done due to its unstable nature during the preparation phase. At no point can the mixture be brought up to room temperature, as that is enough induce decomposition. When isolating the product, it was noted through experience that the solids should not be filtered.
through suction filtration such that the solids are dry of any solvent. Drying the solids to dryness will lead the product to quickly and exothermically decompose into a white solid that has faint odors of ammonia. Only after sufficient washes with methanol and acetone to remove any leftover potassium permanganate and acetic acid was it able to be dried overnight over Drierite.

![Image of Fremy's reagent](image)

**Figure 22. Purified Fremy’s reagent in its solid form (left) and dissolved in water as well as precipitated during the precipitation step of the preparation (right).**

Preparing the reaction solution containing Fremy’s reagent, disodium monohydrogen phosphate and 1 resulted in a dark purple solution that was stirred for 5 hours at room temperature. After stirring, the solution began to turn a dark red colour, similar to literature reports stating that 4 is a dark red crystal. Similar to the crude mixture from preparing 3, a number of different products were formed. It was noted that even though the crystals were expected to be red, and the crude reaction mixture was red, when fractions were being collected after purification via FCC, some fractions were yellow despite the TLC indicating that it was just 4. Further investigation determined that at low concentrations, the solution is yellow, and begins to turn red as the concentration increases. The red liquid in addition to the different $R_f$ values between the product and starting material fortunately made isolation via FCC easy.
Figure 23. Compound 4 during FCC purification (left) and in its solid crystal form (right).

Once isolated, the product was left in the fridge under inert atmosphere to prevent it from degrading. If left at room temperature or with access to oxygen, the red crystal will lose its colour and form a black solid, similar to that found in the FCC column during purification. Identification of 4 was verified by comparison with previously reported literature.51

During multiple attempts at synthesizing 4, an unexpected compound was made instead. As seen in the image below, doublet of doublet is seen at 8.11 and 7.79 ppm as well as a singlet at 7.00 ppm, each integrating for 1H. After some investigation, it was determined that this compound was napthoquinone, a common oxidation product of 1 under high temperatures.28,42 The proposed mechanism that this occurs is that the amine hydrogen from 1 is abstracted, and the aminyl radical is reacted with a peroxyl radical (in the context of the Fremy’s PAN reaction, it is most likely the Fremy’s reagent that is present) to yield a nitroxyl radical. The nitroxyl radical is then attacked via another peroxyl radical at the C4 position of the naphthyl group, resulting in a nitron compound. Loss of the peroxyl group results in a product similar to the expected 4, but with a nitron group instead of amine. Further attack by another peroxyl group, this time at the C1 position and then loss of an alkoxide radical results in nitrosobenzene and 1,4-naphthoquinone.
Figure 24. $^1$H NMR spectrum of 1,4-napthoquinone formed during various attempts at preparing 4.

Scheme 16. Top: The formation of 4 based off previous literature.\textsuperscript{42} Bottom: The proposed mechanism of the formation of nitrosobenzene and napthoquinone during the preparation of 4 based off the previously mentioned free radical oxidation mechanism.\textsuperscript{30,27} In the context of preparing 4, ROO• may be substituted with Fremy’s reagent.
2.1.6 Carbon-Nitrogen Coupled Dimer 5

Scheme 17. The reaction scheme for the synthesis of carbon-nitrogen coupled PAN dimer using 2,2'-bipyridine, Cul, 18-crown-6, K$_2$CO$_3$ and DMPU.

Previous literature$^{52}$ reported the synthesis of the carbon-nitrogen coupled dimer (known as CN PAN (5)) through the use of a pressure vessel and heated to 240 °C. In order to reduce the risk of fire, we opted to use a microwave reactor instead of a pressure vessel/kettle. Unfortunately, preliminary attempts along these lines proved to be problematic.

An initial reaction with the microwave set for 3 hours at 180 °C and with scaled down amounts showed the reaction mixture was heating up and reacting. However, it was noted that the thin cylindrical nature of the microwave vial would cause some issues. One of the major reagents by weight is K$_2$CO$_3$. This was one of the reagents added last, and therefore accumulated at the top of the vial, while the rest of the reagents (1, Cul, and 2,2’-bipyridine (BIKY)) were near the bottom because they were added first. Of all the reagents present, K$_2$CO$_3$ has the highest melting point (891 °C). This led to all the chemicals reaching their melting point and collecting at the bottom of the vial, but the K$_2$CO$_3$ would
still be near the top, preventing it from participating in the reaction. Subsequent reactions were prepared by homogenizing the mixture before adding it to the pressure vial to prevent this issue from happening.

Figure 25. The reaction vessel containing the CN PAN crude mixture before it was heated to 240 °C (left), after (middle left), and during quenching with dilute HCl (middle right).

