Plasma Methods for the Clean-up of Organic Liquid Waste

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Table 6.2 Summary of results of the GAD plasma-liquid degradation of dodecane using batch and recycling treatment. The total volume of oil removed is calculated after 1 hour of treatment. Initial volume of dodecane was 15 ml in the batch treatment and 60 ml in the recycling treatment. GC-MS analysis has been performed to quantify the amount of liquid by-products in the samples after the treatment.
Abstract

This thesis has studied the low-temperature atmospheric pressure plasma as a potential technological application for the degradation of waste oils. The study has been approached initially by investigating the degradation of oil in gas phase only, in order to understand the gas chemistry and elucidate the plasma-chemical degradation mechanism. Gaseous odourless kerosene and dodecane have been used as simulants to waste oil and their plasma-chemical degradation has been studied using a BaTiO$_3$ packed bed plasma reactor and a gliding arc discharge reactor. Kerosene showed similar degradation behaviour to dodecane and the latter one was chosen as a surrogate to allow quantitative analysis. The dodecane plasma degradation efficiency and the distribution of end-gaseous products have been studied under these two reactors in different gas compositions. Optical emission spectroscopy was used to identify intermediate excited species and calculate the rotational and vibrational temperature profiles. Differences in the dodecane degradation gas chemistry between the packed bed and the gliding arc plasma are discussed and postulated mechanisms are presented for each condition. Gliding arc discharge demonstrates higher degradation efficiency and it will be used mainly for the plasma-liquid treatment.

The plasma-liquid dodecane treatment is firstly studied using argon dielectric barrier discharge. The effect of different reactor configuration, humidity and temperature to the discharge characteristics and degradation efficiency will be discussed.

The study of the liquid dodecane degradation is extended by using the gliding arc discharge. Using N$_2$ and Ar in both dry and humid conditions for the batch treatment of dodecane, the degradation efficiency, gas chemistry and liquid chemistry are discussed and correlated to the gas chemistry observed during the plasma treatment of gaseous dodecane under the same conditions, in order to gain an overall understanding of the plasma-liquid clean-up process.

Finally, the gliding arc plasma treatment of liquid dodecane is studied using the recycling method and shows a significant improvement to the degradation efficiency.
Declaration

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>CCD</td>
<td>Charged coupled device</td>
</tr>
<tr>
<td>DBD</td>
<td>Dielectric barrier discharge</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infra-red</td>
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<tr>
<td>GAD</td>
<td>Gliding arc discharge</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>HV</td>
<td>High voltage</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectroscopy</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitrogen oxides</td>
</tr>
<tr>
<td>OES</td>
<td>Optical emission spectroscopy</td>
</tr>
<tr>
<td>OK</td>
<td>Odourless kerosene</td>
</tr>
<tr>
<td>PBDBD</td>
<td>Packed bed dielectric barrier discharge</td>
</tr>
<tr>
<td>$P_d$</td>
<td>Discharge power</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>Input power</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>SIE</td>
<td>Specific input energy</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
“As you set out for Ithaka, hope the journey will be a long one, full of adventures, full of discovery…

...keep Ithaka always in your mind, arriving there is what you are destined for. But do not hurry the journey at all. Better if it lasts for years, so you are old by the time you reach the island, weathly with all you have gained on the way, not expecting Ithaka to make you rich. Ithaka gave you the marvellous journey. Without her, you would not have set out. She has nothing left to give you now. And if you find it poor, Ithaka won’t have fooled you. Wise as you will have become, so full of experience, you will have understood by then what these Ithakas mean.”

C.P. Cavafy
Chapter 1

1. The problem of organic liquid waste in nuclear industries and introduction to plasma technology

1.1 Introduction to nuclear waste

Nuclear wastes are by-products of nuclear power generation, nuclear weapon production plus residuals of radioactive materials used by industry, medicine, agriculture and academia. It is their radioactive nature and potential hazard that make nuclear waste the most dangerous type of waste, but also the most controversial and regulated with respect to disposal.

Radiation is measured in terms of its effects on people and materials. Radiation emitted from radioactive materials is known as ionising radiation and can be in the form of three main types.

Alpha particles are positively charged helium nuclei of very low penetration and do not give rise to a measurable external radiation, but can give higher doses when incorporated into the body by inhalation or ingestion. Beta particles are equivalent to electrons. These can give an external dose, especially those of high energy that will penetrate through two cm of aluminium. Gamma – rays are very penetrating passing through up to 6 mm of concrete. X-rays are equivalent to low energy gamma rays. Radioactivity per unit weight is fixed for any specific radioelement no matter in what chemical or physical state, and for this reason can be expressed in decay periods.

Figure 1.1 Penetration characteristics of various ionising radiation
The SI unit for radioactivity is Becquerel (Bq) which is equal to one disintegration per second. A common term also used to express radioactivity is half-life, which is the time needed for the radioactivity of a radioelement to decay to one-half of its original value.

Radioactivity can spread to the environment and may cause severe health effects in humans. The physiological effect of very large whole-body doses is radiation sickness and early death, while large organ doses lead to local cell destructions and possibly organ death. The effect of lower doses are cell changes like decreased surviving fraction, decreased rate of division, chromosomal aberrations and more [2]. For man, the unit that is used to measure ionising radiation is Sievert (Sv). In humans, it has been calculated that a 5 Sv is usually fatal, and the lifetime risk of dying from radiation-induced cancer from a single dose of 0.1 Sv is 0.8%, increasing by the same amount for each additional 0.1 Sv increment of dosage.

Radioactive contamination can enter the body through ingestion, inhalation, absorption, or injection. Radioactive contamination may also be ingested as the result of eating contaminated plants and animals or drinking contaminated water or milk from exposed animals.

![Image](Figure 1.2 Potential radionuclide pathways from nuclear waste (taken from [3]))
The main radioactivity by definition reduces over time, so in principle the waste needs to be isolated for a particular period of time until its components no longer pose a hazard. This depends on the components’ half-life and it can mean hours to years for some common medical or industrial radioactive wastes or many thousands of years for high-level wastes, such as plutonium-239 in spent fuel. The main approaches to managing radioactive waste so far have been segregation and storage for short-lived waste, near-surface disposal for low and some intermediate level waste, and deep and secure burial for the long-lived high-level waste.

The object of radioactive management is to concentrate the radioactive material as far as possible into a small volume that can be isolated indefinitely from human contact. If streams such as water from fuel storage ponds are too bulky for anything but release into the environment, all radioactivity or harmful material that poses a significant risk has to be removed [4].

1.2 Classification of radioactive waste

Waste can be classified according to activity (low, medium or high) and physical state (gas, liquid or solid package). The four main types according to activity are given below [4, 5].

*Exempt or very low level waste* (VLLW) is sometimes described as “below regulatory concern” and contains very low concentrations of radioactivity. The associated radiological hazards are considered negligible as they are less than the naturally occurring radioactivity (each 0.1 m$^3$ of material or single item containing less than < 400 kBq or 40 kBq beta/gamma activity, respectively).

*Low Level waste* (LLW) is generated from hospitals, laboratories, industries as well as nuclear fuel and defence program cycles. It comprises paper, rags, tools, clothing, filters and other lightly contaminated materials containing small amounts of short-lived radionuclides. It is easy to handle but must be disposed of more carefully than normal garbage, often buried in shallow monitored landfill sites. To reduce its volume, it can be either compacted or incinerated (in a closed container) before disposal. Worldwide it constitutes 90% of the volume but only 1% of the radioactivity associated with other radioactive waste (not exceeding 4 GBq alpha or 12 GBq beta/gamma activity).
Intermediate Level Waste (ILW) contains higher amounts of radioactivity and requires the use of special shielding before operation. It could be materials like resins, filters, chemical sludge, reactor components, or contaminated materials from reactor decommissioning and it usually needs to be solidified into concrete or bitumen for disposal. Whilst short-lived waste can be buried, long lived waste from nuclear fuel reprocessing is usually subject to deep geological disposal. ILW contains 4% of the radioactivity of all radioactive wastes.

High Level Waste (HLW) generally refers to materials requiring permanent isolation from the environment. When nuclear fuel from nuclear reactors is chemically processed, wastes include highly concentrated liquid solutions with fission products and transuranic elements generated in the reactor core. It is highly radioactive and often thermally hot. Although HLW is small compared to the total radioactive waste produced, it contains over 95% of the total radioactivity.

1.3 The nuclear fuel cycle

The nuclear fuel cycle is the series of industrial processes which involve the production of electricity from uranium in nuclear power reactors. A schematic of the nuclear fuel cycle is given in Figure 1.3. Where fuel discharged from a reactor is reprocessed and the uranium or plutonium returned for further use, at least some of the material follows a closed loop or cycle. Reprocessing for this purpose is often described as closing the Back End of the fuel cycle [3]. The genuine nuclear fuel cycle comprises: mining and milling the ore, purifying the ore concentrate, etching the U-253 content if necessary and manufacturing fuel, utilising the fuel in reactors of various kinds, reprocessing the discharged fuel to separate uranium and plutonium from waste, returning the uranium and plutonium for further use and disposing of wastes.

Discussing how to manage waste from the nuclear power industry, the Fuel Cycle divides into two parts. The Front End, which consists of the activities beginning with mining and milling up through and including burning the uranium fuel in a nuclear reactor. The Back End of the nuclear cycle is the remaining activities, where the vast majority of the waste is generated and managed.
The three major options resulting from the Back End fuel cycle according to the waste management are as follow: 1) the once-through cycle and direct disposal as HLW, 2) the reprocessing fuel cycle (RFC) with mixed oxides (MOX), recycling of U and P in light water or fast breeder reactors and then disposal of HLW or 3) the advanced fuel cycle (AFC), as an extension of the RFC in which the wastes are partitioned or transmuted to reduce radiotoxicity [5].

The nuclear industry’s common option is reprocessing, where the unused uranium and the plutonium produced are recovered leaving the minor actinides with the fission products as HLW. This method would give recovered fuel to produce more energy while, the volume of the HLW would be significantly reduced. This method follows the rule of making full use of the valuable energy resources of mankind.

1.4 The origin of the organic liquid nuclear waste

The majority of the organic liquid radioactive waste in the nuclear industry consists of lubricating oils and extraction solvents.
Lubricating oils are mostly paraffins and could come from primary heat transport pumps, hydraulic fluids from fuelling machines, and turbine oils. These are normally low level wastes containing only relatively small quantities of beta/gamma emitting radionuclides. They can become waste as a result of regular servicing of equipment, or when an item of equipment is discarded.

Organic extraction solvents are used both in the Front End for uranium ore purification processes and in the reprocessing plants in the Back End of the nuclear cycle. At the present time, the PUREX (Plutonium Uranium Redox Extraction) process is universally employed as the preferred aqueous chemical processing technology for reprocessing spent nuclear fuel. It is a wet chemical process that uses mixtures of 20% or 30% tributylphosphate (TBP) in diluents (usually odourless kerosene or dodecane) to co-extract U (VI) and Pu (IV) from a strongly acidic nitrate solution (3-4 M HNO₃) [2, 4-6].

Specifically inPUREX process after the extraction, the uranium and plutonium are transferred by intensive mixing to the organic phase of the tributylphosphate (TBP) in kerosene, while the fission products remain in the aqueous nitric phase (Figure 1.4). Further process steps enable the subsequent separation of uranium and plutonium from one another. The chemical reactions that describe the extraction of uranium and plutonium in the PUREX process are as follows [4]:

\[
\text{UO}_2^{2+} + 2\text{NO}_3^-\text{aq} + 2 \text{TBP} \rightarrow \text{UO}_2(\text{NO}_3)_2(\text{TBP})_2\text{org} \quad \text{Equation 1.1}
\]

\[
\text{Pu}^{4+} + 4\text{NO}_3^-\text{aq} + 2 \text{TPB} \rightarrow \text{Pu}(\text{NO}_3)_4(\text{TPB})_2\text{org} \quad \text{Equation 1.2}
\]

The PUREX process yields two product streams, which are chemically-purified uranium and plutonium that are further separated from each other with selective extraction and repetitive cycles of “steam-stripping” to remove any by-products. Two main waste streams are the aqueous remains including nitrates of actinides and fission products as HLW, and the organic extractants (TBP/kerosene) with small residues of radioactive actinides (U, Pu) and fission products (Ru, Zr, Nb) and a small amount of solvent degradation by products such as dibutyl or monobutylphosphate caused by radiolysis as a result of the intense radiation arising primarily from fission product decay [2].
A smaller fraction of the overall organic liquid radioactive waste produced in the nuclear industry could also be scintillation liquids used in routine radiochemical analyses (e.g. toluene, xylene), decontamination agents used to remove radionuclides (e.g. citric acid, ethylene diamine tetra acetate (EDTA) and other miscellaneous halogenated organic solvents used for cleaning and degreasing [8].

1.5 The nuclear waste management- the challenge of organics

The nuclear fuel cycle generates a large variety of wastes that can result from any stage in this cycle. A lot of effort has been made in order to solve the problems of nuclear waste treatment over the last fifty years. Governments around the world are considering a range of waste management and disposal options [9, 10], such as incineration, compaction, cementation, vitrification or ion exchange as initial treatment to reduce and immobilise the waste and then package it into an appropriate material, such as metallic drums, concrete boxes or containers, so it can be safe for long term storage or geological disposal.

Figure 1.5 depicts a map with the 35 sites of the major radioactive waste producers in the UK, excluding Northern Ireland which has only a small contribution [11]. In England, the site that produces most waste apart from the nuclear power reactors is Sellafield, which includes large fuel fabrication, reprocessing and waste storage.
facilities. The national Low Level Waste Repository facility (LLWR), is located near the village of Drigg, four miles south of Sellafield. The sites that are most involved in the production, storage or treatment of LLW/ILW radioactive oils are Sellafield, Dounreay in Scotland and Trawsfynydd in Wales.

Figure 1.5 Major radioactive waste production sites in UK, excluding Northern Ireland and minor nuclear companies and research institutions (adapted from [11])

Organic liquid nuclear waste includes a small amount of radionuclides, so it could be considered as LLW or ILW. This type of waste is mainly disposed of by incineration or decomposed by hydrolysis and pyrolysis with the view of forming inactive hydrocarbons, and active phosphoric acid, which is treated together with other aqueous wastes. Nevertheless, these methods are not yet standardised as they have
many disadvantages. Table 1.1 summarises the possible waste treatments and their limitations.

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct incineration</td>
<td>Conceptually straightforward</td>
<td>Burnout, plant life, ventilation clean up</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Avoids corrosive fume</td>
<td>Intractable residues</td>
</tr>
<tr>
<td>Phosphoric acid split</td>
<td>Possible recycling</td>
<td>High temperature moving parts, undesirable distribution of activity</td>
</tr>
<tr>
<td>Encapsulation</td>
<td>Conceptually straightforward</td>
<td>High volume of solid waste</td>
</tr>
<tr>
<td>a) Direct encapsulation</td>
<td>Conceptually straightforward</td>
<td>Low fractional incorporation, weepage</td>
</tr>
<tr>
<td>b) Absorption and cementation</td>
<td>Conceptually straightforward</td>
<td>High volume of solid waste</td>
</tr>
<tr>
<td>Ultraviolet irradiation</td>
<td>No reagents needed</td>
<td>Highly inefficient, high energy costs</td>
</tr>
<tr>
<td>Gamma radiation</td>
<td>Conceptually elegant process, radiation available, continuous degradation</td>
<td>Very high energy required, practical demonstration lacking, safety engineering problems</td>
</tr>
<tr>
<td>Microbial degradation</td>
<td>Potential low temperature, modern technology</td>
<td>Large waste volumes, large plant required</td>
</tr>
<tr>
<td>Dealkylation (Friedel-Craft)</td>
<td>Chemically elegant</td>
<td>Poor performance, by products difficult to handle</td>
</tr>
<tr>
<td>Distillation</td>
<td>Simple process, reduces interim storage acquirement.</td>
<td>Partial process, OK* distillate not suitable for recycling</td>
</tr>
<tr>
<td>Emulsification and sea discharge</td>
<td>Simple and cheap</td>
<td>Extremely large effluent volumes, discharges and organics</td>
</tr>
<tr>
<td>Silver II electrochemical</td>
<td>Potential versatile</td>
<td>Energy costs, needs excessive development with no guarantee of success</td>
</tr>
</tbody>
</table>

*Odourless Kerosene

Table 1.1 Unsuitable solvent destruction processes (adapted from [4])

It is the characteristics of liquid organic radioactive waste that makes its management and treatment complicated and expensive. In general, the organic components of radioactive waste can change form more easily than most inorganic components, for example due to their low melting point, their response to radiolysis or their volatility. They will drain under gravity and contribute to the spread of contamination, so they need to be effectively contained. Many are volatile and combustible, or will support
combustion of other wastes. They can also provide a source of nutrients for microbial activity. Their immiscibility with water require special care due to their potential to migrate rapidly in the environment (the lighter fraction can float on water whereas the dense fraction cannot), or some of the decontaminants (chelating agents) can form water soluble complexes with radionuclides. This distinction may be of significance for waste collection, storage and processing [8].