The synthesis was repeated but now at full scale, thus requiring a larger vial that no longer had the pointed bottom since the smaller pressure vial would not be able to contain all the reagents. This proved to be detrimental because once the reaction mixture was heated to the required temperature of 240 °C, the reagents would go from the solid state which was not as condensed and took up a fair amount of volume in the vial, to a melted liquid state, reducing the overall volume. This would bring the volume of the reagents lower than the minimum volume that the vial requires in order to operate. This led to inaccurate heating from the instrument. The pressure in the vial would sometimes fluctuate between different runs. For example, some runs the pressure would be stable at around 3-5 bar, but some runs it would continue to rise as the temperature rose. This would lead to either the machine detecting the constant rise in pressure and aborting the run early, or to the structural integrity of the cap failing and leading to expulsion of the built-up pressure in the vial.
There was an attempt to scale up the reaction using a bigger pressure vial as it would better contain the pressure build up during the reaction. The microwave was set to heat up to 80 °C for 3 minutes before it was left to cool. The mixture was observed before it was placed back in the microwave reactor and this time the temperature was increased to 120 °C, and this was repeated up to the required 240 °C. The goal was to observe what was occurring in the flask during the heating process. In the reaction mixture, the vast majority of the reagents are in the solid state with only a fraction of it being the liquid solvent (about 2 grams of solid versus the 150 µL of solvent). As seen in Figure 26, the low melting point reagents (1, BIPY) began to melt, which can be seen from the increase in liquid in the reaction mixture. As the temperature continues to rise, the reaction mixture began to take on a red appearance.

Figure 26. The reaction vessel containing CN PAN crude mixture, heated to various temperatures (from left to right: 80, 120, 160, 200, 240 °C).

After multiple failed runs with the microwave reactor, the method of heating was changed to a standard oil bath. The reaction vessel was placed in an oil bath that was heated to 240 °C. Not only were the contents of the vessel observable during the reaction, but the temperature was also monitored with far greater ease and accuracy.

Originally, the protocol called for the reaction mixture to be quenched with diluted HCl before filtering off the precipitate, and finally washing the organic precipitate with ammonium hydroxide and water. However, when put in practice, the precipitate would be a brown oil and would either get stuck in the filter paper or make it through entirely. This
made it difficult because the product would now have to be extracted from the filter paper. Instead, the solution was diluted in ethyl acetate and extracted using aqueous HCl instead. This modification made the work up process easier and removed the possibility of the organic precipitate getting lost in the filter paper.

Figure 27. The TLC of CN PAN crude mixture in short wavelength (left) and long wavelength (right) UV. A large smear (right lane, left image) can be seen and hides the presence of other spots which can be seen in the long wavelength (right lane, right image) UV. PAN (left lane, both images) is used as the reference. The middle lane in each image is the co-spot of PAN and the reaction mixture.

The TLC of the crude mixture (right lane) in short wavelength (254 nm) (Figure 27, left image) shows that there is still some starting material present, but there is also a large smear starting at the baseline, which could be the product or any of the reagents. Under long wavelength UV (365 nm) (Figure 27, right image), the TLC shows that there are multiple products that are hiding behind this smear.
A quick look at the $^1$H NMR spectrum of the crude mixture shows two doublets at around 8.7 ppm and 8.4 ppm which were hypothesized to be the two characteristic protons in the structure that are flanked by both nitrogens (as seen in the structure shown in Figure 28). However this proved to not be the case once the product was purified. Two main products were obtained after purification by FCC. The other minor products that were observed to be hidden by the baseline smear under the low wavelength UV in the TLC were not present in any of the fractions. The $^1$H NMR spectra of the fractions (shown below in Figure 29) showed that two compounds were present. The first was the starting material PAN, and the second was BIPY, which was discovered to be the compound that gave the brown smear at the baseline when performing TLC.
Figure 29. Comparisons between the NMR spectrum of CN PAN crude mixture (bottom), PAN 1 (middle) and BIPY, one of the recovered products from after FCC (top).

Despite the $^1$H NMR spectrum of the crude reaction mixture providing only peaks that correlate to the starting material and BIPY, the TLC showed that there are other products being formed. One hypothesis was that the two known products are so abundant in the NMR tube that any products have such small quantities in comparison that they don’t provide an NMR signal.

While trying to develop a solution to this problem, the contents of the aqueous phase and organic phase were being investigated. This is because during the extraction step using dilute HCl, a dark red emulsion would develop, which would sometimes prove difficult to fix. This emulsion was separated, and the contents of both the emulsion and aqueous solution were run examined via TLC. The only spot in either lane was a brown smear near the baseline, which was determined earlier to be BIPY. This was proven to be true when the aqueous phase was extracted with ethyl acetate. The solution quickly crystallized upon concentration and the $^1$H NMR spectrum showed that it indeed was BIPY.
After this discovery, the reaction was repeated but this time the number of dilute HCl washes was increased. Each subsequent wash was monitored by TLC to ensure the removal of BIPY. The process worked and the products hidden in the TLC were now more visible, which would in theory provide an easier time in isolating these products via FCC and for the signals to appear when performing NMR spectroscopy.

Figure 30. TLC plates before (left) and after the removal of BIPY (right). As seen in the right lane, the presence of the smear is greatly reduced after several washes with dilute acid.

Separation of the different products proved to be difficult because of the similar $R_f$ values between the starting material and different products. The method that was developed was to run multiple separations using FCC. The purpose of the first separation was to remove as much of the starting material as possible. Each fraction was monitored until the PAN spot was no longer present. The rest of the products were then eluted from the column, concentrated, and a second column was then prepared. The second column employed a lower polarity eluent, with the purpose of separating each product. The separation proved successful, with the production of a slight orange powder that would fluoresce very brightly under long wavelength UV.
Figure 31. TLC of purified CN PAN (left), purified CN PAN in its solid form (center), and CN PAN fluorescing in solution under UV light (right).

Once each individual spot on the TLC was separated and concentrated, the next step was to determine which spot was the desired product. The identities of the other products will be discussed in Section 2.2. One of the products was indeed 5 (seen via the NMR in Figure 33), which was confirmed by comparison with the reported peaks. However other peaks which were unexpected were also seen in the NMR. It was unsure if these peaks were from a contaminant or were part of the product that was being made. It was unlikely to be a contaminant due to the presence of only one spot in the TLC, however these peaks were not listed in the previous report of the synthesis of 5.

Figure 32. COSY spectrum of CN PAN with Fremy’s PAN contaminant (left), COSY spectrum of the same CN PAN sample left in the NMR tube for 4 hours (center) and COSY spectrum of pure 4 as reference (right).

Proton and COSY NMR spectra were acquired on the same NMR tube a couple hours later because the colour of the NMR tube turned from a slight orange to a darker,
more red colour. The purpose was to see if there were any changes in the NMR spectra from the first time it was run. When the proton NMR spectrum was acquired in preparation for the COSY experiment, the spectrum showed that the peaks that correlated to 5 were no longer present, and the unexpected peaks were what was left. It was concluded that in the time between each NMR spectrum being acquired, 5 had degraded and what was left is presumed to be the degradation product (which will be mentioned later in Section 2.2).

![Figure 33. Comparison between the 1H NMR spectra before the degradation of 5 (bottom) and after (top).](image)

Unfortunately, all further attempts at trying to obtain an NMR spectrum of 5 would result in the same outcome. Often the spectrometer would have trouble locking and it would produce a spectrum with no signal except for the expected chloroform signal. It was suspected that trace acid found in the deuterated chloroform solvent was reacting with the product, causing it to degrade. At this point we elected to acquire the NMR spectrum using deuterated benzene as a solvent instead. This led to successful acquisition of an 1H NMR spectrum that can be used to validate future preparations of 5.
Figure 34. NMR spectrum of the carbon-nitrogen PAN dimer using deuterated chloroform (black) and deuterated benzene (red)

2.1.7 Phenyl Oxidation

There were two different proposed routes to get to the phenyl oxidized PAN derivative (also known as phenol PAN (6)), with the goal of eventually synthesizing the quinone imine derivative. The first attempted route was using 1-naphthol and 4-aminophenol in the presence of excess sodium bisulfite. The mixture was heated at reflux before extraction with ethyl acetate and purification via FCC. The product was dark purple flakes that crystallized without difficulty. Preparing an NMR spectrum using CDCl₃
produced a spectrum that had the expected peaks but was missing the characteristic OH peak. Rerunning the NMR using DMSO-$d_6$ as a solvent instead not only showed the proper OH peak but rendered the N–H peak sharper, as opposed to the broader peak observed in CDCl$_3$. Due to the success with the first route, the second route was not attempted. Further transformation to the carbonyl derivative could not be done due to lack of time and delays due to COVID-19.

Figure 35. NMR spectrum of 6 in CDCl$_3$ (bottom) versus Phenol PAN in DMSOD$_6$ (top). Note the presence of the hydroxyl and amine groups in the DMSO-$d_6$ spectrum that were not present in the CDCl$_3$ spectrum.

2.2 Findings From Synthesizing PAN Derivatives

Previously, it was noted that crude 1 from the manufacturer has a red-pink colour, and when recrystallized, this colouration is no longer present and purified 1 is white. Throughout the course of purified 1 in experiments, it was repeatedly exposed to the
atmosphere, and over time the pink colour would slowly return. However multiple to determine the identity of what was causing the pink colour by performing NMR resulted in no change in the spectrum. One possible reason is that the small amounts of degradation was enough to cause a pink colour, but not in sufficient quantity to be seen in NMR. Once pure 4 was prepared and characterized, it was hypothesized that the pink colour could be to small amounts of 4 accumulating as 1 degrades. Unintentionally due to the COVID-19 pandemic, a small amount of freshly recrystallized 1 was left in the fridge for 4 months and was not filled with inert gas. It was observed that the pink colour had returned, this time more intense than usual (presumably due to the prolonged time that it was left to stand). The sample was analyzed by the \(^1\)H NMR to see what it had degraded to while kept in the fridge. The NMR spectrum indeed shows that 4 is present, with the characteristic peaks at 8.54, a doublet at 8.23, as well as a doublet at 6.74 ppm present.

Figure 36. Comparison between the NMR spectrum of 1 (top), 4 (middle), and 1 after 4 months (bottom). Note the presence of peaks characteristic of 4 in the bottom spectrum.
Prioritizing 2 as the first PAN derivative to investigate was inefficient. This was because the reaction leads to multiple products, and the lack of knowledge of any other PAN derivatives made it difficult to interpret or otherwise utilize the results. However, after preparing a couple of different PAN derivatives, investigating the previous NMR spectra that were obtained led to some interesting discoveries. Looking back at the nitroxyl radical reaction that was done under inert atmosphere and using anhydrous benzene, some of the previously unidentifiable peaks can now be correlated to the peaks characteristic of 4 as well as 3. As seen in the stacked NMR plot below (Figure 37), there is a doublet in the nitroxyl radical NMR spectrum at 8.54, a doublet at 8.23, as well as a doublet at 6.74 ppm. These are all peaks that are characteristic of 4. Additionally, there are doublets at 8.15, 7.51, and 7.12 ppm, which are all characteristic of 3.