It is the complexity of this waste in conjunction with the lack of appropriate treatment and management policy that leads to the option of storing a huge generation of LLW/ILW liquid organics since 1950’s until now. Nowadays, the amount of this waste volume in Sellafield is equivalent approximately to an Olympic size swimming pool. Degradation and leakage with time made this waste even more complicated and very difficult to transport. For that reason, the interest in the recent years has been focused on searching for treatment solutions. Looking in that direction, this project investigates the potential of low temperature plasma application to the clean-up of liquid organic waste, supported by Nuclear Decommissioning Authority (NDA) in collaboration with National Nuclear Laboratory (NNL).

1.6 Low temperature plasma potential application in nuclear waste management

No commercial-scale treatment has yet been universally established for the treatment of radioactive organic liquid waste. The criteria for solvent treatment process may be summarised as follows [12]:

- Reasonable chance of successful development on an acceptable timescale
- Demonstrated to be safe with small uncertainty and compatible with associated plants
- Simple and easy to control with minimal steps and operation units
- Acceptable lifetime costs

Taking into account the above consideration, the objective for this piece of work is to investigate the potential application of atmospheric pressure, low-temperature plasma destruction or conversion of oils in the nuclear industries liquid waste management.
Furthermore, the investigation of the plasma-chemical oxidation and degradation of liquid hydrocarbons has yet much information to yield.

The next sections introduce the plasma technology and give a literature review on the history and current findings of plasma-gaseous or plasma-liquid organics treatment with relevance to the nuclear decommissioning.

1.7 Plasma Technology

1.7.1 Introduction to plasma

It is from the ancient times that the Greek philosopher Empedocles (490-460 BC) suggested that everything is made up of four elements; earth, water, air and fire and that every matter can be formed by transmutation between these. This is principally correct if the four elements are interpreted as being the gaseous, liquid, solid and fire is interpreted as energy (or plasma). In 1929, the American chemist Irving Langmuir was the first who used the term plasma while he was trying to describe the oscillations of the electron cloud during electrical gas discharges [13]. Plasma is also known as the fourth state of matter [13, 14]. As temperature increases, a substance transforms in the sequence of solid, liquid, gas and finally plasma. Molecules become more energetic by heating until they dissociate to form gas atoms and then a mixture of gas particles freely moving in the plasma state. Some of these particles are charged particles such as electrons and ions or neutral particles, freely moving in random directions being on average, electrically neutral. Figure 1.6 illustrates the four states of matter. The origin of plasma was lately found that could be from the universe formation, and the Big Bang theory. According to this scientifically accepted theory, over fifteen million years ago, the matter and energy of the universe was squeezed into a small and unstable ball that exploded, causing the Big Bang. The matter was so hot, that it was in a state of plasma. Plasma exists in space, the Sun and the stars, but can also be man-made in laboratory, as a result of thermal, electric, microwave or radio frequency induced processes.
Figure 1.6 The four states of matter (taken from [15])

Plasma can occur over a wide range of pressure and it is commonly classified in terms of electron temperature and electron densities. Most plasmas of practical significance in laboratory have electron energies of 1-20 eV and electron densities of $10^6-10^{18}$ cm$^{-3}$ [16]. Figure 1.7 shows electron temperatures and densities of typical natural and man-made plasmas.

Not all particles need to be ionised in the plasma and the ionisation degree can be very different between various types. When the ionisation degree is close to unity, it is called *completely ionised plasma*, such as thermonuclear systems. The main interest for plasma-chemical applications is *weakly ionised plasmas*, with a low degree of ionisation in a range of $10^{-4}$-$10^{-7}$ [16].

The plasma medium is usually described macroscopically by its temperature and density and changes in the plasma are calculated by using conservation equations such as energy, momentum and mass. Microscopically, plasma is described using statistical probabilities distribution for calculating positions and velocities of all particles.
Figure 1.7 Operating regions of nature and manmade plasma (taken from [16])

Plasma is generated by supplying energy to a neutral gas causing the formation of charge carriers [17]. There are various ways to supply the energy for the plasma generation and a schematic of this is given in Figure 1.8.

Figure 1.8 Principles of plasma generation (adapted from [17])
The most common way of generating and sustaining low temperature plasma for technological applications is by applying an electric field to a neutral gas. Free charged particles are formed and accelerated by the electric field and while colliding with other atoms, molecules, or the electrode’s surfaces, new charged particles may be created. This leads to an avalanche of charged particles, but while some charge carrier losses also occur, eventually balance is created and steady-state plasma develops.

The plasma which is generated by applying electrical energy, is also called electrical gas discharge, initially defined the process of “discharge” of a capacitor into a circuit containing a gas gap between the electrodes. If the electrical field is sufficiently large, breakdown occurs, the gas becomes a conductor and the capacitor discharges. More recently, electrodeless electrical field induced breakdown became also possible to cause a gas discharge.

Depending on the type of energy supply and the amount of energy transferred to the plasma, the properties of the plasma change in terms of electron density and temperature. These parameters can be used to group plasma into different categories.

1.7.2 Plasma properties and classification

The different plasma generation methods and large range of plasma sources create multiple characteristics and variations in plasma. The main characteristics of plasma such as density, temperature pressure and electric field can be altered by different types of discharge, power supply or operating temperature and pressure. That leads to a promising technology with a wide choice of technical applications [17].

- Plasma conductivity and electromagnetic field

The presence of a non-negligible number of charge carriers makes the plasma electrically conductive so that it responds strongly to electromagnetic fields. This is the main property that distinguishes plasma from neutral gas, which is an electrical insulator. Like gas, plasma does not have a definite shape or a definite volume unless enclosed in a container; although unlike gas, in the influence of a magnetic field, it may form structures such as filaments, beams and double layers. Although, plasma is quasi-neutral, which means that the total density of the positive charge carriers are equal to the total density of the negative charge carriers.
Moving charged particles of plasma create magnetic fields (Figure 1.9) and magnetic fields can apply forces on other charged particles which affect the motion of the original moving particles in a continuous cycle [13]. Due to this chaotic energetic motion, mutual collisions are taking place and the charged particles in the plasma may emit radiation.

![Figure 1.9](image.png)

**Figure 1.9** The motion of electrons and ions in a magnetic field, taken from [13]

Plasma can be classified by the nature of the electric field that causes the discharge. Basically, they can be categorised as direct current (DC), or non-direct current (non-DC) discharges. The DC discharges can be continuous with a constant current (arc, glow) or can be sustained in a pulsed-periodic regime (pulsed corona). Pulsed DC discharges can provide the advantages of better control of plasma regime and afterglow by varying the duty cycles and increasing power for cold plasmas at atmospheric pressure. Figure 1.10 shows different types of plasma dc discharges depending on the applied voltage and the discharge current. The Townsend discharge is a self-sustained discharge created at low discharge current. Transition to a glow discharge is marked by voltage decrease and an increase in current. At very high currents, the discharge undergoes a glow-to-arc transition [17].

Non-DC discharges can be sinusoidal with low or high frequency. Alternating current (AC) dielectric barrier discharges (DBD) can be generated at low frequencies between 0.5-1 MHz [17], while high frequencies include electrodeless induced radiofrequency (RF) discharges between 1-100 MHz and microwave (MW) discharges commonly generated at 2.45 GHz [17]. These electrodeless discharges play an important role in technologies where electrode erosion is undesirable, but their operational cost is generally higher.
**Figure 1.10** The dependence of voltage upon current for various kinds of DC discharges (taken from [17])

- **Plasma temperature**

The gas translational temperature is defined as the average kinetic energy of the particles in thermal equilibrium. Thus, plasma can not be described by a single temperature, unless sufficient collisions occur between particles to equilibrate [14]. Nevertheless, the electron mass is much more less than the mass of heavy particles such as atoms, molecules or ions and many collisions are required for this to occur. Even with a high frequency of collisions at higher pressure, the electron and particle temperatures may be different. A more elaborate profile of plasma temperature is presented when different forms of plasma energy are studied separately such as electron temperature ($T_e$), heavy species temperature ($T_n$) - such as vibrational or rotational temperature- or translational gas temperature ($T_g$).

A parameter which determines the electron energy in a plasma is the reduced field ($E/n$), where the electric field ($E$) is divided by the neutral gas density ($n$) [14]. If the ratio $E/n$ is really small, elastic collisions between hot electrons and heavy particles are more likely to occur and subsequently their temperature can approach each other to create a thermodynamic equilibrium. In this conditions where the electrons temperature is close to the particles temperature ($T_e = T_n$), the plasma is called *equilibrium or thermal plasma*. When the electrons in the plasma have a much higher energy or temperature than the gas neutral particles ($T_e > T_n$), then the plasma is called as *non-equilibrium or non-thermal plasma*. In discharge physics, the reduced
field is measured in Townsend (Td), where one Townsend equals $10^{-17} \text{ V cm}^2$. Only in very low values of reduced energy ($< 1\text{ Td}$) equilibrium conditions can be expected.

Physics, chemistry, engineering aspects or application areas are quite different for thermal and non-thermal plasmas. Thermal plasma is usually more powerful, while non-thermal plasma is more selective to chemical reactions. This is the main advantage of non-thermal plasma in plasma chemistry. If only a small fraction of the gas atoms or molecules are desired to be excited, only non-thermal plasma can provide electrons or ions at the right energy. The bulk of the gas is more or less left untouched and the losses are kept at the minimum. Table 1.2 summarises up the main characteristics of thermal and non-thermal plasmas.

<table>
<thead>
<tr>
<th>Thermal Plasma</th>
<th>Non-Thermal Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e = T_n$</td>
<td>$T_e &gt;&gt; T_n$</td>
</tr>
<tr>
<td>$(\approx 10,000 \text{ K})$</td>
<td>$T_e \approx 10,000-100,000 \text{ K}$</td>
</tr>
<tr>
<td>High Electron Density</td>
<td>Lower Electron Density</td>
</tr>
<tr>
<td>$10^{21} - 10^{26} \text{ m}^{-3}$</td>
<td>$&lt;10^{19} \text{ m}^{-3}$</td>
</tr>
<tr>
<td>Inelastic collisions between electrons and heavy particles create plasma reactive species whereas elastic collisions heat the heavy particles and electron energy is consumed</td>
<td>Inelastic collisions between electrons and heavy particles induce plasma chemistry. Heavy particles are slightly heated by only a few elastic collisions</td>
</tr>
</tbody>
</table>

Table 1.2 Main characteristics of thermal and non-thermal plasmas (adapted from [14])

- Operating pressure

Another plasma property is the pressure which affects also the plasma density and temperature. The plasma pressure can be controlled by the operating pressure. The most commonly used pressures in plasma technology are atmospheric pressure (1 bar) or under low pressure (< 1 bar). Low pressure plasmas ($10^{-6}-10^{-4} \text{ bar}$) are weakly ionised non-thermal plasmas. The inelastic collisions between electrons and the heavy particles are excitative or ionising and the temperature of the heavy particles is lower than the electronic one. When the pressure becomes higher, collisions could be also elastic that increase the temperature of heavy particles and the plasma state becomes close to thermal [18]. A typical example of low pressure discharge is the glow discharge that are widely used as light sources and surface
treatment applications and it can operate between $10^{-6}$ bar to near atmospheric pressure. Above atmospheric pressures, glow discharge can transform to thermal arcs that can operate at high pressures exceeding 10 atm. The plasma in that case is so dense that most of the discharge power (80-90 \%) is converted into radiation [16]. Non-thermal low temperature plasmas can be operated in atmospheric pressure and are attractive to plasma-chemical applications. In the next section characteristic atmospheric pressure low temperature gas discharges that are in relevance to this work will be described.

1.7.3 Low temperature atmospheric pressure discharges and their applications

- Corona discharge

The corona discharge consists of relatively low power electrical discharges that take place at or near atmospheric pressure. They appear when the field at one or both electrodes is stronger than in the surrounding gas, thus they are easily formed near sharp points, edges or thin wires. Coronas have frequently been observed at high voltage transmission lines, lightning rods and ships masts during electrical storms, where the discharge takes the shape of a crown (from which corona takes its name) [19].

A corona discharge can be formed by applying either continuous or pulsed DC voltage between two electrodes. The electrodes are most commonly arranged as a grounded cylindrical outer electrode with a high voltage wire or rod inner electrode or as a point-to-plate, or point-to-point electrode configuration. The area between the electrodes where the corona is formed is occupied by a static or continuous flow gas. Corona discharges can take on several forms depending on the relative polarity of the electrodes. For a point-to-plate electrode configuration, the different types of corona discharge are shown in Figure 1.11, where the applied voltage increases from left to right. In a positive corona, the initial breakdown of the gas produces a burst pulse, limited to the area surrounding the electrode. Increasing the voltage creates additional charged species, leading to the formation of streamers. In this mode, the corona occupies a relatively large active volume and has a low temperature of \(~ 27 \degree C\) [19]. However, application of the continuous corona discharge is limited by low current and low discharge power. Increasing the electrical field the active corona can reach the opposite electrode, causing a spark (Figure 1.11). Spark channels result
in local overheating and plasma non-uniformity which is not acceptable for applications. The generation of higher discharge power corona streamers without the formation of sparks, is possible with the pulsed-periodic voltages.

![Diagram of corona discharges](image)

**Applied Voltage**

**Figure 1.11** Schematic diagrams showing different forms of corona discharges in a point-to-plate electrode configuration (adapted from [19])

Corona discharges were first applied for the first electrostatic precipitator of Lodge [20], and after that they have been spread to other applications such as electrophotography, static control in semiconductor manufacture and ionization instrumentation. Furthermore, their ability of generating high concentration of active atoms and radicals in atmospheric pressure without heating the gas have made them very attractive for other applications such as surface treatment and cleaning of gas and liquid waste streams.
• **Dielectric Barrier Discharges (DBD)**

The dielectric barrier discharge (DBD) or silent discharge - as they were originally known due to the prevention of noisy spark formation - are non-thermal plasma that can operate to about atmospheric pressure. It was originally proposed in 1857 by Siemens, for ozone generation from air or oxygen [21]. DBDs can form stable discharges in a range of different gases at relatively high discharge powers, making them particularly suitable for many industrial applications. The DBD reactor consists of two electrodes with one or more dielectric barriers positioned in the discharge gap, in the path of current flow. Materials with high relative permittivity such as quartz, glass and ceramics are suitable for use as dielectric barriers. There are several configurations for a DBD which could be planar, cylindrical as shown in Figure 1.12, or in the form of a surface discharge.

![Common planar and cylindrical dielectric-barrier discharge configurations](image)

**Figure 1.12** Common planar and cylindrical dielectric-barrier discharge configurations [22]

To ensure stable plasma operation, the gap which separates the electrodes is limited to a few millimetres wide. The discharge is ignited by means of sinusoidal AC or pulsed current, as the dielectric being an insulator, cannot pass the DC current. Plasma gas can flow or be static in the gap. The DBD can be operated in a wide range of pressure (mbar up to atmospheric) and the frequency range could be between of 50 Hz to 1 MHz [17].
Normally, in DBD configurations a filamentary discharge can be obtained. A filamentary discharge is a non-uniform plasma discharge that consists of many tiny breakdown channels known as microdischarges or filaments on the surface of the dielectric material and extend across the discharge gap. The dielectric barrier limits the flow of current causing the microdischarges to become extinguished, leaving significant charge deposition on the dielectric surfaces. As the polarity of the electrodes is rapidly changing, the microdischarges are reformed at the point where the breakdown voltage is reached in the next half cycle of the AC voltage sine wave. This results in the continuous formation of nanosecond microdischarges at a frequency which is twice that of the applied frequency [22]. The microdischarges appear as “spikes” on the current waveform. In appearance, the microdischarges are randomly distributed over the surface of the dielectric. In reality, the position of the microdischarge formation is dependent on the residual charge distribution on the dielectric surface due to memory effect as described in detail in [23, 24]. The lifetime of the filaments is very short (1-10 ns), minimising overheating. The current density in the filaments is $10^2 - 10^3$ A cm$^{-2}$, the electron density is $10^{14}$-$10^{15}$ cm$^{-3}$, and typical electron energies are in the range 1-10 eV.

The advantage of the DBD over other discharges is the option to work with non-thermal low temperature plasma at atmospheric pressure and the comparatively straightforward scale up to larger dimensions. Industrial applications include ozone generation, surface treatment, high power CO$_2$ lasers, UV excimer lamps, plasma displays [21] pollution control in gas and liquid streams [21, 25] and recently has been attracting interest in plasma medicine applications [16, 26, 27].

- **Packed bed plasma reactor**

A variation on typical DBD systems is the packed bed reactor. A packed bed reactor consists of dielectric pellets within two electrodes, possibly with a dielectric layer between the pellets and the electrodes, as shown in Figure 1.13, and that could be either catalytic or non catalytic. Typical dielectric materials used are glass, quartz, aluminium oxides and ferroelectrics. Ferroelectric plasma reactors are a common name for packed bed reactors filled with perovskite oxides. The most common ferroelectric is barium titanate (BaTiO$_3$), which has a dielectric constant of 2000-10000.
The major characteristic of packed bed reactors is the presence of contact points between the pellets themselves and pellets-electrodes. When the ferroelectric materials are exposed to an external electric field, a spontaneous polarisation occurs in the direction of the electric field, resulting in a high electric field at the contact points of the pellets [25]. High dielectric constant materials reduce the breakdown voltage and that generally leads to a higher discharge power. Thus, packed bed reactors can be categorised as high electron energy but low plasma density devices, typically with a maximum energy up to 10 eV, mean electron energy of about 4 - 5 eV and electron density of $10^8 \text{cm}^{-3}$ [28, 29]. Despite the low electron density, a packed bed reactor can generally achieve a better energy efficiency for ozone generation or pollution removal [30].

**Figure 1.13** Schematic configurations of packed bed reactors, a) without a dielectric layer between electrodes, b) parallel plate packed bed with dielectric layer and c) cylindrical packed bed with dielectric layer (b, c taken from [28])

- **Gliding Arc Discharge (GAD)**

The Gliding Arc Discharge (GAD) or “glidarc” was first proposed by Lesueur et al. [31] and developed by Czernichowski et al. mainly for the removal of species such as $\text{H}_2\text{S}$ or $\text{N}_2\text{O}$ from industrial gases [32-34] and later for the conversion of light hydrocarbons [35]. Its characteristics made it an attractive tool for both academic and industrial research [33] and while it was initially developed for gas treatment
applications, it soon was developed also for solids treatment [36-38] or liquid waste treatment [39].

A GAD is an auto-oscillating phenomenon developing between at least two diverging electrodes placed in a fast laminar or turbulent gas flow. It operates at atmospheric pressure or higher and the power at non-equilibrium conditions could exist up to 40 kW power [40]. A high voltage generator can provide the appropriate electric field to initially breakdown the gas at the upstream shortest gap between the two electrodes and create a plasma arc column between the electrodes. The gas flow gently pushes the arc downstream along the electrode axis so its length increases until it extinguishes and reignites itself again at the minimum gap between the electrodes starting a new cycle. The gliding arc plasma can be either thermal or non-thermal depending on the power and gas flow applied, but also can be operated at the transitional regime. In that case is also described as low-temperature quenched plasma, because it includes both regions of thermal and non-thermal plasma. The initial arc breakdown region is characterised by quasi-equilibrium phenomena, but as its length increases, the temperature of the heavy species decreases, so it becomes non-thermal quenched plasma upon breaking into a plasma plume. The physical characteristics and dynamics of this Fast Equilibrium to Non-Equilibrium Transition (FENETRe) regime have been studied considerably by several researchers [40-43]. Figures 1.14 and 1.15 illustrate that phenomenon.

The advantage of gliding arc is that by combining both thermal and non-thermal plasma characteristics, it can successfully provide high power and electron density, whilst simultaneously maintaining a high electron temperature and low gas temperature that is favourable in plasma-chemical applications. Many people have worked on the development of gliding arc discharge. Czernikowski tried three-phase, three-electrode gliding arc discharge for removing H₂S as early as 1993 [44]. Cormier and co-workers [45] and more recently Fridman and his group have studied rotating discharges [46]. Stryczewska and co-workers studied the improvement of power supply especially for a three-electrode configuration [47]. Three different gliding arc configurations are given in Figure 1.16.
Figure 1.14 Phases of the gliding arc evolution i) (A) gas break down, (B) equilibrium heating phase, (C) non equilibrium reaction phase, ii) Argon GAD showing the transition (when flow is $Q = 5 \text{ L min}^{-1}$ and input power is $P_{in} = 100 \text{ W}$)

Figure 1.15 Argon GAD generated in are laboratory ($Q = 5 \text{ L min}^{-1}$, $P_{in} = 100 \text{ W}$). Photographs are taken using a Nikon 5100 digital single-lens reflex camera, at different exposure times. Time-spaced 1/200 s exposures show the arc evolution in the gliding arc discharge
Figure 1.16 Different Gliding arc discharge configurations: a) bi-dimensional gliding arc discharge [16], b) vortex flow rotating gliding arc discharge [16, 46] and c) three-electrodes gliding arc discharge [47]

1.8 Non-Thermal Plasma Composition and Generation of Active Species

Plasma discharges can cause molecular dissociation and produce radicals, and in oxygen source gas mixtures that will create oxidative environment and promote the chemical reactivity. The chemical effects occurring in an electrical discharge are the consequence of the energy injection into a gas stream by electron impact reactions under the influence of the electric field [25]. Collisions of electrons with neutral particles may produce ionisation, fragmentation of molecules, electronic, vibrational and rotational excitation of the neutral gas. The importance of its reaction is based on its timescale as shown if Figure 1.17.

Chemical processes in non-thermal plasma are divided into a primary and a secondary process depending on the timescale. Primary process includes ionisation, excitation, and dissociation, light emission and charge transfer. Table 1.3 lists these reactions occurring in the plasma phase. The secondary process is the subsequent chemical reactions between products of the primary process such as electrons, ions,
excited molecules and radicals. Additional radicals or reactive molecules may be formed from radical-neutral recombination reactions in the secondary process.

**Figure 1.17** Timescale of events in elementary processes in non thermal plasma (adapted from [25])

Figure 1.18 shows an example of possible reaction pathways of radicals in non-thermal plasma treatment of a pollutant. Channel 1 (CH-1) is the most desirable pathway of the radical-pollutant reactions. Unfortunately, high reactivity usually means a poor selectivity. Competing reactions (CH-2, CH-3) also occur at the same time. These competing reactions may lead to a poor selectivity of the O, OH radical reaction with the pollutant, especially when degrading dilute pollutants.

**Figure 1.18** Reaction pathways of radicals (taken from [25])
Type of reaction | Reaction | Type of reaction | Reaction
---|---|---|---
**Excitation by** | Heavy particles | A+ B → A+B⁺ | **Recombination by** | atoms | A+ A+B → B + A₂
Photon | A+ hv → A⁺ | e⁻/ion | A⁺⁺e → A + hv
Electron | A+ e → A⁺ + e | ion/ion | A⁺ + B⁺ → AB
Transfer | A+B⁻ → A⁺+B | Radicals | A + B → AB
Ionisation by | De-excitation/photon | A⁺ → A + hv | A⁺ + B → A + B⁻
| heavy particles impact | A+B→A⁺ + B + e | Heavy particles impact | A₂⁺ B→ A + A + B
electron attachment | A+ e → A⁻ | Heavy particles attachment | A⁺ + BC → AB + C⁺
Photon impact | A+ hv → A⁺ + e | electron impact | A₂⁺ e → A +A + e
electrons impact | A+ e → A⁺ + 2e | electron attachment | A₂⁺ e → A⁻ + A
photon impact | A⁺⁺hv → A + A

**Table 1.3** Typical reactions occurring in non thermal discharges (adapted from [48])

In this work, the plasma gases used were argon, nitrogen and N₂-O₂ mixtures in dry or humid conditions. A short description of the primary generated species is given below.

- **Argon plasma species**

In argon plasmas electron impact reactions generate species such as excited neutral argon atoms Ar⁺⁺(4s), Ar⁺⁺⁺(4p) or Ar⁺⁺⁺⁺(5p) (Ar I lines) and ground Ar⁺, or excited singly ionised argon atoms, Ar⁺⁺ (Ar II lines). Among them, the first excited state Ar⁺⁺⁺ belongs to metastable states with a natural decay lifetime of about 1.3 s [49]. It is expected to be the most populated among the other states and thus it is considered important in the plasma-chemical reactions.
Figure 1.19 Energy level diagrams for argon showing the first two excited configurations. The two metastable levels are indicated by the letter “m.” The Paschen designation for each level is indicated at the top of the table, along with the corresponding value of $J$ [49]

The most pronounced population mechanism for $\text{Ar}_m^*$ is direct electron impact excitation, but direct or stepwise electron impact excitation to $\text{Ar}^*$, $\text{Ar}^{**}$ and then cascade to $\text{Ar}_m^*$ is also possible. Ionisation can initially occur by direct electron impact but Penning ionisation from argon metastables or other excited species in the discharge can also occur. However, direct electron impact mechanisms are more important in cold discharges with high electron temperatures and moderate excited heavy species. Stepwise electron impact mechanisms become more important in more energy-intense plasmas where the concentration of highly excited species is higher [16].

Direct electron impact excitation

$$R_{1.1} \quad e + \text{Ar} \rightarrow e + \text{Ar}_m^*, \text{Ar}^* \text{ or Ar}^{**} \quad \Delta E = 11.5 - 11.7, 13.08 - 13.33 \text{ or } 14.7 \text{ eV}$$

Stepwise excitation

$$R_{1.2} \quad e + \text{Ar}_m^* \text{ or Ar}^* \rightarrow \text{Ar}^{**}$$

Direct Electron impact ionisation

$$R_{1.3} \quad e + \text{Ar} \rightarrow \text{Ar}^+ + 2e \quad \Delta E = 15.7 \text{ eV}$$
Penning Ionisation

R 1.4  \[ M^+ + Ar \rightarrow e + Ar^+ + M \]

Stepwise ion excitation

R 1.5  \[ e + Ar^+ \rightarrow Ar^{*+} + e \quad E_j = 19.6 - 24.3 \text{ eV} \]

While ground state singly ionised argon \( Ar^+ \) is fairly unreactive, excited singly ionised argon atoms \( Ar^{*+} \) can contribute to the plasma-chemical reactions. However, due to their high ionisation energy, \( Ar^{*+} \) can be neglected as their relative concentration is expected to be very low compared to the neutral excited argon atoms \( Ar_m^* \), \( Ar^* \) and \( Ar^{*+} \).

- **Nitrogen plasma species**

Diatomic nitrogen is held together by a very stable triple bond – \( N_2 \) bond dissociation energy is 9.79 eV - which is difficult to break in standard conditions. However, under plasma conditions active nitrogen species can be generated by energetic electron collisions, such as excited neutral molecular \( N_2^* \), ground or excited molecular \( N_2^+ \) ions and ground or excited atomic N. Figure 1.2 illustrates the potential energy curves for \( N_2^* \) and \( N_2^{*+} \).

Among the molecular excited states, the first electronically excited metastable state is the triplet \( N_2(A^3\Sigma_u^+) \) with an energy threshold of 6.2 eV and a natural decay lifetime close to 2 s [50]. For those reasons, it is the most populated molecular excited state and is considered to play a key role in promoting plasma chemical reactions. Higher excited triplet states \( N_2(C^3\Pi_u) \) and \( N_2(B^3\Pi_g) \) are also formed mainly by direct electron impact excitation or stepwise excitation from the lower excited states which is most common in lower electrical field discharges [50, 51]. Then, cascading to the metastable \( N_2(A^3\Sigma_u^+) \) state with photon emission or quenching collisions with other existing species in the discharge can occur. Energetic electrons or heavy species can cause ionisation generating ground state molecular \( N_2^+(X^2\Sigma_g^+) \) or excited state \( N_2^+(B^2\Sigma_u^+) \) ions, while higher energy ionisation can be neglected. The molecular transitions \( N_2^+ B \rightarrow X \), \( N_2 C \rightarrow B \) and \( N_2 B \rightarrow A \) are often called **first negative** (1\textsuperscript{-}), **second positive** (2\textsuperscript{+}) and **first positive system** (1\textsuperscript{+}) respectively, and their emissions can be easily obtained in discharges [52].
Figure 1.20 Schematic diagram of the potential energy curves of molecular $\text{N}_2$ and $\text{N}_2^+$ (adapted from [53, 54])

Direct electron impact excitation

R 1.6 $\text{e} + \text{N}_2 \rightarrow \text{e} + \text{N}_2(A), \text{N}_2(B) \text{ or } \text{N}_2(C)$ $\Delta E = 6.2, 7.3, 11.1 \text{ eV}$

Stepwise excitation

R 1.7 $\text{e} + \text{N}_2(A) \rightarrow \text{N}_2(B) \text{ or } \text{N}_2(C) + \text{e}$ $\Delta E = 1.1, 4.9 \text{ eV}$

Direct Electron impact ionisation

R 1.8 $\text{e} + \text{N}_2 \rightarrow \text{e} + \text{N}_2^+$ $\Delta E = 15.7 \text{ eV}$

Stepwise ion excitation

R 1.9 $\text{e} + \text{N}_2^+ \rightarrow \text{N}_2^+(A), \text{N}_2^+(B) + \text{e}$ $E_j = 16.2$-$18.7 \text{ eV}$

$\text{N}_2$ dissociation can lead to different states of atomic nitrogen such as ground state $\text{N}(^4\text{S})$ and the metastable states $\text{N}(^2\text{D})$ and $\text{N}(^2\text{P})$ as shown in Figure 1.21. $\text{N}(^4\text{S})$ is fairly unreactive, however it will react with unstable radical species and it is often given the simple notation of N. Possible excited states of atomic nitrogen include
N(²D) and N(²P). The ²D configuration is at a lower energy than ²P so it is assumed that it will be more involved in plasma reactions and is often referred to as \( N^* \).

- **N₂-O₂ plasma species**

The key reactive oxygenated species in air mixtures plasma are dissociated oxygen radicals (the molecular O₂ energy diagram is given in Figure 1.21). Oxygen dissociation takes place mainly through electron impact as follows:

\[
\begin{align*}
R 1.10 & \quad e + O₂ → e + O(³P) + O(³P) & \Delta E = 5 \text{ eV} \\
R 1.11 & \quad e + O₂ → e + O(³P) + O(¹D) & \Delta E = 7 \text{ eV}
\end{align*}
\]

![Figure 1.21](image)

**Figure 1.21** Potential energy diagrams of various states of O₂ (adapted from [55, 56])

However, the different electron impact reactions in air plasmas that will initiate the plasma chemistry are different in different types of plasmas and are dependent on the mean electron energy that different discharges can sustain. The dissipation of input electrical power in atmospheric air plasma as a function of the mean kinetic energy
of the electron is given in Figure 1.22a. With regards to the efficiency of a particular electron-impact process, this can be expressed in terms of the $G$-value [57]. The $G$-value gives the number of events relating to particular collision processes per 100 eV energy input. It is the ratio of the number of reactions to the amount of energy expended by the electrons. Figure 1.22b shows the calculated $G$-values for various electron impact dissociation and ionisation processes as a function of the electron mean energy in the discharge plasma. It can be seen that for low mean energy discharges (e.g. gliding arc discharges), most of the energy produces vibrational excitation of $N_2$ and dissociation of $O_2$ in discharges with higher mean electron energy. At typical cold atmospheric plasma and mean electron energy $< 10$ eV, oxygen dissociation will dominate over nitrogen dissociation. This means that an oxidising environment of O radicals will be produced when oxygen is present.