Figure 37. Comparison between the NMR spectrum of 2 under inert atmosphere (bottom), 3 (center), and 4 (top). Note the presence of some of the characteristic peaks that are attributed to 3 and 4 are found in the nitrooxide radical mixture.
Looking at the TLC of the nitroxy radical crude mixture shows even more evidence that other products are present. Spots that correlate to 3, 4 and even 5 are present when looked at using the low wavelength UV light.

Figure 38. TLC of the nitroxy radical PAN after one week. Note the presence of PAN (1), CN PAN (2), CC PAN (3), Fremy’s PAN (4) in the mixture.

Figure 39. The potential products that can be formed with the nitroxy radical PAN derivative as an intermediate.
When the synthesis of 3 was done, it was noted that a red side product was being formed. It was unclear at the time what this was, but a sample of it was kept and NMR spectra were acquired for future reference. It was ultimately discovered to be 4. Comparing the NMR spectra between the pure freshly prepared 4 and the fractions that contained a red or yellow colour showed presence of the characteristic peaks. The same behavior where dilute concentrations of 4 were yellow was also found to be present, which explains the yellow to red and back to yellow gradient seen in the fractions, as this indicates where 4 was eluting.

![NMR spectra comparison](image)

*Figure 40. Comparison between the NMR spectrum of 3 crude mixture (bottom) and 4 (top). Note the presence of some of the 4 characteristic peaks found in the crude mixture.*

With the preparation of 5 being one of the last PAN derivatives to be prepared, it was easy to figure out what the side products were because of the array of information that
had been gathered for the previous PAN derivatives. It wasn’t clear at first but when the NMR sample of 5 was degraded, it was clear that the remaining peaks were that of 4. The characteristic peaks at 8.54, 8.23, and 6.74 ppm were all present. Additionally, the colour would turn red as it degraded, which coincides with the red colour of 4. Not only was 4 present when preparing 5 dimer, but 3 was also found. One of the last products to elute during the separation of the crude mixture provided a $^1$H NMR spectrum that lines up with 3.

![Figure 41. Comparison between the NMR spectrum of CN PAN crude mixture (bottom), separately prepared 4 (top), and degraded CN PAN mixture (middle) to show the characteristic peaks attributed to 4.]

Of the numerous PAN degradation products synthesized, it was noted that 3 was the most stable, even more stable than 1 itself. As previously shown in Section 2.1.2 purified PAN would gradually degrade into 4 as seen via the NMR and by the onset of a slight pink colour in the otherwise white powder. After 2 weeks of constant exposure to
the atmosphere from accessing 1 for use in experiments, performing TLC showed the presence of degradation, and another recrystallization would be required. Although it was present by TLC, it was never in sufficient quantities to be seen via NMR spectroscopy. 3, however, was found to be stable after 4 months in the similar storage conditions. The only difference being that it wasn’t continuously exposed to atmosphere. A sample of 3, after being stored in the fridge for 4 months resulted in no change in the NMR spectrum, indicating that no degradation had occurred. 5, on the other hand, was found to be quite unstable in comparison. When stored under the same conditions (inert gas and at 4 °C), 5 would degrade after a couple days, even less so if it was not stored under inert gas. 4 was found to be more stable than 5, but will still degrade after a couple days, as indicated by the disappearance of its red colour and the appearance of black crystals in its place.
Chapter 3: Conclusions and Future Directions

The goal of the project was to synthesize PAN oxidation products in pure form and sufficient quantities for use in the development of in-line sensors by GasTops Ltd. The purpose of these sensors would be to monitor the remaining serviceable lifetime of the oil lubricant of industrial scale applications. To summarize, various oxidation products of PAN were synthesized, purified and provided to GasTops: carbon-carbon coupled dimer, carbon-nitrogen coupled dimer, naphthyl oxidized PAN, phenyl oxidized PAN, and nitroxyl radical PAN. These compounds were identified to be common occurring products and attempts were made to synthesize these compounds. The synthesis of carbon-carbon coupled PAN dimer resulted in a grey powder that when stored under nitrogen and in 4 °C temperatures, would be stable for a several months. It was also discovered that in the process of synthesizing this PAN product, the formation of Fremy’s PAN would also occur. The synthesis of Fremy’s PAN resulted in red crystals that would degrade into nitrosobenzene and napthoquinone. Storage under nitrogen and at 4 °C temperatures would slow down, but not stop this decomposition. It was discovered that PAN, when left for a prolonged period with access to oxygen, will auto-oxidize to Fremy’s PAN, as evident via NMR spectroscopy and via the appearance of a pink colour that is characteristic of Fremy’s PAN. Synthesis of carbon-nitrogen coupled PAN dimer resulted in the synthesis of a slightly yellow powder that would degrade into Fremy’s PAN after a couple days of storage under nitrogen and at 4 °C. During the synthesis of this PAN oxidation product, it was discovered that both carbon-carbon coupled PAN dimer and carbon-nitrogen PAN dimer would be synthesized as well. Synthesis of nitroxyl radical PAN resulted in a highly unstable product that would degrade into the other products that were previously
mentioned: carbon-carbon coupled, carbon-nitrogen coupled dimer, as well as Fremy’s PAN. Synthesis of phenyl oxidized PAN resulted in violet crystals.