![Graph of G-values and electron mean energy](image)

**Figure 1.22** a) Power dissipation in an atmospheric-pressure dry air discharge, showing the percent of input power consumed in the electron impact process of vibrational excitation, dissociation and ionisation of $N_2$ and $O_2$ and b) calculated $G$-values for the dissociation and ionisation processes in dry air, all as a function of average kinetic electron energy [57, 58]

- **Humid plasma species**

The addition of humidity is used in many plasma-chemical organic waste processing applications in order to produce extra strong oxidants such as OH, HO$_2$ or O radicals which could enhance the oxidation. In humid gas mixtures plasma, H$_2$O dissociates
to produce OH and H radicals. In low mean electron energy discharges, this dissociation can occur via mainly three types of reactions:

Direct impact dissociation

R 1.12  \[ e + H_2O \rightarrow e + H + OH \]

Dissociative electron attachment

R1.13  \[ e + H_2O \rightarrow H^- + OH \]

Penning dissociation or dissociative attachment

R 1.14  \[ M^* + H_2O \rightarrow M + H^+ OH \rightarrow MH + OH \]

In O\(_2\) gas mixtures plasmas O\(^1\text{D}\) can also significantly contribute to the water dissociation in atmospheric plasma by increasing the production of OH radicals, according to Reaction 1.14. Figure 1.23 shows the contributions of these reactions in a mixture of 5% O\(_2\), 10% H\(_2\)O, 15% CO\(_2\) and 70% N\(_2\), as calculated from Penetrante et al [57].

![Diagram showing contributions of various processes to the production of OH in an atmospheric pressure plasma of 5% O\(_2\), 10% H\(_2\)O, 15% CO\(_2\) and 70% N\(_2\)]

**Figure 1.23** Contributions of various processes to the production of OH in an atmospheric pressure plasma of 5% O\(_2\), 10% H\(_2\)O, 15% CO\(_2\) and 70% N\(_2\) [57]
1.9 Low temperature plasma treatment of organic liquid waste - a literature review

1.9.1 Introduction

Gaseous pollution control, solid and liquid waste treatments have been developed into commercial processes based on incineration, catalysis, adsorption, disposal with landfill, etc. More recently, technology based on plasmas has become significant for these environmental applications due to the advantages such as lower costs, higher treatment, energy efficiencies and smaller space volume.

During the last two decades, non-thermal plasmas in and in contact with higher density media, like liquids, have attracted much attention. Due to their nature, they can produce a high active species density with short quenching times and with simultaneous UV radiation, making them particularly suitable for environmental applications such as water decontamination, sterilisation and purification processes. Although such plasmas have been known for a long time, they are still considered as a new aspect of plasma science, and further research is needed to understand its effect and learn how to control them.

1.9.2 Classification of discharges in and in contact with liquids

Discharges in and in contact with liquids can be divided into three main types such as direct liquid phase discharges, discharges in the gas phase with one or more liquid electrodes and discharges creating into bubbles in liquids [59]. Figure 1.24 illustrates examples of those three main categories. Non-thermal direct liquid-phase discharges are often called direct liquid streamer or corona discharges and are almost always generated by pulsed excitation in a pin-to-plate or in plate-to-plate configuration [60, 61].

Discharges in the gas phase with liquids are in principle gas discharges. Nevertheless, the properties of these discharges can be different as the discharge current is transported through the liquid electrode by ions which have smaller mobility than electrons in gases. Configurations used to generate this type are shown in Figure 1.25. Discharges in gas-liquid phase can be generated by dc, pulsed or ac excitation. Discharges created in bubbles in water are usually treated as a separate group, as they are completely surrounded by the liquid which serves as an electrode.
Figure 1.24 Typical electrode configurations in and in contact with liquids (taken from [59]). a) Direct liquid phase discharge reactor, b) gas phase discharge with liquid electrode and c) bubble discharge reactor

Figure 1.25 Overview of the different electrode configurations used to study electrical discharges with liquid electrodes (taken from [62]). (a) Discharge reactor between two liquid electrodes, (b) setup to study discharges between two droplets, (c) water surface discharge setup (flashover), (d) gliding arc reactor with active water electrode [63], (e) gliding arc reactor with passive water electrode (standard gliding arc configuration) and (f) hybrid reactor ([64])

Many different configurations have been used such as bubbling systems, capillary or diaphragm systems. The gliding arc discharge configuration belongs to the plasma “in contact” with the liquid treatment method as shown in Figure 1.25 e.
1.9.3 Non-Thermal Plasma Treatment of Liquid Waste

Environmental applications of electrical discharges in liquid treatment are being considered increasingly, as they could present many potential advantages [65]:

- Direct in situ production of multiple reactive chemical species;
- Enhancement of gas phase reactions through quenching of gas reaction products into the liquid and species formed in liquid reactions and transferred to the gas;
- Facilitation and enhancement of both gas and liquid phase reactions;
- Control of relative amounts of reactive species by adjusting the applied electric field and the gas-liquid flow rates;
- Simultaneous production of UV light and shock waves.

Many of the different plasma-liquid configurations have been centred on waste water treatment and water purification processes [65, 66]. The corona discharge [61, 65, 67-70], and optimised hybrid reactors [71], the gliding arc discharge [39, 72], as well as dielectric barrier discharges have been tested for their efficiency in this field [73-76]. A review on water purification by plasma comparing the energy efficiency for different reactors is given by Malik [77]. A recent review and discussion on different plasma-liquid treatment methods in aqueous systems even with the use of catalyst is given in the book edited by Parvulescu, Maguraneu and Lukes [78].

Changing the liquid in the plasma-liquid process would significantly affect the plasma properties and chemistry, for example going from a high salt containing liquid to high purity water or an organic liquid which generally have lower conductivity properties and it could be more difficult or more energy demanding to create an in-liquid discharge. For that reason, we find extended literature on the treatment of organics in aqueous systems and wastewater, however, the literature on plasma-liquid treatment of organic waste is more limited. However, plasma in contact with organics can be found in literature as early as 1978, when Sharbaugh et al. used benzene as an example to study the breakdown phenomena in insulating dielectric liquids [79]. Later in 1982, Suhr reviewed on the organic plasma-chemical reactions in organic plasma synthesis and [80] some of his later work with co-workers using low-pressure RF discharge can be found on [81-83]. In atmospheric
plasma processing of organic liquids, Prieto et al studied the conversion of heavy oil to lighter hydrocarbons [84] and soon, research was extended to the field of plasma reforming for the production of hydrogen rich gases using different configurations such as corona discharges [85-89], dielectric barrier discharges [90-92] or gliding arc discharge [35, 93].

1.9.4 Gliding Arc Applications on Organic Liquid Waste Treatment

The interest in the gliding arc discharges in interaction with liquids has also started to increase in the last few years and soon a standardised reactor configuration for the treatment of aqueous waste was developed [39]. The main reason for its use is because it can provide plasma with both useful properties from thermal (large electron densities, currents and power) and non-thermal plasma (low operating gas temperature). Gliding arc was mainly developed in France [94-96] and Algeria [97, 98], but now it is considered as an easy technique to use and it is further developed in other groups in Unites States [99-101], Far East [102, 103], Cameroon [104-106] and Eastern Europe [37, 107].

Regarding the treatment of organic liquid waste, Moussa and Brisset were the first to treat an organic solvent rather than an aqueous solution using the gliding arc configuration [94]. The treatment was performed using tributylphosphate (TBP) under humid air batch conditions and results show that TBP is degraded mainly to CO$_2$ and H$_3$PO$_4$ by means of highly reactive species (e.g. HO$^\cdot$) formed in the plasma arc and the plasma-liquid contact surface. Similar work has been performed by the same group in trilaurylamine (TLA) [96]. In addition to batch treatment, a recycling device for the treated liquid was developed in order to improve the kinetic rate. Further work has been done in organophosphorous compounds (triethylphosphorate, TEP) using a modified version of a gliding arc discharge with an auxiliary pair of electrodes in order to control the discharge energy and decrease the operating voltage [95].

An important development in the use of gliding arc discharge for liquid treatment has been performed by Burlica, Locke and their co-workers, using a spraying nozzle injection system of the treated solution directly to the plasma plume [99, 108, 109].
1.10 Objectives and thesis structure

The objective of this thesis is the study of low-temperature atmospheric pressure plasma as a potential technological application for the degradation of organic liquid waste found in nuclear industries. Literature supports the idea that low-temperature plasma technology and especially the unique properties of gliding arc discharge have much potential for the nuclear decommissioning and the treatment of organic liquid waste. However, limited literature is found for the plasma treatment of liquid organics and fundamental aspects of the chemical process still remain to be unravelled.

For this reason, the study has been approached initially by investigating the degradation of oil in gas phase only, in order to understand the gas chemistry and elucidate the plasma-chemical degradation mechanism. Gaseous odourless kerosene and dodecane have been used as simulants and their plasma-chemical degradation has been studied using a BaTiO₃ packed bed plasma reactor (Chapter 3) and a gliding arc discharge reactor (Chapter 4). The effect of different gas composition to the plasma-chemical degradation has been studied and overall degradation ability and efficiency is compared and discussed.

The plasma-liquid dodecane treatment is firstly studied using Ar dielectric barrier discharge (Chapter 5), testing the effect of different reactor configuration, humidity and temperature to the discharge characteristics and degradation efficiency will be discussed. The study of the liquid dodecane degradation is then extended by using the gliding arc discharge (Chapter 6). Using N₂ and Ar in both dry and humid conditions for the batch treatment of dodecane, the degradation efficiency, gas chemistry and liquid chemistry are discussed and correlated to the gas chemistry observed during the plasma treatment of gaseous dodecane under the same conditions, in order to gain an overall understanding of the plasma-liquid clean-up process. Finally, the gliding arc plasma treatment of liquid dodecane is studied using the recycling method investigating the effect to the reactivity and degradation efficiency.
1.11 References


[53] S. V. Pancheshnyi, Starikovskaia, S. M., Starikovskii, A. Yu, "Collisional deactivation of N$_2$(C$^3\Pi_u$, v=0, 1, 2, 3) states by N$_2$, O$_2$, H$_2$ and H$_2$O molecules," *Chemical Physics*, vol. 262, pp. 349-357, 2000.


Chapter 2

2. Analytical Techniques

2.1 Introduction

This chapter aims to give a background on the main analytical techniques used in this work. These were Fourier Transform Infrared (FTIR) spectroscopy, Optical Emission Spectroscopy (OES) spectroscopy, the combined Gas Chromatography and Mass Spectroscopy (GC-MS) technique and Flash Colum Chromatography. The following sessions will present a short description of the principles and the operating conditions that were used for each technique, while further description of the experimental set-ups used are given separately in the next chapters.

2.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR absorption spectroscopy has been used in this work for the quantitative and qualitative gaseous analysis using real time in-line sampling system, as well as for qualitative characterisation of off-line liquid samples. The next sections will present a background on the principles of IR spectroscopy, instrumentation and methods used.

2.2.1 Outline of Basic Spectroscopy

Spectroscopy is the study of interaction between electromagnetic radiation and matter studied as a function of frequency (ν), or wavelength (λ). According to the quantisation of energy, the energies of various forms of motions in atoms and molecules are limited to certain discrete values, those which correspond to the so-called stationary states. When an atomic or molecular system absorbs or emits light, the system goes from one quantised energy level to another. The Bohr frequency condition states that the difference in the energy level must equal the energy of the light absorbed or emitted:

\[ \Delta E = h \nu \]  

Equation 2.1

where, \( h = 6.626 \times 10^{-34} \) J s, the Planck constant, \( \nu = \) frequency (s\(^{-1}\)), \( E = \) energy (J)
Emission and absorption spectroscopy give the same information about energy level separations, but practical considerations generally determine which technique is employed. In emission spectroscopy, a molecule undergoes a transition from a state of high energy to a state of lower energy and emits the excess energy as a photon. In absorption spectroscopy, the net absorption of incident radiation is monitored and its frequency is varied.

Electromagnetic radiation is described as a transverse waveform. By this is meant that it consists of oscillating electric and magnetic fields which point transversely to the direction of propagation of the wave. Both electric and magnetic field are oscillating at the same frequency $v$ (in units s$^{-1}$ or Hz) and the light wave travels through a vacuum at a speed of $c = 2.9979 \times 10^8$ m s$^{-1}$. The distance between adjacent crests at a given point in time is called the wavelength:

$$\lambda = \frac{c}{v} \quad \text{Equation 2.2}$$

The characteristics of the wave are also reported by giving the wavenumber, $\tilde{\nu}$ (cm$^{-1}$) of the radiation, where

$$\tilde{\nu} = \frac{v}{c} = \frac{1}{\lambda} \quad \text{Equation 2.3}$$

Electromagnetic radiation is commonly divided in separate sections, as each section has different effects on its surroundings. The various regions of the electromagnetic spectrum with their defining frequencies and wavelengths are shown in Figure 2.1. Photons involved in transitions can have energy of various ranges in the electromagnetic spectrum, such as X-ray, ultraviolet, visible light, infrared, or microwave radiation, depending on the type of transition.

![Figure 2.1](image-url)

**Figure 2.1** a) Energy level separations on the four types of molecular motions and b) regions of the electromagnetic spectrum [1]
Translational energy levels are practically continuous and can be calculated as kinetic energy using classical mechanics. An energy unit often used in spectroscopy is eV, the amount of energy an electron acquires when it is has been accelerated through a potential of 1 V. A table of conversion factors for energy units is given in Appendix I.

### 2.2.2 Principles of IR spectroscopy

Infrared (IR) spectrometers have been used and developed since 1800 when Sir William Herschel did the first experiment passing sunlight through a prism in his laboratory [2]. IR spectroscopy today is one of the most common spectroscopic techniques used by organic and inorganic chemists. Spectra of gaseous, liquid and solid samples can all be measured and so functional group information can be gathered easily with no special sample-handling techniques. More profound information of the molecular structure can be also obtained in the high resolution gaseous analysis. This section will focus mainly on the gaseous IR analysis as it constitutes the majority of the analysis used in this work.

Infrared radiation is divided into three subsections of far IR (13,000 – 4,000 cm$^{-1}$), mid IR (4,000 – 200 cm$^{-1}$) and near IR (200 – 10 cm$^{-1}$). The mid IR is the most frequently used, also used in conventional FTIR spectrometers (4000 – 400 cm$^{-1}$). In this range, vibrational transitions of a molecule can be observed. When dealing with vibrational spectra of polyatomics, the gross selection rule is that the normal mode of vibration must result in a change of dipole moment for that mode to be IR active [1, 2]. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation, causing a higher amplitude vibration and rotation until de-excitation happens. Different IR frequencies correspond to different types of vibrations. Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes (x, y, z). A polyatomic molecule of $n$ atoms has 3$n$ total degrees of freedom. However, 3 degrees of freedom are required to describe the translation, of the entire molecule through space and 3 or 2 additional degrees of freedom to describe the rotation of a non-linear or linear molecule, respectively. Therefore, the remaining 3$n$ – 6 degrees of freedom are true, fundamental vibrations for non-linear molecules, where linear molecules possess 3$n$ – 5 fundamental vibrational modes. Among these
fundamental vibrations (also known as normal modes of vibration), those that produce a net change in the dipole moment may result in an IR activity. However some vibrations leave the net dipole moment unchanged (e.g. symmetric stretching) corresponding to IR inactive modes. Major types of vibrations are stretching and bending and typical examples of carbon dioxide and water gas molecules are given in Figure 2.2 and 2.3. More complex polyatomics can exhibit bending, rocking or wagging. Figure 2.4 depicts the vibrational modes of two atoms attached in a stationary one, as in the case of a hydrocarbon.

**Figure 2.2** Normal modes of vibration of CO$_2$ A: Symmetric stretching (IR inactive), B: antisymmetric stretching, C: in plane deformation, D: out of plane deformation (C and D result in same frequency, the so-called two-fold degenerate deformation vibration [3]).

**Figure 2.3** Normal vibrational modes of water

**Figure 2.4** Vibrational modes of two atoms attached on a stationary atom
2.2.3 FTIR spectrometer components

The basic instrumentation of an IR absorption spectrometer includes the radiation source, the dispersive element and the detector. Early IR spectrometers introduced in the mid 1940’s are the dispersive spectrometers. They use a monochromator as a dispersive element that separates light into different frequencies. The intensity of radiation at each frequency is then analysed by a suitable detector. Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy (the Multiplex or Felgett Advantage).

Common radiation sources that could be used for both dispersive and FT spectrometers are the Plank (or black-body) radiator, thermal radiator, Nerst rod and high pressure lamp. Common reference source is the He-Ne laser that can produce two lines in the mid-IR (1.152 μm and 3.391 μm) that cannot be detune easily [2].

Instead of a monochromator in dispersive spectrometers, FTIR spectrometers use an interferometer. After the radiation is emitted, the beam enters the interferometer where spectral splitting takes place allowing a wavelength dependent radiation modulation. The most common and widely used type of interferometer is the Michelson interferometer. The Michelson interferometer consists of two mutually perpendicular plane mirrors. One can move either at a constant velocity or is held at equidistant points for fixed short time periods and rapidly stepped between these points. Between the fixed and moveable mirror there is the beamsplitter. The IR beam from the source reaches the beamsplitter where is split into two partial beams that are reflected on the fixed mirror and on the movable mirror back to the beamsplitter where they recombine and are brought to interfere. A shift of the movable mirror changes the optical pathlength into the interferometer. That results in a phase difference between both partial beams, hence a change of the interference amplitude happens. The intensity signal from the detector, as a function of the change of the optical pathlength corrected by a constant component, is called an interferogram. After the interference, the IR modulated beam enters the sample compartment where specific frequencies of energy unique to the sample, are
absorbed. In gas FTIR analysis, sampling happens into gas cells. Figure 2.5 depicts a general instrumentation layout of a FTIR spectrometer including the long path cell illustration and Figure 2.6 shows a typical interferogram.

Figure 2.5 Schematic layout of a FTIR spectrometer (adapted from [3])
The gas cell used in this work was a Specac Tornado T5 long path 1.3 L cylindrical borosilicate cell using gold coated mirrors and KBr windows. Within the cell, the beam is deflected by a plane mirror horizontally by 90° and reflected back and forth many times until it finally leaves the cell exit KBr window having travelled a defined pathlength of 5 m. Long pathlengths can increase sensitivity, as the longer the pathlength at a fixed concentration the more molecules the IR beam passes through. However they might also cause considerable radiation loses, that is why most frequently used pathlengths are up to 10 m. After the long path gas cell, the beam finally passes to the detector for final measurement. The measured signal is digitalised and sent to the computer where the mathematical Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

FTIR spectrometers do not require slits to achieve resolution and therefore they can succeed high spectral resolution with a much higher throughput compared to dispersive spectrometers. In FTIR, the spectral resolution is determined by the maximum achievable optical path difference between the two parallel beams in the interferometer. The bigger the optical path difference results in a longer interferogram, thus more data points present to allow higher resolution. High resolution reduces spectral overlap allowing the detection of narrow absorbance peaks at specific frequencies. However, high resolution spectra require longer

**Figure 2.6** A typical interferogram and the single beam spectrum after the Fourier Transform (adapted from [2])
measurement time and produce more noise, reducing the signal-to-noise ratio. Thus, high resolution spectra are taken only if needed, and multiple scanning might increase the measurement time, but improve the signal-to-noise ratio.

2.2.4 Attenuated Total Reflectance (ATR) FTIR spectroscopy

The ATR FTIR technique was used for the analysis of off-line liquid samples during this work. Although traditional liquid or solid sample FTIR analysis requires pretreatment of the sample to allow good transmittance of IR beam and nice spectra, the ATR technique eliminated this problem allowing quick sample analysis and the generation of reproducible spectra. In the ATR technique, the IR radiation emitted by the source is internally reflected in a high refractive index, optically dense crystal which is in direct contact with a “less dense” sample. In practice, part of the radiation penetrates the surface before reflection occurs, the so-called evanescent waves [4]. Evanescent waves interact with the sample and the IR spectrum can be obtained. The penetration depth \( d_p \) is determined by the wavelength of incident radiation \( \lambda \), the angle of incidence \( \theta \), and the refractive index of crystal \( n_1 \) and sample \( n_2 \) and can be expressed using Equation 2.1. For a typical refractive index of an ATR crystal at the mid-IR wavelength, the penetration depth is less than 1 micrometer. Common ATR crystals used are germanium, zinc selenide and diamond. Figure 2.7 illustrates a schematic of the ATR crystal. For our liquid analysis, a Bruker Alpha Platinum ATR spectrometer was used using with a diamond crystal \(( n \sim 2.4)\).

\[
d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta + \frac{n_2}{n_1} - 1}}
\]

Equation 2.4

![Figure 2.7 Schematic of ATR crystal cell in FTIR spectroscopy](image)
2.2.4 Qualitative and Quantitative Analysis Using FTIR Spectroscopy

The gaseous analysis of the plasma processing end-products has been performed using a FTIR spectrometer (Shimadzu 8300). Analysis can be both qualitative and quantitative and methods are described in the following sections.

Qualitative analysis in IR spectroscopy is mainly used in two ways, structural elucidation and compound identification. Structural elucidation is possible, as many functional groups give characteristic IR absorption at specific, narrow frequency ranges, regardless of their relationship with the rest of the molecule. This method is routinely used in organic chemistry and characteristic group frequencies are well given in literature. Figure 2.8 shows the regions of mid-IR, in which functional groups absorb. However, spectral interpretations should not be confined to one or two bands and the whole spectrum should be examined. To confirm or gain more information of an unknown substance, other analytical information provided by nuclear magnetic resonance (NMR), mass spectrometry (MS), or other chemical analysis should also be used where possible. Furthermore, compound identification can be more easily achieved by using a reference IR spectrum that matches that of the unknown compound. A large number of reference spectra for vapour and condensed phases are available in printed and electronic formats.

![Figure 2.8 Regions of IR functional groups](image-url)
Quantitative analysis in FTIR spectroscopy follows Beer-Lambert law. Using the Beer-Lambert law the absorbance can be converted to concentration [4]:

\[ A = \varepsilon CL \]  

Equation 2.5

where, \( A \) = absorbance, \( \varepsilon \) = molar absorption coefficient which is constant for a specific compound, \( C \) = sample concentration, \( L \) = optical pathlength of absorbance.

In this work, compound identification and quantitative analysis was performed using the gaseous IR reference spectra from the QASoft database by Infrared Analysis Inc [5]. Bruker’s Opus 4.2 software was used for the interpretation of the experimental IR spectra and comparison with the reference. Measuring the absorbance peak heights of specific bands at characteristic frequencies the concentration of the compound can be obtained according to the equations below. The reference spectrum of dodecane is given as an example of the calculation as shown in Figure 2.9.

**Figure 2.9** The dodecane reference spectrum with major absorbance peaks annotated. Dodecane reference concentration is \( C_o = 100 \) ppm, mixed in \( \text{N}_2 \) at pressure 1 atm. The optical pathlength is \( L_o = 1 \) m and the spectral resolution is 1 cm\(^{-1}\).

For a known compound reference spectrum the absorbance of a characteristic peak at specific frequency is:
\[ A_o = \varepsilon \ C_o \ L_o \]  

Equation 2.6

In case of dodecane, at specific frequency 2863cm\(^{-1}\) the absorbance is \( A_o = 0.1176 \), \( C_o = 100 \) ppm, \( L_o = 1 \) m

The concentration value of dodecane in an experimental sample spectrum under the same spectral conditions can be obtained using the following equations:

\[ A_s = \varepsilon \ C_s \ L_s \]  

Equation 2.7

Where, the optical path length in the long path cell used was \( L_o= 5 \) m

Equations 2.6 and 2.7 can give Equation 2.8 and finally Equation 2.9:

\[ \frac{A_s}{A_o} = \frac{C_s L_o}{C_o L_s} \]  

Equation 2.8

\[ C_s = \frac{100 A_s}{0.1176 \cdot 5} \]  

Equation 2.9

Using the Equation 2.9 relationship between the dodecane concentration and its absorbance, the same method is used for the quantitative analysis of the plasma processing gaseous end-products using the reference QASoft database.

2.2.5 Operating Conditions

A Shimadzu 8300 FTIR spectrometer was mainly used for the experimental measurements and a Bio-Rad 4000 FTIR spectrometer was used for the work described in Chapter 5. The operating conditions are summarised in Table 2.1.

<table>
<thead>
<tr>
<th>FTIR Spectrometer</th>
<th>Cell</th>
<th>Pathlength</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shimadzu 8300</td>
<td>Specac Tornado T5, 1.3 L</td>
<td>5 m</td>
<td>1 cm(^{-1})</td>
</tr>
<tr>
<td>Bio-Rad 4000</td>
<td>Infrared Analysis Inc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Excalibur series</td>
<td>Mini series 6-PA, 0.5 L</td>
<td>6 m</td>
<td>1 cm(^{-1})</td>
</tr>
</tbody>
</table>

Table 2.1 Operating conditions of the FTIR spectrometers used
In all cases the measurements were in-line with the gas sample flowing continuously through the gas cell. The sampling temperature is laboratory temperature at 24 °C and pressure is atmospheric. Considering the nature of the gas sample which consists of narrow peaks, a high resolution of 1 cm\(^{-1}\) was necessary in all measurements. In order to improve the signal to noise ratio (S/N) 10 multiple scans were used and the spectrometer automatically gives the average spectrum of the sample. The standard deviation in concentration values was calculated from 5 repetitive samples in each case.

2.3 Optical Emission Spectroscopy (OES)

2.3.1 Introduction

Optical emission spectroscopy (OES) is commonly employed in the diagnosis of laboratory plasmas and it was also used in this work, in both gaseous and plasma-liquid treatment. A short introduction to the technique is given below.

Atomic or molecular emission is based upon the emission of light upon the relaxation of an electron from an excited state of an atom or molecule. In plasma emission spectroscopy, light emitted from the plasma itself is recorded. One of the basic underlying processes is the excitation of particles (atoms, molecules, ions) by electron impact and the decay by spontaneous emission. The intensity of emission line is correlated with the particle density in the excited state \[6\].

2.3.2 OES Instrumentation

The basic components of a spectrometer are the entrance slit, the wavelength dispersion element, the imaging mirrors and the exit slit equipped with a detector. A monochromator uses a prism as the dispersive element and the slits at fixed positions where the prism needs to be rotated to change wavelength. Spectrographs use diffraction grating as the dispersive element in a fixed position, and the angle of diffraction varies with the wavelength. The principle of the spitting of a wide range spectral region into numerous sub-spectra by a classic ruled grating is described by the grating equation (Equation 2.10) and illustrated in Figure 2.10 \[7\]. The relationship between an incident and a diffracted parallel light beam for a grating is:
where, $k$ is the diffraction order number, $\lambda$ is the wavelength, $d$ is the groove distance, $\alpha$ is the angle of incidence and $\beta$ is the angle of diffraction.

**Figure 2.10** A classic ruled grating showing the diffraction principle. $N$ is the grating normal, $d$ the groove distance, $\alpha$ is the angle of incidence and $\beta$ is the angle of diffraction and $\vartheta$ is the blaze angle [7].

The spectrograph used in this work uses the common Czerny–Turner configuration as illustrated in Figure 2.11. A triple grating turret is used as the grating element, which changes easily to three different gratings, selectable by computer control. The exit plane is equipped with an array charge-coupled device (CCD) detector. The light source, i.e. the plasma, is either imaged by an imaging optics onto the entrance slit or coupled by optical fibres to the slit. The latter is very convenient, particularly when direct access to the plasma light is difficult. Light enters the entrance slit and is collected by the collimating mirror. Essentially what a spectrograph does is to form an image of the entrance slit in the exit focal plane with each position in the plane representing a different wavelength. Collimated light strikes the grating and is dispersed into individual wavelengths (colours). Each wavelength leaves the grating at a different angle and is reimaged onto the CCD detector at the exit focal plane. As each wavelength images at a different horizontal position, the spectrum of the input light is spread across the CCD. Individual wavelengths focused at different horizontal positions along the exit port of the spectrograph are detected simultaneously. Rotating the diffraction grating scans wavelengths across the CCD, allowing the intensity at individual wavelengths to be readily measured.
Figure 2.11  a) A general and b) a more detailed schematic of the OES spectrograph with the Czerny–Turner diffraction configuration and the CCD detector [9]

The CCD refers to a semiconductor (usually silica oxide) matrix array that charge is collected, transferred and converted into measurable voltage [8]. In principle, they are consisted of many single pixels in arrays, which generate photoelectrons and transport them by vertical and horizontal shifting to the read-out amplifier [7, 8]. CCDs have various applications in imaging and they are considered ideal detectors in spectroscopy, due to their mechanical accuracy and photometric performance.

2.3.3 Operating conditions

A Princeton 320PI spectrograph was used for the optical emission spectroscopy measurements of various plasma conditions in this work and the operating conditions are given in below.

<table>
<thead>
<tr>
<th>Princeton 320PI CCD spectrograph</th>
<th>200-850 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>grating</strong></td>
<td>150gr/mm</td>
</tr>
<tr>
<td><strong>resolution</strong></td>
<td>0.52nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Muti-mode quartz optical fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Numerical Aperture (NA)</strong></td>
</tr>
<tr>
<td><strong>Optical field diameter</strong></td>
</tr>
</tbody>
</table>

Table 2.2 Operating conditions of the OES plasma spectroscopy used in this work
2.4 Gas Chromatography and Mass spectroscopy (GC-MS)

2.4.1 Gas Chromatography

Gas chromatography is the type of chromatography where the mobile phase is a gas. Separation occurs by partitioning gaseous samples between a carrier gas and a stationary phase. The gas chromatograph enables a small amount of sample (gas or vaporised liquid) to be introduced into an inlet system where it is vaporised and passed into a column. The column is held within an oven and a flow of the inert carrier gas passes through it. A detector is fitted to the column exit to monitor the eluted and separated components. The detector creates the electrical signal which is amplified and sent to the recording or data-processing device, from which results can be obtained [10].

Different gas species pass through the column at different rates depending on the strength of interactions with the walls of the column. This causes the gas mixture to become separated into individual components that reach the end of the column and are detected at different times. By measuring the retention time of each species in the column, the component gases can be identified either by comparison with chromatograms for known species or coupled with an identification technique (e.g. GC-MS). Retention times are affected by the gas concentration, flow rate and pressure as well as the column material and temperature [11], therefore selection of appropriate column materials and operating conditions are critical for resolution of the gas mixture.

Common carrier gases are usually high purity inert gases like helium, nitrogen, or argon, normally determined by the detector used. GC columns originally consisted of a tube containing a packing of solid support material with various liquid or solid coatings depending on the type of mixture being separated. Most GCs now use capillary columns, which offer several advantages over packed columns. The stationary phase is coated uniformly on the inside of a capillary eliminating problems associated with uneven packing. They are made of a flexible material so that longer lengths can be wound into compact coils that allow for a better resolution of the separated gas mixture.
Figure 2.12 Schematic for simple gas chromatography (taken from [4])

Figure 2.13 An example of a chromatograph from a plasma-dodecane post treatment sample. Most abundant component is untreated dodecane, however, traces of other alkanes were identified

2.4.2 Mass Spectroscopy

Mass spectrometry is a widely used instrumental technique that relies on separating gaseous charged ions according to their mass-to-charge ratios [4]. Atomic, ionic and molecular weights are normally expressed in terms of atomic mass units (amu). One atomic mass unit is defined as one-twelfth the mass of a $^{12}$C atom.
The basic components of a mass spectrometer involve a sample inlet, an ioniser, an ion accelerator by an electric field, an ion dispersion chamber where ions are separated according to their mass-to-charge ratio and finally a detector which identifies ions and sends digitised signal to signal processing and data output device.

A small quantity of sample (0.5-2 ml < 100 ppm) is first introduced into the sample inlet. Inlet systems usually combine an atomiser with a heater in order to vaporise sample before the ionization. The sample is then bombarded with electrons, photons, molecules or ions and a stream of ions is produced, mostly positively, but also negatively charged. Due to their charge, they can be accelerated under electric field and pass into the mass analyser where they can be dispersed or physically segregated according to their mass-to-charge ratios ($m/z$). Ions are finally detected, characterized and recorded in forms of mass spectrums.

Mass spectroscopy is extremely powerful and widely used analytical tool for both qualitative and quantitative information relating to both inorganic and organic compound into mixtures. There are many different types which best result in different applications, but this section is limited only to common types of the combined GC-MS technique.

### 2.4.3 Gas chromatography-Mass Spectroscopy combined technique

Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas chromatography and mass spectrometry to identify different substances within a test sample. Mass spectrometers can be used as the detection system, as sample substances are separated and eluted from a gas chromatograph. Figure 2.14 shows the basic components of a GC-MS instrument.

![Figure 2.14 A typical GC-MS system diagram [12]](image-url)
Electron ionisation (EI) and chemical ionization (CI) are the two most widely used ionisation techniques in GC-MS. In this work both EI and CI ionisation was used for the GC-MS samples, in order to obtain complementary information.