![Chemical structures](image)

Thanks to the work of Timothy Mack, a solution of 1 was dissolved in decylacetate (decac) was heated to 175 °C under 4 bar of O₂ and HPLC was performed on samples that were heated for 4, 12, and 20 hours. By using samples of the various compounds that were prepared, the retention times of compounds 1, 2, 3, and 5 were determined and compared to the results from the oxidation experiments previously described. As seen in Figure 42, the targeted compounds were present in the oxidation experiment. After 4 hours, as well as 12 hours, 4 and 5 could be seen as oxidation products. After 20 hours, 4 is seen to be the most prominent oxidation product while the amount of PAN has begun to decrease.
There is still much work that can be done in the future to help support the sensor development. The identification of some of the other degradation products resulting from the oxidation of nitroxy radical PAN would be beneficial and could potentially lead to other PAN products that were not investigated. Investigation using radical trappers such as TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl can be used to isolate and purify the radical derivative. Scaling up the nitroxy radical PAN reaction can possibly lead to the synthesis of multiple products, which in theory can be isolated and subsequently used as pure samples that can be used by GasTops and other members of the project. Further refinement of the synthesis of carbon-nitrogen coupled PAN dimer would also be beneficial. Further oxidization of phenyl oxidized PAN from the alcohol to the quinone imine is a synthesis that can be done in the future. As seen in the work (Figure 42)
conducted by Timothy Mack, another member of the project, the CN PAN derivative is a common oxidation product and by further refining the synthesis would help in providing the samples for future work. Since the compounds are shown to be present during oxidation experiments using O₂, the fluorescence characteristics of the PAN oxidation products can be monitored and the changes can be observed. This information can then be used for the sensor as it would monitor the disappearance of PAN as it is consumed and the appearance of the PAN oxidation products.
Chapter 4: Experimental Procedures

4.1 General Experimental

All chemicals were used as received unless explicitly stated. All reactions involving air- or moisture-sensitive reagents or intermediates were performed under a nitrogen atmosphere in oven-dried glassware. When referring to reaction temperatures, they refer to the temperature of the cooling/heating bath. Volatile solvents were removed under reduced pressure using a Heidolph Laborata 4011 rotary evaporator at 40 °C (temperature of water bath). TLC was performed on Silicycle 250 μm thickness silica plates. Plates were visualized using fluorescence quenching under UV light using an Entala UVGL-25 UV Lamp using either short or long wavelength. FCC was performed using Silicycle 40-63 μm particle size silica. Filter Agent Celite 545 was use as a plug for filtrations when mentioned. Gravity and suction filtration used Fisherbrand P8 coarse porosity filter paper. Compounds that were dried under high vacuum refers to a reduced pressure of ~20 mTorr. FTIR spectra were recorded on ABB Bomem MB Series FTIR spectrometer. 1H and 13C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for 1H and 75 MHz for 13C and were obtained at the indicated field as solutions in CDCl3 (stored over activated 4 Å molecular sieves) unless otherwise stated. Chemical shifts were referenced to TMS (δ = 0.00 ppm) and are reported in parts per million (ppm). Coupling constants (J) are reported in Hz and the splitting abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Yields refer to purified compounds unless explicitly indicated as crude.
4.2 Purification of N-Phenyl-1-naphthylamine (PAN)

5.00 g of unpurified PAN was dissolved in 50 mL of ethanol heated to 70 °C and stirred for 5 minutes. 1.51 g of decolourizing charcoal was added and the solution was stirred for another 10 minutes and kept on the hot plate. After sufficient stirring, the black opaque suspension was filtered (while hot) by gravity. The filtrate was returned on the hot plate (70 °C) and another portion of decolourizing charcoal was added and stirred for an hour. After stirring the solution was filtered a second time. If the solution was deemed still impure (the filtrate was determined to be impure if the purple tint remained), a third round of decolourizing charcoal and stirring was used. Once the solution appeared colourless, the solution was filtered into a beaker and set aside to cool to room temperature. Once cooled, 50 mL distilled water cooled to 0 °C via an ice bath was slowly added to precipitate the dissolved PAN. The solution was then placed in the fridge and stored at 4 °C to finish precipitating overnight. The solution was then filtered via suction filtration, and left with the suction on for 30 minutes with occasional stirring to ensure that any residual ethanol was evaporated, and any residual water was filtered. The resulting white amorphous crystals (3.64 g, 72% recovery) were then stored in the fridge. If the recrystallized PAN was deemed impure (judged by a change in the white crystal to an off-pink colour), one repetition of decolourizing charcoal and filtration was used for repurification.