EI is produced by accelerating electrons from a hot filament through a potential difference, usually of 70 eV. Organic molecules that eluted from a GC column will be ionised and fragmented. The initial product of EI is a radical cation, resulting from the removal of one electron from the analyte molecule. This cation is called molecular ion (M⁺) and provides the molecular weight of the substance, whereas smaller pieces of the analyte molecule are called fragment ions. EI method is a well understood method that can create reproducible spectra. The fragmentation provides useful structural information for the analyte and there are available mass spectra libraries where compounds can be identified based of their EI “fingerprint”. Limitations of this method are that the analyte must be volatile and stable and the M⁺ is frequently weak or absent from spectra. Usually, CI is used instead of EI to provide molecular weights in GC-MS work.

The CI method uses ion-molecule reactions to produce ions from the analyte. The chemical ionization process begins when a reagent gas such as methane or ammonia is ionised by electron impact. A high reagent gas pressure (or long reaction time) results in ion-molecule reactions between the reagent gas ions and reagent gas neutrals. Some of the products of these ion-molecule reactions can react with the analyte molecules to form ions. Advantages of this method are that molecular weight information of the analyte can be obtained with the molecular-like ions such as [M-H]⁺ - even when EI cannot produce a M⁺ - and the limited fragmentation creates simple spectra. Limitations are that the analyte must be thermally volatile and stable and that spectra are not reproducible enough to allow library searches. The final mass spectra depend on the reagent gas type, reagent gas pressure or reaction time, and nature of the sample.

Figure 2.15 shows an example of 1-dodecanol mass spectrum via EI and CI approaches.
Figure 2.15 Mass spectrum for 1-decanol via a) chemical ionisation and b) electron impact ionisation methods [4]

GC-MS instruments most commonly employ quadrupole mass filters, magnetic sectors analyzers or ion trap detector as mass analyzers. A brief description of quadrupole mass filters is given below, as it was applied in this work.

The quadrupole consists of four parallel metal rods of hyperbolic or circular cross-section. A radio frequency (RF) potential and DC voltage is connected opposite pairs of rods. Ions are injected into the oscillating electric field by a small accelerating voltage (10-20 V) and undergo complex oscillations. Mass separation is achieved by varying (scanning) the voltages on the quadrupole rods, while keeping the RF/DC ratio constant. Only ions of a certain m/z will reach the detector for a given ratio of voltage while other will collide with the rods. At any one point in the scan only one mass can pass through the system. A scheme of a quadrupole mass analyzer is given in Figure 2.16.

Figure 2.16 Schematic of a quadrupole mass analyser [4]
2.4.4 GC-MS Operating Conditions

In this work, GC-MS was carried out in order to identify potential end-products in post-treated samples of liquid dodecane after the gliding arc plasma treatment. A Agilent 5975C Triple Axis GC-MS system was used along with a non-polar capillary column HP-5MS (5%-phenyl)-methylpolysiloxane) dimensions of 30 m length, 250 μm i.d., 0.25 μm film thickness and He as a carrier gas. In order to collect complementary information about our sample analysis, both CI and EI were run for every sample. CI method using CH₄ as the chemical reagent provided molecular weight information for the unknown product in most cases in the form of [M-H]⁺ ions, while EI produced more informative spectra with higher fragmentation. Complementary information and the NIST EI mass spectral database were all used in order to identify unknown end-products. The method used, along with the temperature control applied for the separation of the end-products, are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Agilent 5975C Triple Axis GCMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-5MS column</td>
</tr>
<tr>
<td>Method for both EI &amp; CI</td>
</tr>
<tr>
<td>°C /min °C Hold / min Run / min</td>
</tr>
<tr>
<td>Ramp 1</td>
</tr>
<tr>
<td>Ramp 2</td>
</tr>
<tr>
<td>Final temperature</td>
</tr>
</tbody>
</table>

Table 2.3 Methods used in GC-MS analysis of plasma post-treated liquid dodecane

2.5 Flash Column Chromatography

Overall, the GC-MS analysis of the dodecane plasma post-treated liquid samples under different conditions showed the formation of < 1 % liquid impurities / end-products within the untreated liquid dodecane. In order to facilitate a more profound GC-MS and identify potential plasma chemical end-products in the liquid phase, flash column chromatography was used to separate the samples to polar and non-polar fractions. A description of the method is given below.
Flash column chromatography is a method of liquid chromatography (LC). The original form of chromatography introduced by Tswett in 1903 was LC carried out in columns by gravity elution but its most important development started after 1960’s to achieve today various powerful and versatile high performance liquid chromatography (HPLC) separation techniques. Although HPLC is used for μl sample size separation and forensic analysis, flash column chromatography is still the most common large scale purification technique used in chemical laboratories and can be performed in different scales columns for ml to litre size liquid samples. LC differs to GC in that both the stationary and mobile phase affect the separation of the solute sample and interactions occur between all the phases. The most common stationary phase in flash column chromatography is an absorbent material such as silica gel containing active sites such as OH groups which interact with the polar portions of the molecules. Gas pressure is used to push the eluent through the microporous silica gel to achieve faster separation which is based on the different polarities of molecules in the sample. A schematic of the column characteristics used in this work is shown in Figure 2.17.

![Figure 2.17](image)

**Figure 2.17** Column characteristics used in this work. Various samples were < 7 ml

Packing of the column was done by the wet method, using a slurry of silica gel and hexane poured into the column, avoiding any air bubbles. Preserving the stationary phase wet, the sample was added on the top. In order to separate our samples in two non-polar and polar group fractions for further analysis, 100% hexane was used initially as the mobile phase to “flash” the non-polar fraction and secondly, 100% of
diethyether was used to “flash” any polar molecules from the column. The fractions collection was monitored via the TLC technique. After evaporation of of the solvents used, samples were collected for GC-MS analysis.

## 2.6 References


Chapter 3

3. Plasma-chemical degradation of vapour phase kerosene and dodecane in an atmospheric ferroelectric packed-bed plasma reactor

3.1 Introduction

Petroleum-based products, ranging from fuel oil and hydraulic fluid to lubricating greases and oils, can be found in all power generating plants. Specifically in nuclear plants, hydrocarbon oils are also used in ore purification and spent fuel reprocessing extraction processes leading to a large amount of waste oils, normally characterised as low level radioactive waste (LLW) [1]. Among them the most common oils used are odourless kerosene and dodecane (C$_{12}$H$_{26}$). Non-thermal plasma technology could be a promising method for the treatment of this waste as it can essentially provide the same outcome as incineration but at low temperatures, thus providing advantages such as lower process cost and construction simplification. In addition, plasma systems could be produced in almost any scale for waste treatment, giving the potential of portable plasma devices for on-site or spillage treatment. The plasma-liquid clean-up process in its different forms involves reactions in the gas phase with the evaporated liquid, but also reactions at an interface between the gaseous plasma and the target liquid. The latter one takes place either as a gas-surface process or by diffusion of the reactive species into the bulk of the liquid. Thus, it was considered important as a first step to study the plasma degradation of the target liquid pollutant in the gas phase, as a key for the second step, the study of the degradation mechanism in the liquid phase.

This chapter investigates the use of a ferroelectric BaTiO$_3$ packed bed plasma for the plasma-chemical degradation of gaseous kerosene and dodecane, considering them as VOCs that can be found in power plants, but also getting a forehand insight of the gaseous degradation mechanism as necessary step applying plasma technology for the liquid waste oil treatment.

Ferroelectric bed reactors were first developed as electrostatic precipitators [2] and then they were widely studied for the VOC decomposition, for a variety of hazardous
compounds [3-7]. The most widely used ferroelectric material is barium titanate (BaTiO$_3$), which has a high dielectric constant of ~10,000. The advantage of the BaTiO$_3$ packed bed beads, is the formation of microdischarges between the short contact distances, which significantly enhance the electrical field. Despite the fact that the electron energy density is lower compare to the non-packed reactors [8], ferroelectric packed bed reactors can still achieve a good efficiency for pollution removal, as shown in numerous studies [9].

Regarding the use of ferroelectric barrier discharge reactors for hydrocarbon destruction, Ogata and co-workers [6] have studied the destruction of methane in nitrogen and air plasmas, while Pringle et al. [10] have extended the study with varying oxygen concentrations and developing a model to compare the experimental results. Futamura and co-workers have investigated the destruction of butane in dry and humid nitrogen and air working gases [5], also presenting a more profound investigation of the intermediates in [11]. However, there is no literature evidence of the use of ferroelectric packed bed reactor for the treatment of longer chain hydrocarbons.

In this work, the plasma-chemical decomposition of oil vapour was investigated in a BaTiO$_3$ packed bed dielectric barrier discharge reactor (PBDBD). The degradation of kerosene and n-dodecane mixed in nitrogen and air plasmas was studied with varying specific input energy of the reactor and end-products distribution has been measured using FTIR spectroscopy. However, kerosene is a mixture of saturated hydrocarbons with no defined structure ($C_nH_{2n+2}$, $n = 9-16$) which does not allow quantitative analysis, thus, n-dodecane was used as a surrogate instead. The influence of the varying oxygen concentration in the N$_2$-O$_2$ plasma gas mixture for the destruction and end-products distribution is discussed. Optical emission spectroscopy was used to study the plasma under different conditions, and the mechanism of the plasma-chemical dodecane decomposition will be discussed.

3.2 Experimental Set-up

A schematic diagram of the experimental configuration is given in Figure 3.1 and more detailed view of the reactor in Figure 3.2. The reactor used in these experiments was an atmospheric pressure non-thermal packed bed dielectric barrier
discharge (PBDBD) reactor. It is consisted of a glass quartz tube, 25 mm i.d and 16.5 cm length. The electrode distance is 40 mm and a packed bed of BaTiO$_3$ beads (o.d = 3.2 mm, $\varepsilon = 2000-10000$) is used to fill in the space between them creating a discharge gap of approximately 0.4 mm. These dimensions result in a discharge volume of 7.5 cm$^3$ and a treatment residence time of 0.23 sec.

Figure 3.1 Schematic diagram of experimental set-up

An AC voltage at a frequency of 10 kHz is applied between the two electrodes. The power supply is computer controlled and monitored using the LabView control system (v.6.0, National Instruments) which was originally designed for an adaptive control of NO$_x$ removal in non-thermal plasma processing [12]. This software controls the value of the voltage supplied to the plasma reactor sending a control value in the form of a digital signal (0-127 slider steps) to a high voltage digital potentiometer to produce the final analogue voltage (0-24 kV$_{\text{pk-pk}}$). Figure 3.3a shows an example voltage and current waveforms generated by nitrogen discharge and Figure 3.3b plots the charge as a function of the discharge voltage at the same conditions to obtain the Lissajous figure. The area integration of Q-U Lissajous figures has been used as a method to obtain the discharge power as introduced by Manley [13] and was described before [14]. Discharge power calculations are given in Appendix A in more detail. Carrier gases used through the plasma reactor were N$_2$, air (N$_2$ 80%, O$_2$ 20%) and mixtures of N$_2$ and O$_2$ and they were supplied by BOC Gases (99.998%). The total flow was stable at $Q = 2$ L min$^{-1}$ and the vapour oil concentrations used were 35 or 65 ppm for dodecane and 80 ppm for kerosene. In-line FTIR spectroscopy (Shimadzu 8300) with a long path IR cell (SpecacT5, 5 m) at
resolution 1 cm⁻¹ was used for the identification and concentration determination of the gaseous products. Optical emission spectroscopy measurements occurred along the discharge in a central and parallel position to the reactor, and by integration of a 2.4 cm diameter optical field, using a multi-mode quartz optical fibre. The spectrograph CCD Princeton Instrument 320PI spectrograph was used, with a 150 or 600 g/mm grating (0.52 or 0.13 nm resolution) and in the range of 200 – 800 nm.

Figure 3.2 The BaTiO₃ packed bed DBD reactor

Figure 3.3 An example of current and voltage waveforms during the BaTiO₃ packed bed nitrogen discharge and the Q-U plot for the calculation of discharge power per cycle, Pd = 0.7 W. The spikes on the current waveform correspond to microdischarges formed from the contact points between the beads and it is of nanosecond duration.
Calculations of reactant conversions, product selectivity and carbon balance in the gas stream are defined as shown in equations 3.1 – 3.4.

\[
\% \text{ Degradation} = \frac{C_i - C_o}{C_i} \times 100
\]

Equation 3.1

where, \( C_i \) and \( C_o \) are the input and output dodecane or kerosene gas concentration respectively.

\[
\% \text{ Product Selectivity} = \frac{n \times C_{\text{product}}}{12 \times (C_i - C_o)} \times 100
\]

Equation 3.2

where, \( n \) is the number of carbon atoms in the end-product with concentration \( C_{\text{product}} \).

\[
\% \text{ Carbon Balance} = \frac{[C_{\text{HCN}} + C_{\text{CO}} + C_{\text{CO}_2} + C_{\text{CH}_4} + 2 \times (C_{\text{C}_{12}\text{H}_{26}} + C_{\text{C}_{12}\text{H}_{26}})]}{12 \times (C_i - C_o)} \times 100
\]

Equation 3.3

The specific input energy (SIE), is a term often used in technological plasmas in a manner of describing the energy efficiency and it was also used this work. It is defined as the energy deposited in the gas per unit volume and it can be calculated by dividing the discharge energy per second (\( P_d \), W) over the gas flow rate \( L_s^{-1} \) as shown in equation 3.5.

\[
\text{Specific Input Energy, SIE (} J L_s^{-1}) = \frac{P_d (Js^{-1})}{Q (Ls^{-1})}
\]

Equation 3.5

The uncertainty in the measurement of the gas concentrations to one standard deviation is less than 2\%. The associated uncertainty in conversion and selectivity to one standard deviation is typically less than 4\%.

### 3.3 Results & Discussion

#### 3.3.1 Gas effect to the plasma-chemical degradation of kerosene and dodecane

The BaTiO₃ packed bed dielectric barrier discharge reactor has been used for the degradation study of kerosene \( \text{C}_n\text{H}_{2n+2}, \ n = 9-16 \) and dodecane \( \text{C}_{12}\text{H}_{26} \) as target gaseous pollutants. The effect of different discharge gas such as nitrogen and air to the degradation efficiency and product distribution is studied as a function of the specific input energy (SIE). However, dodecane only was used for both qualitative and quantitative analysis, while kerosene was studied only qualitatively, as it has no defined chemical structure. Both chemicals seem to have similar behaviour under the
N₂ or air plasma treatment resulting in the same degradation products. The FTIR spectra in Figure 3.4 show the degradation products observed when nitrogen and air discharge in maximum discharge power (Pₐ) was applied for the treatment of dodecane.

![FTIR Comparative Spectra](image)

Figure 3.4 FTIR comparative spectra of 65 ppm dodecane when plasma was off, and in nitrogen or air discharge at maximum power Pₐ = 1.4 W and SIE = 42 J L⁻¹. Spectral resolution is 1 cm⁻¹.

Figure 3.5 shows the degradation rate as a function of the specific input energy. Overall both dodecane and kerosene appear to have similar degradation rates with a maximum destruction of 21%. The degradation rate increases almost linearly with increasing energy density, which increases the generation of the active species and promotes the chemical reactions. The degradation rate in the nitrogen discharge for both chemicals seems higher than the air in less powerful discharges when SIE < 30 J L⁻¹, but beyond that energy there is no significant influence of the different gas used. Futamura et al. has studied the decomposition of butane in a BaTiO₃ packed bed discharge and he observed a higher decomposition efficiency in a nitrogen discharge rather than air, especially at lower electrical field [11].
More specifically, in the case of N$_2$ plasma of dodecane, end-products concentration distribution is plotted as a function of the discharge energy density in Figure 3.6. Dodecane in a nitrogen discharge is decomposed mainly to HCN, NH$_3$ and CO, but also lower concentrations of C$_2$H$_4$, C$_2$H$_2$, CH$_4$ and N$_2$O are observed. All products concentrations show a linear correlation with increasing the energy of the discharge.
The formation of the oxygenated products CO and N$_2$O could be formed by impurities of the N$_2$ gas used (2 ppm), but the high selectivity towards CO could also suggest that the lattice oxygen in BaTiO$_3$ plays an important role in surface reactions taking place between the beads as suggested from Ogata et al. [6] and also Futamura et al. [11, 15] and will be further discussed in section 3.3.2.

In air treatment dodecane degrades mainly to CO and CO$_2$, linearly with increasing the discharge energy, where CO > CO$_2$ and only traces of CH$_4$ are observed. The characteristic formation of nitrogen oxides is also seen with NO > NO$_2$ and N$_2$O.