*RF* 0.52 (10% EtOAc/hexanes; UV). *IR* (film): 3389, 3051, 1600, 1497, 791, 776 cm⁻¹

*1H NMR* (CDCl₃, 300 MHz): δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.68, 1H), 7.51 (dd, *J* = 2.1, 7.1, 1H) 7.43 (dd, *J* = 1.47, 6.84Hz, 1H), 7.38 (dd, *J* = 2.85, 7.74 Hz, 1H), 7.31 (m, 2H), 7.19 (m, 2H), 6.88 (m, 3H), 5.81 (s, 1H). *13C NMR* (CDCl₃, 300 MHz): 144.7, 138.7, 134.7, 129.4, 128.6, 127.7, 126.1, 126.0, 125.7, 123.0, 121.8, 120.5, 117.4, 115.9 ppm.
4.3 Synthesis of Nitroxyl Radical PAN 2

The procedure was adapted from Forrester et al.\textsuperscript{53} PAN (1.00 g, 4.57 mmol, 1.00 equiv) was dissolved in 30 mL anhydrous benzene at room temperature. Ag\textsubscript{2}O was prepared by adding an aqueous solution of NaOH (6.62 g in 200 mL, 0.16 mol, 1.0 equiv) to an aqueous solution of AgNO\textsubscript{3} (2.74 g in 50 mL, 0.16 mol, 1.0 equiv). The precipitate was collected and rinsed thoroughly with water until neutral pH. Ag\textsubscript{2}O (3.00 g, 12 mmol, 2.8 equiv) was added along with anhydrous MgSO\textsubscript{4} (1.80 g, 15 mmol, 3.5 equiv). The solution was stirred for 30 minutes before filtered by gravity. The filtrate was then concentrated, and the residue was recrystallized using 50 mL hexane to yield 0.72 g of a dark brown oil that proved to be a complex mixture whose composition changed over time (see Section 2.2).
4.3 Synthesis of C-C coupled PAN dimer 3

The procedure was adapted from the original works by Li et al.\textsuperscript{48} 6 mL of 1,2-dichloroethane was added to a round-bottom flask containing K$_2$CO$_3$ (0.14 g, 1.0 mmol, 1.0 equiv), PAN (0.22 g, 1.0 mmol, 1.0 equiv) and stirred for 5 minutes at room temperature. After stirring, FeCl$_3$ (0.19 g, 1.2 mmol, 1.2 equiv) was added in one portion. The reaction mixture was then stirred for 1 at room temperature. As the reaction stirred, a brown colour began to form. Once the reaction was deemed complete by TLC, 1 ml of Et$_3$N was added and the reaction mixture was stirred for additional 5 min. A pad of celite was prepared and the solution was filtered through and washed with EtOAc (3 x 20 mL). The organic filtrates were combined, dried over anhydrous MgSO$_4$, and concentrated. The residue was then purified by column chromatography (10:90 EtOAc /hexanes) to yield fluffy grey foam (0.132 g, 0.3 mmol, 30%). The compound is stable for at least 2 months when stored under inert atmosphere at 4 °C.

$R_f$ 0.28 (10% EtOAc/hexanes; UV). IR (thin film): 3392, 3043, 3011, 1600, 1497, 752, 693 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.15 (d, $J = 8.4$ Hz, 2H), 7.46 (m, 8H), 7.29 (t, $J = 7.5$ Hz, 6H), 7.10 (d, $J = 8.5$ Hz, 4H), 6.93 (t, $J = 8.9$ Hz, 2H), 6.25 (s, 2H). $^{13}$C NMR
The original synthesis was reported by Zimmer et al. A slurry of Celite Filter-Aid was made using 15 g of Celite Filter-Aid and 75 mL of ethyl acetate. A Buchner funnel with the Filter-Aid slurry was prepared prior to beginning the synthesis so that it was immediately available when needed. An aqueous solution of NaNO₂ (5 M, 14 g in 40 ml dH₂O, 0.16 mol, 1.6 equiv) was prepared and the solution was poured into a 1 L beaker with 80 g of chopped/crushed ice. A separate solution of aqueous NaHSO₃ (5M, 21 g in 40 ml dH₂O, 0.21 mol, 1.0 equiv) was prepared and added to the reaction mixture over 1 min and followed by addition of 8 mL of glacial acetic acid in one portion. The reaction was deemed to be complete after 2-3 min, when the colour of the solution darkens. A small sample of the solution was used to treat an aqueous solution of iodine. If it failed to decolourize then the reaction was deemed complete. A concentrated solution of aqueous ammonia (15 ml, 30% w/w) was added and the mixture was cooled in an ice bath, with fresh ice continuously added to ensure that the reaction mixture temperature remained below 15 °C. A solution of aqueous potassium permanganate (0.2 M, 5 g in 150 mL dH₂O, 0.03 mol, 0.3 equiv) was cooled using an ice bath added dropwise into the reaction mixture.
over the course of 1 hour. The precipitated manganese dioxide was removed via suction filtration over the previously prepared Celite Filter-aid into a filter flask containing saturated KCl (saturated at 0 °C, 100 ml). A sample of the filtrate was set aside and treated with an equal portion of saturated potassium chloride solution to start the precipitation. After filtration the solution was placed back in an ice bath and small portions of the separately precipitated Fremy’s salt was added occasionally to promote the crystallization process. An extra 150 mL of aqueous KCl solution was then added dropwise over 10 min. Once the addition was finished, the solution was left on ice for 45 minutes to promote further crystallization. The orange precipitate was collected using suction filtration but not to dryness. It was placed back into a beaker and to it a cold mixture of 5 ml of concentrated aqueous NH₃ in 75 ml of methanol was added. The washing step was repeated two more times to insure the removal of residual potassium permanganate. It was then washed with a solution of ammoniacal saturated KCl solution (5% v/v 30% aqueous ammonium hydroxide), then twice with ammoniacal methanol (5% v/v 30% aqueous ammonium hydroxide), and finally with acetone. Once the final wash with acetone was done, the precipitate was finally filtered to as dry as possible without letting air through the filter. The crude Fremy’s salt was spread on a watch glass for 10-15 minutes to let the acetone evaporate. It was then dried over overnight in vacuo. The final result was long orange rods (20.56, 0.07 mol, 75%). The compound was stored under nitrogen at 4 °C.