![Figure 3.7 Effect of specific input energy effect on gaseous products at the destruction of 65 ppm dodecane in air PBDBD](image)

It must be noted that in both nitrogen and air plasma treatment experiments, the overall carbon balance determined by the FTIR measurements was poor, at 56% and 51% respectively. This is a limitation of the FTIR spectroscopic technique that has to be accepted when measuring the degradation of heavy molecules such as dodecane. The formation of other nitrogenated or oxygenated organics is possible, such as RNH$_2$, RCN, ROH, RCHO, R$_1$R$_2$CO, where R is alkyl group that could be a C$_1$-C$_{11}$ carbon group. However, if these exist as traces and go under the IR detection limit, they cannot be identified but they would affect the carbon balance. This limitation does not give a full range of the intermediate products formed, however
does not affect our conclusions which are based on the major products formed and interpretation of comparative results.

### 3.3.2 OES diagnostics of packed bed plasma in different gas compositions

Optical emission spectroscopy (OES) is a common diagnostic tool for low-temperature plasma under different conditions, as it uses the intensity of the light emitted at particular wavelengths from an electronically-excited state to calculate the concentration of the species, rotational \((T_r)\) and vibrational \((T_v)\) temperature of these species, as well as the electron temperature \((T_e)\) [16]. In this work emission spectra were collected under different gas compositions BaTiO\textsubscript{3} packed bed dielectric barrier discharge such as nitrogen, air and with addition of low concentration dodecane (\(~65\) ppm). Table 3.1 compares the intermediate excited species observed by OES with the end-products formed in each case as measured by FTIR.

<table>
<thead>
<tr>
<th>PBDBD Plasma</th>
<th>OES Intermediate species</th>
<th>Region/nm</th>
<th>Intensity ratio (N_{2(2+)}/N_{2}^{+}(1-))</th>
<th>FTIR end-products</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>N\textsubscript{2}</strong></td>
<td>(\text{NO}<em>{2}\gamma) (N</em>{2}^{+}B^2\Sigma^+_u - X^2\Sigma^-_g) ((2+))</td>
<td>247.8, 259.5, 272.2</td>
<td>12.3</td>
<td>((\text{N}_2\text{O}))</td>
</tr>
<tr>
<td></td>
<td>(N_{2} C^{3}\Pi_u - B^{3}\Pi_g) ((1-))</td>
<td>315.9, 337.1, 353.6, 357.7</td>
<td>391.4, 427.8</td>
<td></td>
</tr>
<tr>
<td><strong>Air</strong></td>
<td>(N_{2} C^{3}\Pi_u - B^{3}\Pi_g) ((2+)) (N_{2}^{+}B^2\Sigma^+_u - X^2\Sigma^-_g) ((1-))</td>
<td>315.9, 337.1, 353.6, 357.7</td>
<td>391.4, 427.8</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>N\textsubscript{2}/C\textsubscript{12}</strong></td>
<td>(\text{NO}<em>{2}\gamma) (N</em>{2} C^{3}\Pi_u - B^{3}\Pi_g) ((2+)) (N_{2}^{+}B^2\Sigma^+_u - X^2\Sigma^-_g) ((1-))</td>
<td>247.8, 259.5, 272.2</td>
<td>315.9, 337.1, 353.6, 357.7</td>
<td>391.4, 427.8</td>
</tr>
<tr>
<td></td>
<td>(\text{CN} B^2\Sigma^- - X^2\Sigma^-) ((1-))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Air/C\textsubscript{12}</strong></td>
<td>(N_{2} C^{3}\Pi_u - B^{3}\Pi_g) ((2+)) (N_{2}^{+}B^2\Sigma^+_u - X^2\Sigma^-_g) ((1-))</td>
<td>315.9, 337.1, 353.6, 357.7</td>
<td>391.4, 427.8</td>
<td>1.78</td>
</tr>
</tbody>
</table>

**Table 3.1** Comparison of excited species and end-products in different gas mixtures in PB DBD
In all spectra the characteristic second positive nitrogen $\text{N}_2 \rightarrow \text{B}$ and first negative $\text{N}_2^+ \rightarrow \text{X}$ systems are observed as are commonly formed in discharges by the primary steps of electron impact excitation and ionisation, shown in reactions R 3.1-3.3. The electron impact dissociation of molecular nitrogen and oxygen also occurs as shown is reactions R 3.4 and R 3.5, however the N and O atomic lines needs high sensitivity and resolution and they could not be detected.

R 3.1  $e + \text{N}_2 (X) \rightarrow \text{N}_2 (A) + e$  
*electron impact excitation*

R 3.2  $e + \text{N}_2 (A) \rightarrow \text{N}_2^+ + 2e$  
*stepwise ionisation*

R 3.3  $e + \text{N}_2 (A) \rightarrow \text{N}_2 (B, C) + e$  
*stepwise excitation*

R 3.4  $e + \text{N}_2 (X) \rightarrow \text{N} (\tilde{2}D) + \text{N} (\tilde{2}P)$  
*electron impact dissociation*

R 3.5  $e + \text{O}_2 \rightarrow e + \text{O} (\tilde{3}P) + \text{O} (\tilde{1}D)$  
*electron impact dissociation*

where, $\text{N}_2 (A)$, $\text{N} (\tilde{2}D)$ or $\text{N} (\tilde{2}P)$ and $\text{O} (\tilde{3}P)$ or $\text{O} (\tilde{1}D)$ are often referred as $\text{N}_2^*$, $\text{N}^*$ and $\text{O}^*$ respectively.

The intensity of $\text{N}_2 \rightarrow \text{B}$ and thus the relative concentration is much weaker in the air discharge where oxygenated species are also formed. It is interesting to note that the emission of NO-$\gamma$ is observed in nitrogen discharge where also forms traces of $\text{N}_2\text{O}$ as an end-product, but surprisingly not in case of air, where NO and NO$_2$ undoubtedly exist as end-products but also $\text{N}_2\text{O}$ forms. Figure 3.8 illustrates the emission spectra collected in case of pure nitrogen and pure air discharge with 0.52 nm resolution. A suggested explanation for the appearance of NO-$\gamma$ in $\text{N}_2$ plasma could be due to the microdischarges and surface discharges that are formed between the BaTiO$_3$ beads, which could allow the energetic nitrogen metastables to interact with the lattice oxygen species. This could lead to the formation of excited species of NO and finally $\text{N}_2\text{O}$ as an end-product, as shown in reactions R 3.6, 3.7 and R 3.10.

R 3.6  $\text{N}_2^* + \text{O} \rightarrow \text{NO}^* + \text{N}$

R 3.7  $\text{N}_2^* + \text{NO} \rightarrow \text{NO}^* + \text{N}_2$

R 3.8  $\text{N}^* + \text{O} \rightarrow \text{NO}^*$

R 3.9  $\text{N}_2^* + \text{O} \rightarrow \text{N}_2\text{O}$

R 3.10  $\text{N}_2^* + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}^*$
Furthermore, the formation of N$_2$O traces that are formed in the nitrogen discharge could be also due to the plasma surface interaction as shown in reactions R 3.9, R 3.10. Reaction R 3.10 was first suggested from Malcombe-Lawes [17] and studied thoroughly from Zipf [18] in corona discharges, where he suggests that the energy-rich metastable N$_2$(A) molecules that can be formed efficiently with large cross sections, can produce N$_2$O in the stratosphere and aurora zone.

The occurrence of surface discharges and reactions has been discussed from several researchers in the past. Tu et al. [19] discusses the transition behaviour from filamentary microdischarges to surface discharges around the contact points between the BaTiO$_3$ beads. Yamamoto et al. [3] has observed the formation of Ti and Ba ions suggesting that it is caused by local heating and energetic electron bombardment near the contact points on the surface of BaTiO$_3$ pellets in air discharge. Ogata et al. [6] has suggested that lattice oxygen in BaTiO$_3$ plays an important role in surface reactions and to the N$_2$O formation. A few years later, Futamura et al. [15] in an attempt to investigate any catalytic effect of BaTiO$_3$ to the packed bed reactor, agree that BaTiO$_3$ can act as monoxygenated agent and produce CO and N$_2$O in N$_2$ plasma, but the contribution of this reaction is negligible under air plasma. The formation of

**Figure 3.8** Emission spectra of 0.52 nm resolution from pure N$_2$ and air packed bed plasma, at power $P_d = 1.4$ W and $Q = 2$ L min$^{-1}$
N₂O and CO has also been observed from other researchers when using nitrogen BaTiO₃ PBBD to treat VOC [7, 10, 20, 21]. The fact that that NO⁺ is not observed in air discharge in Figure 3.8, indicates that surface reactions are suppressed and metastables N₂⁺ and N⁺ preferably react with the gaseous oxygen to form NOx as shown in reactions R 3.11 and R 3.12.

\[
\text{R 3.11} \quad \text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}
\]

\[
\text{R 3.12} \quad \text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}
\]

**Figure 3.9** Emission comparative spectra in packed bed discharge in pure N₂ and N₂/dodecane, pure air and air/dodecane gases, when dodecane concentration is 65 ppm, total flow is \( Q = 2 \text{ L min}^{-1} \) and discharge power is \( P_d = 1.4 \text{ W} \). The spectral resolution is 0.13 nm with exposure time \( t = 2 \text{ sec} \).

Emission spectra from the treatment of dodecane in a nitrogen and air discharge are shown in Figure 3.9. The \( \text{N}_2 \rightarrow B \) is the dominant band in both cases, and \( \text{N}_2^+ \rightarrow B \rightarrow X \) is also observed, however the \( \text{N}_2 \rightarrow B \) intensity in the nitrogen dodecane discharge is about four times weaker when comparing with pure nitrogen. This could be an indication that the relative concentration of N₂⁺ metastables is decreased due to reactions with dodecane and fragments as a part of the degradation mechanism. The
CN violet system is also observed, which is correlated with the HCN formation, one of major end-products. In case of air, when adding dodecane, there is no significant change to the $N_2 \rightarrow B$ intensity, but the ratio of $N_2 \rightarrow B+X + N_2 \rightarrow B$ decreases as $N_2 + B \rightarrow X$ emission becomes stronger. This could suggest that $N_2$ metastables preferably react with oxygen leading to the formation of NO, NO$_2$ and N$_2$O as end products as shown before in reactions R 3.6 – R 3.12.

The emission spectra in the different gas mixture BaTiO$_3$ packed bed discharge were also used to obtain vibrational and rotational temperatures of the $N_2 \rightarrow B$ in the different conditions. The rotational temperature ($T_r$) is determined by a comparison between the experimental spectrum of molecular band of $N_2 (C^3\Pi_u - B^3\Pi_g, \Delta v = -1$, at 357 nm) and a simulated one by using Specair [22], while vibrational temperature is calculated using the Boltzmann plot method.

The intensity of the spectral line is given by:

$$\frac{\lambda_{ij} I_{ij}}{h c A_{ij} q_{ij}} = \frac{n}{U(T_v)} \exp \left(-\frac{E_j}{k_B T_v}\right)$$

where $I_{ij}$ and $\lambda_{ij}$ are the intensity and wavelength that corresponds to transition $i$ to $j$ respectively, $h$ is the Planck’s constant, $c$ is the speed of light, $n$ the number density of emitting species, $U(T_v)$ the partition function, $A_{ij}$ the transition probability between level $i$ and $j$, $k_B$ the Boltzmann’s constant, $T_v$ the vibrational temperature, $q_{ij}$ the Franck-Condon factor and $E_j$ the upper energy level in eV unit.

Equation 3.2 gives a linear relationship when $\ln\left(\frac{\lambda_{ij} I_{ij}}{h c A_{ij} q_{ij}}\right)$ versus $(E_j)$ is plotted, and then $T_v$ can be determined by the plot’s slope. The Frank-Condon factor and transition probabilities can be found in [23].

$$\ln\left(\frac{\lambda_{ij} I_{ij}}{h c A_{ij} q_{ij}}\right) = -\frac{1}{k_B T_v} (E_j) + \ln\left(\frac{n}{U(T_v)}\right)$$

Figure 3.10 shows the gas mixture effect to the $N_2 \rightarrow B$ vibrational and rotational temperatures. The difference between the vibrational and rotational temperature is expected in our packed bed dielectric barrier discharge system, indicating the significant degree of non-equilibrium state. Generally, in low temperature non-thermal plasmas, the rotational temperature is taken to be a good indicator of the gas temperature, involving the assumptions that the rotational population is following Boltzmann’s law and the rotational temperature is equilibrated with the translational
temperature by fast intermolecular relaxation [22, 24]. The nitrogen or air discharge with or no addition of dodecane vapour had no influence to the rotational temperature of N$_2$ $C \rightarrow B$, which was measured at $T_r \approx 750$ K (0.06 eV). The vibrational temperature is much higher at $T_v = 2500$ K (0.21 eV) in nitrogen discharge while the dodecane vapour appears to have no effect. However, it slightly increases in air discharge $T_v = 2750$ K (0.24 eV), and with the addition of vapour dodecane $T_v = 2900$ K (0.25 eV).

![Figure 3.10](image.png)

**Figure 3.10** Rotational and vibrational temperature of N$_2$ $C \rightarrow B$ in different gas mixture BaTiO$_3$ packed bed discharge, at maximum discharge power, $P_d = 1.4$ W

### 3.3.3 The Oxygen Effect on dodecane degradation and end-products formation

The effect of oxygen concentration in the N$_2$-O$_2$ discharge feed gas on the dodecane decomposition was studied in order to identify potential optimal processing conditions, as increased oxygen concentration is generally believed that it can promote the oxidation rate. Figure 3.11 shows the results of PB DBD degradation of dodecane (35 ppm) when (0-40) % concentration of oxygen was used at a fixed energy density, $SIE = 42$ J L$^{-1}$. As observed, variation even up to high oxygen concentration $\leq 40\%$ hardly influences the degradation efficiency, which lies within the experimental error at $\sim 24\%$. This is not surprising in case of packed bed plasma treatment of hydrocarbons, as previous literature has shown that best destruction rates have been noted in the absence of oxygen in dry nitrogen packed bed plasma of methane [10] and butane [11].

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Figure 3.11. Oxygen concentration effect on 35 ppm dodecane plasma degradation in N$_2$-O$_2$ mixtures, at fixed power $P_d = 1.4$ W and $Q = 2$ L min$^{-1}$

Figure 3.12 illustrates the end-product distributions under the same conditions.

Figure 3.12 Oxygen concentration effect on the end-products formation of 35ppm dodecane plasma degradation in N$_2$-O$_2$ mixtures, at fixed power $P_d = 1.4$ W and $Q = 2$ L min$^{-1}$

Increasing the oxygen concentration has no effect to the concentration of CO and CO$_2$ products. However, the formation of NO$_2$ and NO is almost linearly increased.
with a ratio of NO$_2$/NO < 1 that increases at higher doses of oxygen. This shows that the oxygen does not participate to the plasma-chemical degradation of dodecane, but rather recombines with N atoms to form NO$_x$. The N$_2$O formation is not affected by the various oxygen concentrations, another indication that N$_2$O forms in the air ferroelectric discharge due to the reactions of N$_2$ metastables with oxygen atoms in the BaTiO$_3$ lattice.

Figure 3.13 illustrates the effect of dodecane on the NO, NO$_2$ and N$_2$O production with increasing oxygen in the N$_2$/O$_2$ BaTiO$_3$ packed bed discharge. As observed, the NO$_x$ distribution with the presence of hydrocarbon appears similar as in its absence, as a function of increasing oxygen concentration. However, the concentrations of NO$_x$ are decreased in the presence of dodecane, more significantly in the case of NO, and less in NO$_2$ and N$_2$O. This suppression is expected at some level, due to either the competitive electron impact reactions with dodecane, nitrogen and oxygen molecules at the primary steps, or due to the competitive radical reactions of O with the hydrocarbon, rather than nitrogen to form NO$_x$. Furthermore, previous studies have shown that the formation of peroxy radicals as intermediate hydrocarbon oxidation products promote the oxidation of NO to NO$_2$ [25-28].