The crude Fremy’s salt was purified through recrystallization using 2 M sodium bicarbonate solution heated to 47 °C and then cooled to room temperature before cooling further on ice and finally isolated using suction filtration and dried overnight in vacuo to
yield a fine orange powder (13.71 g, 66% recovery). The IR spectrum matched an authentic sample purchased from Sigma Aldrich.

**IR (ATR):** 1277, 1250, 1038, 844 cm\(^{-1}\).

### 4.5 Synthesis of Naphthyl Oxidized PAN 4

![Synthesis of Naphthyl Oxidized PAN 4](image)

The procedure was adapted from previous literature reported by Forrester et al.\(^{42}\) A solution of PAN (0.22 g, 1.0 mmol, 1.0 eq) in 30 mL of acetone was prepared. In a separate beaker, to a solution Fremy’s salt (0.67 g, 2.5 mmol, 2.5 equiv) in dH\(_2\)O (50 mL) and NaH\(_2\)PO\(_4\) (0.16M, 4mL) Once both solutions were prepared, the PAN solution was added in one portion to the Fremy’s salt solution, and the mixture was stirred at RT for 5 h. The acetone was removed from the mixture using the rotary evaporator at room temperature. The aqueous phase was then extracted with CHCl\(_3\) (3 x 30 mL). The extracts were combined, dried over anhydrous sodium bicarbonate and concentrated into a dark brown oil. The oil was then purified using column chromatography (10:90 EtOAc /hexanes) to yield bright red crystals (0.126 g, 0.5 mmol, 54%). The \(^1\)H NMR data matched previously reported literature.\(^{51}\)

\(R_f\) 0.22 (10% EtOAc/hexanes; UV). **IR** (thin film): 3297, 3041, 2921, 1735, 1653, 1299, 738 cm\(^{-1}\) **\(^1\)H NMR** (CDCl\(_3\), 300 MHz): \(\delta\) 8.51 (d, \(J = 7.6\) Hz, 1H), 8.19 (d, \(J = 7.6\) Hz, 1H), 7.73 (dtd, \(J = 1.5, 7.4, 20.5\) Hz, 2H), 7.44 (t, \(J = 6.5\) Hz, 2H), 7.25 (m, 3H), 6.93 (d, \(J = 8.2\) Hz, 2H), 6.71 (d, \(J = 10.5\) Hz, 1H) **\(^{13}\)C NMR** (CDCl\(_3\), 300 MHz): 133.9, 133.1, 131.3, 130.3, 129.4, 129.3, 129.0, 128.8, 128.6, 126.1, 125.7, 125.4, 125.2, 120.3 Hz.
4.6 Synthesis of Carbon-Nitrogen Coupled PAN Dimer 5

The original preparation was reported by Zhang et al.\textsuperscript{52} The reactions were performed under nitrogen gas using dried solvents. A mixture of PAN (0.88 g, 4.0 mmol, 1.0 equiv), 2,2'-bipyridine (0.63 g, 4.0 mmol, 1 equiv), CuI (0.10 g, 0.50 mmol, 0.1 equiv), 18-crown-6 (0.05 g, 0.13 mmol, 0.03 equiv), K\textsubscript{2}CO\textsubscript{3} (1.11 g, 8.0 mmol, 2.0 equiv) and DMPU (0.15 ml) was placed in a Synthware cylindrical pressure vessel under nitrogen gas and placed in an oil bath already heated to 240 °C and a blast shield was placed as a safety precaution. The mixture was then left to stir for 5 h while the reaction vessel was closely monitored to ensure safety. Once the reaction time was complete, the heat was turned off and the system was left to cool. Once cooled the mixture was quenched with 10% w/w aqueous HCl solution. The aqueous solution was extracted with EtOAc (3 x 30 mL). The organic layers were combined, dried over anhydrous magnesium sulphate, filtered and concentrated using a rotary evaporator. The resultant brown oil was then purified using column chromatography (10:90 EtOAc /hexanes) to yield a light brown powder (0.52 g, 1.1 mmol, 28%). The \textsuperscript{1}H NMR data matched previously reported literature.\textsuperscript{52}
$R_f$ 0.37 (10% EtOAc/hexanes; UV). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.18 (m, 3H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.14$ Hz, 2H), 7.38 (dt, $J = 8.4$ Hz, 3H), 7.33-7.18 (m, 5H), 7.14 (t, $J = 7.5$ Hz, 2H), 7.00 (d, $J = 7.6$ Hz, 2H), 6.91 (dt, $J = 21.8$, 7.17 Hz, 2H), 6.71 (d, $J = 7.3$ Hz, 2H), 5.92 (s, 1H) Hz.

4.7 Synthesis of Phenyl Oxidized PAN

A mixture of 1-naphthol (1.00 g, 6.9 mmol, 1.0 equiv), 4-aminophenol (1.01 g, 9.26 mmol, 1.39 equiv) and sodium bisulfite (5.2g, 50 mmol, 7.2 equiv) in 30 mL of dH$_2$O was refluxed for 36 hours under nitrogen gas. The reaction mixture was cooled via an ice bath to 0 °C and diluted with 50 mL of dH$_2$O. It was then extracted with EtOAc heated to 40 °C (3 x 50 mL). The organic layer was separated and washed with dH$_2$O (1 x 50 mL), dried over anhydrous MgSO$_4$, filtered, and concentrated using a rotary evaporator to yield a purple solid. It was then purified by flash chromatography (10:90 ethyl acetate: hexanes). The final product resulted in purple flakes (0.83 g, 3.59 mol, 52%).

$R_f$ 0.17 (10% EtOAc/hexanes; UV). IR (thin film): 3500-3200, 2110, 1229, 960, 703 cm$^{-1}$

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 10.11 (s, 1H), 9.10 (s, 1H), 8.27 (d, $J = 9.6$ Hz, 1H), 8.14 (d, $J = 9.9$ Hz, 1H), 7.82 (m, 3H), 7.45 (m, $J = Hz$, 2H), 7.04 (d, $J = 8.73$ Hz, 2H), 6.77 (d, $J = 8.73$ Hz, 2H) $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 8.02 (d, $J = 9.6$ Hz, 1H), 7.87 (d, $J = 9.9$ Hz, 1H), 7.49 (m, 3H), 7.34 (t, $J = 7.59$ Hz, 1H), 7.11 (d, $J = 7.23$ Hz, 1H) 7.03 (d, $J =
8.73 Hz, 2H), 6.82 (d, J = 8.73 Hz, 2H). $^{13}$C NMR (DMSO-$d_6$, 300 MHz): 153.0, 142.8, 135.3, 134.9, 128.4, 127.8, 126.8, 124.9, 123.3, 122.7, 122.4, 118.7, 116.23,
Appendices

A.1  \(N\)-Phenyl-1-naphthylamine (PAN)

Figure A1. \(^1\)H NMR spectrum of \(N\)-phenyl-1-naphthylamine.

Figure A2. \(^1\)H NMR spectrum of unpurified \(N\)-phenyl-1-naphthylamine.
Figure A3. $^{13}$C NMR spectrum of $N$-phenyl-1-naphthylamine.

Figure A4. COSY spectrum of $N$-phenyl-1-naphthylamine.
A.2 Nitroxyl Radical PAN 2

Figure A5. $^1$H NMR spectrum of nitroxyl radical PAN.

Figure A6. $^1$H NMR spectrum of nitroxyl radical PAN after one week.
Figure A7. $^1$H NMR spectrum of nitroxyl radical PAN with broad NMR peaks (expansion of Figure A5).

Figure A8. $^1$H NMR spectrum of nitroxyl radical PAN performed under inert atmosphere.
A.3 Carbon-Carbon Coupled PAN Dimer 3

Figure A9. $^1$H NMR spectrum of carbon-carbon coupled PAN dimer.

Figure A10. $^{13}$C NMR spectrum of carbon-carbon coupled PAN dimer.
Figure A11. COSY spectrum of carbon-carbon coupled PAN dimer.

Figure A12. $^1$H NMR spectrum of carbon-carbon coupled PAN dimer with broad peaks.
A.4 Naphthyl Oxidized PAN/Fremy’s PAN 4

Figure A13. $^1$H NMR spectrum of naphthyl oxidized PAN.

Figure A14 – $^{13}$C NMR spectrum of naphthyl oxidized PAN.
Figure A15. COSY spectrum of naphthyl oxidized PAN.

Figure A16. $^1$H NMR spectrum of napthoquinone, a side product of naphthyl oxidized PAN synthesis.
Figure A17. $^1$H NMR spectrum of carbon-nitrogen coupled PAN dimer showing only peaks characteristic to PAN starting material and BIPY.

Figure A18. $^1$H NMR spectrum of BIPY recovered after FCC on the carbon-nitrogen coupled PAN dimer crude mixture.
Figure A19. $^1$H NMR spectrum of PAN starting material recovered after FCC on the carbon nitrogen coupled PAN dimer crude mixture.

Figure A20. $^1$H NMR spectrum of carbon-nitrogen coupled PAN dimer, with naphthyl oxidized PAN as a contaminant.
Figure A21. $^1$H NMR spectrum of degraded carbon-nitrogen coupled PAN dimer, with peaks characteristic top naphthyl oxidized PAN as a contaminant.

Figure A22. $^1$H NMR spectrum of carbon-nitrogen coupled PAN dimer using deuterated benzene.
Figure A23. COSY spectrum of carbon-nitrogen coupled PAN dimer, with naphthyl oxidized PAN as a contaminant before degradation of carbon-nitrogen coupled PAN.

Figure A24. COSY spectrum of carbon-nitrogen coupled PAN dimer, with naphthyl oxidized PAN as a contaminant after degradation of carbon-nitrogen coupled PAN.
A.6 Phenyl Oxidized PAN 6

Figure A25. $^1$H NMR spectrum of phenyl oxidized PAN in DMSO-$d_6$.

Figure A26. $^{13}$C NMR spectrum of phenyl oxidized PAN in DMSO-$d_6$. 
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