Figure 3.13 The NO$_x$ and N$_2$O distribution as a function of increasing oxygen concentration in the discharge, with or without the addition of 35 ppm dodecane at fixed power $P_d = 1.4$ W and $Q = 2$ L min$^{-1}$
3.3.4 The Plasma-chemical destruction of gaseous dodecane in the ferroelectric packed bed reactor

As discussed earlier in chapter 2, the chemical effects occurring in an electrical discharge are the consequence of the energy injection into the bulk gas by electron impact reactions under the influence of the electric field [29]. Electron collisions with neutral particles cause the primary reactions of ionisation, excitation and dissociation, followed by charge and energy transfer reactions (~10^{-8}s). The secondary processes consist of the radical reactions which are important for the pollutant decomposition, as they last longer (~10^{-3}s). In this part, a postulated plasma chemical decomposition of dodecane in the BaTiO_3 PBDBD reactor will be discussed.

The mean electron energy in most electric discharge reactors operating at atmospheric pressure is typically between 3 – 6 eV [30]. BaTiO_3 packed reactors, due to the contact points between the pellets which enhance the electric field, can be categorised as high electron energy but low energy density devices [31], with a maximum energy up to 10 eV and mean electron energy of about 4 - 5 eV [32]. In this range, the direct electron impact dissociation of dodecane on our diluted gas mixture is not expected to be an important reaction. Although the dissociation energy of the C-C and C-H dodecane bonds are ~ 4.3 eV and 3.8 eV respectively (Table 3.2), the threshold dissociation energy by electron impact is considerably higher at ~ 9 eV. However, one must consider that these reactions become more important in concentrated systems, where the probability of the energetic electrons collision with the hydrocarbon is increased. Moreau et al. [33] have studied by experiments and model predictions the dissociation of propane and propene in N_2 non-thermal plasma and they suggest that the quenching N_2* metastable states by C_3H_8 and C_3H_6 are the most important processes for the removal of the hydrocarbons for concentrations ~ 5500 ppm. In addition, Aerts et al. [34] have used a kinetic model to study the initiation reactions of ethylene destruction in an air DBD plasma, where it is found that electrons have minimum contribution to ethylene plasma destruction compared to N_2(A) metastables and O atoms, up to 10,000 ppm concentration of ethylene.

It is suggested that the initiation mechanism of dodecane plasma-chemical decomposition happens through two main pathways: 1) the cleavage of C–C bond to form smaller hydrocarbon radicals, and 2) the dehydrogenation reaction to form an H
radical and the corresponding C_{12}H_{25} radical. Another pathway is H-abstraction reactions by small radicals including O, OH, N, H, CH_{3}, and C_{2}H_{5}, which are secondary products after initiation reactions. It should be noted that C-H cleavage is more thermodynamically favoured in the C_{4} carbon as shown in Table 3.2. This could create initial dodecyl radicals and subsequent C-C scission with higher probability between C_{5}-C_{6} or C_{5}-C_{4} positions which could be followed by chain radical reactions with simultaneous C_{2}H_{4} elimination by $\beta$-scission, leading to methyl fragments and final oxidation products. The $\beta$-scission reaction in alkyl radical reactions is often used to describe initiation radical reactions in fuel combustion mechanistic studies [35-37]. A schematic of the postulated plasma-chemical initiation mechanism is given in Figure 3.14.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta H^\circ$ (C-H)/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ H + CH_{3}(CH_{2})<em>{10}CH</em>{2}•</td>
<td>4.40</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ H + CH_{3}(CH_{2})<em>{9}CH'CH</em>{3}</td>
<td>4.22</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ H + CH_{3}(CH_{2})<em>{8}CH'CH</em>{2}CH_{3}</td>
<td>4.21</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ H + CH_{3}(CH_{2})<em>{7}CH'(CH</em>{2})<em>{2}CH</em>{3}</td>
<td>4.20</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ H + CH_{3}(CH_{2})<em>{6}CH'(CH</em>{2})<em>{3}CH</em>{3}</td>
<td>4.18</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ H + CH_{3}(CH_{2})<em>{5}CH'(CH</em>{2})<em>{4}CH</em>{3}</td>
<td>4.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta H^\circ$ (C-C)/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ CH_{3}+n-C_{11}H_{23}</td>
<td>3.85</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ n-C_{2}H_{5} +n-C_{10}H_{21}</td>
<td>3.73</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ n-C_{3}H_{7} +n-C_{9}H_{19}</td>
<td>3.71</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ n-C_{4}H_{9} +n-C_{8}H_{17}</td>
<td>3.71</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ n-C_{5}H_{11} +n-C_{7}H_{15}</td>
<td>3.67</td>
</tr>
<tr>
<td>n-C_{12}H_{26} $\rightarrow$ 2 n-C_{6}H_{13}</td>
<td>3.68</td>
</tr>
</tbody>
</table>

**Table 3.2** Bond dissociation enthalpies of C–H and C-C bond in n-dodecane at different C sites (adapted from [37])
Figure 3.14 Schematic of initiation reaction mechanism of the oxidation processes of the n-dodecane

In a nitrogen plasma, the largest fraction of the electron energy is used to create vibrationally-excited nitrogen metastables such as N$_2$(A), and N$_2$(B, C) as shows in reactions R3.1, R3.3. The first excited N$_2$ metastable N$_2$(A), with the lowest threshold energy of 6.2 eV and the longest lifetime $\sim 2$ s, is considered to be the most populated and for that reason to play a central role to plasma processing [38]. The rest of the electron energy is used to electron impact dissociation and ionisation reactions to create N, N* radicals and N$_2^+$, N$_2^{+*}$, N$^+$ and N$^{+*}$ ions. From our OES observations, it can be suggested that N$_2^*$ plays an important role in dodecane decomposition by creating initiation radical reactions through energy transfer reactions which could dissociate the C-H and C-C bonds at the different positions to create initial H and alkyl radicals. Furthermore, H-abstraction from the C-H bond at the various positions can happen from N radicals to create also initial alkyl radicals, but also leading to NH$_3$ formation by stepwise H addition. The methyl radicals can react with N radicals to give H$_2$CN intermediates which can then form HCN by simultaneous H-abstraction. A schematic summary of the plasma-chemical decomposition of dodecane in N$_2$ PBDBD is given in Figure 3.15.

Figure 3.15 Schematic summary of plasma-chemical decomposition of dodecane in N$_2$ PBDBD
In an air plasma, a large amount of the electron energy is consumed in the vibrational excitation of molecular nitrogen, but also a significant amount goes into the electron impact dissociation of oxygen to create O radicals [30] as shown earlier in reaction R 3.5. The O radicals can abstract H atoms to form OH radicals, which in turn can also contribute to the H-abstraction reactions forming H₂O and promoting radical reactions. Both O and OH radicals can add to dodecane and sub-sequential fragments to produce RO and RCHO as intermediates which with subsequent oxidation steps can lead to final oxidation products of CO and CO₂. A schematic summary of the plasma-chemical decomposition of dodecane in air PBDBD is given in Figure 3.16.

**Figure 3.16** Schematic summary of plasma-chemical decomposition of dodecane in air PBDBD

The formation of nitrogen oxides is unavoidable in air discharges and it has been well-studied [39, 40]. It can be initiated by nitrogen metastables as shown in reactions R 3.13- R 3.16.

- **R 3.13** \( \text{N}_2(A) + \text{O}_2 \rightarrow \text{products} \) \( k_{300} = 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [41]
- **R 3.14** \( \text{N}_2(A) + \text{O} \rightarrow \text{NO} + \text{N(D)} \) \( k_{300} = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [38]
- **R 3.15** \( \text{N}_2^* + \text{O} \rightarrow \text{N}_2\text{O} \) no data
- **R 3.16** \( \text{N}_2^* + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}^* \) no data
- **R 3.17** \( \text{N(D)} + \text{O}_2 \rightarrow \text{NO} + \text{O} \) \( k = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [41]
- **R 3.18** \( \text{N(P)} + \text{O}_2 \rightarrow \text{NO} + \text{O} \) \( k = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [41]
- **R 3.19** \( \text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M} \) \( k = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [42]
Our results indicate that increasing the oxygen concentration in the \( \text{N}_2\text{-O}_2 \) mixture plasma does not increase the dodecane destruction. The rapid NOx formation reactions act as competitive reactions to the degradation of the hydrocarbon. This could take place in the radical initiation stage, where nitrogen metastables react faster with oxygen rather than with the hydrocarbon, as shown in reactions R 3.14, R 3.20 (\( \text{C}_4\text{H}_{10} \) was used as the largest hydrocarbon with available kinetic data). From extrapolation of kinetics in reactions R 3.20 – R 3.27 we understand firstly that reaction rates generally become faster for longer unsaturated hydrocarbons as someone could easily suggest, since the longer hydrocarbon, the weaker the C-C and C-H bonds become and thus, easier to breakdown. Secondly, it can be noted that the reaction of metastable \( \text{N}_2\text{(A)} \) with the longer hydrocarbons becomes very important kinetically for the initiation of the radical chemistry, where the H-abstraction reaction by O or OH radicals is slower. Furthermore, although singlet state oxygen \( \text{O(D)} \) reacts quite fast with the hydrocarbons, its relative concentration is thought to be small compared to \( \text{N}_2\text{(A)} \) and thus its contribution cannot be considered significant. For that reason, it is suggested that the reactions of \( \text{N}_2\text{(A)} \) leading to NOx formation inhibit the initiation dodecane breakdown to smaller fragment radicals which could then rapidly react with O and OH radicals as shown in reactions R 3.28-R 3.30, until subsequently complete oxidation.

\[ \text{R 3.20} \quad \text{N}_2\text{(A)} + \text{C}_4\text{H}_{10} \rightarrow \text{products} \quad k_{300} = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [41] \]

\[ \text{R 3.21} \quad \text{N}_2\text{(A)} + \text{CH}_4 \rightarrow \text{products} \quad k_{300} = 3.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [41] \]

\[ \text{R 3.22} \quad \text{O} + \text{C}_4\text{H}_{10} \rightarrow \text{products} \quad k_{300} = 4.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [43] \]

\[ \text{R 3.23} \quad \text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH} \quad k_{300} = 1.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [44] \]

\[ \text{R 3.24} \quad \text{OH} + \text{C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad k_{300} = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [45] \]

\[ \text{R 3.25} \quad \text{OH} + \text{CH}_4 \rightarrow \text{products} + \text{H}_2\text{O} \quad k_{300} = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [46] \]

\[ \text{R 3.24} \quad \text{O (}^1\text{D)} + \text{C}_4\text{H}_{10} \rightarrow \text{products} + \text{OH} \quad k_{300} = 2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [47] \]

\[ \text{R 3.27} \quad \text{O (}^1\text{D)} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH} \quad k_{300} = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [46] \]
R 3.28 \[ \text{CH}_3 + \text{O}_2 \rightarrow \text{products} \quad k_{300} = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [46] \]

R 3.29 \[ \text{CH}_3 + \text{O} \rightarrow \text{products} \quad k_{300} = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [46] \]

R 3.30 \[ \text{CH}_3 + \text{OH} \rightarrow \text{products} \quad k_{300} = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [48] \]

### 3.4 Summary & Conclusions

A ferroelectric BaTiO$_3$ packed bed plasma reactor has been investigated for the plasma-chemical degradation of gaseous kerosene and dodecane, considering it as VOC that can be found in power plants, but also getting a forehand insight of the gaseous degradation mechanism as necessary step applying plasma technology for the liquid waste oil treatment.

The degradation efficiency follows a similar trend for kerosene and dodecane as target pollutants, and thus, dodecane can be used as a surrogate for quantitative analysis. The degradation increases with increasing SIE for both nitrogen and air, however with a higher rate in case in nitrogen at lower electrical field, but with no significant difference with air at maximum 42 J L$^{-1}$ where was found 22%.

Optical emission spectroscopy has been used as plasma diagnostics of the treatment in N$_2$ and air plasma. It can be suggested that the dodecane decomposition in a nitrogen plasma is controlled by the primary steps of electron-induced excited nitrogen metastables which can initiate radical reactions by energy transfer reactions. Interestingly, the excited NO-$\gamma$ is observed only in case of nitrogen, suggesting surface reactions are taking place between the nitrogen metastables and the lattice oxygen of BaTiO$_3$, resulting in the formation of N$_2$O and CO. In an air plasma, the electron impact dissociation of molecular oxygen in the primary steps, create the O atoms which could contribute to the dodecane degradation mechanism, but can also rapidly react with nitrogen metastables to form nitrogen oxides.

Increasing the oxygen concentration between (0–40) % in N$_2$-O$_2$ mixture plasma shows no significant influence to the degradation efficiency, however the yields of NO and NO$_2$ is almost linearly increased with a ratio NO$_2$/NO $< 1$, which slightly
increases at higher oxygen doses. This shows that oxygen does not participate to the degradation mechanism of dodecane, as rapid recombination reactions with nitrogen metastables form NO\textsubscript{x} and hinder the dodecane breakdown initiation reactions. However, the N\textsubscript{2}O formation is not majorly influenced, and remains stable for ≥ 10% oxygen, which also indicates that its origin is related to the lattice oxygen of BaTiO\textsubscript{3}.

Overall, interesting observations have been made for the dodecane treatment in the BaTiO\textsubscript{3} PBDBD. The maximum degradation efficiency found was rather low ~24%, but with a good energy efficiency of 2.63 mg/kJ. For the same configuration ferroelectric plasma reactor, the treatment of dodecane appears more efficient compared to propane studied by Hill et al. [49] and methane treatment studied by Pringle et al. [10] which is calculated at 0.87 mg/kJ and 0.38 mg/kJ, respectively. It can be suggested that a higher energy density and longer residence time treatment would presumably lead to total oxidation of the VOC. Regarding the view on applying plasma technology for the liquid waste oil, the gliding arc plasma reactor is suggested and will be examined in the next chapter.

3.5 References


[34] R. Aerts, Tu Xin, De Bie Christophe, Whitehead J. Christopher, Bogaerts Annemie, "An Investigation into the Dominant Reactions for Ethylene


Chapter 4

4. Gliding Arc Discharge degradation of oil in the vapour phase

4.1 Introduction

Applying low-temperature plasma technology for the treatment of waste oil in power plants, gliding arc discharge (GAD) has been suggested as a favoured type of low-temperature plasma. Its simple and flexible design can build reactors for both gas and liquid treatment and on different scales such as portable reactors for emergency spillage treatment. In addition, its discharge characteristics preserving the dual character of thermal and non-thermal plasma, offer elevated power which is preferable to treat concentrated organics, with possibly the same outcome as incineration, but at lower operating temperatures targeting at cost efficient processing.

Gliding arc discharge (or “glidarc”) was first proposed by Lesueur et al. [1] and developed by Czernichowski et al. mainly for the treatment of gases such as H₂S or N₂O removal from industrial gases [2-4] and later for the conversion of light hydrocarbons [5]. Its characteristics made it an attractive tool for both academic and industrial research [6] and while it was initially developed for gas treatment applications, it soon was developed also for liquid treatment [7]. These physical characteristics and dynamics have been studied extensively by several researchers [8-11].

In this work, gliding arc discharge has been used as a source of low-temperature atmospheric plasma for the study of the degradation of hydrocarbon oils such as odourless kerosene and n-dodecane, under different conditions. The aim of this study focuses only on the vapour phase destruction of the oil as an essential first step to understanding the gas chemistry which would help to elucidate the chemistry of plasma-liquid treatment. Following the same approach as described in Chapter 3, odourless kerosene has been studied only qualitatively and is compared with dodecane which is then used as a surrogate instead to allow quantitative analysis.
FTIR spectroscopy has been used for identification and quantification of the processing end-products. Comparison has been made between different gas streams such as N\textsubscript{2}, air and Ar and the effect of humidity has also been studied. Optical Emission Spectroscopy (OES) was used as a plasma diagnostic tool under different conditions, where reactive excited species were observed and temperature profiles were obtained. In order to investigate the optimal conditions for the oil destruction, the effect of O\textsubscript{2} concentration in the N\textsubscript{2}-O\textsubscript{2} buffer mixtures is also presented in this work.

4.2 Experimental set-up

Non-thermal plasma was generated in a gliding arc discharge (GAD) reactor at low temperature and atmospheric pressure. Figure 4.1 illustrates the experimental configuration.

The GAD reactor consists of two stainless steel diverging electrodes, 50 mm long, 18 mm to 2.4 mm diverging width, 5 mm thick and with an adjustable minimum gap fixed at 3 mm, located under a feeding gas nozzle of i.d. 1.5 mm, as shown in Figure 4.2a. Reactions are performed in a Pyrex glass vessel of ~ 1 L capacity. An AC neon sign power supply provides a high voltage up to 20 kV\textsubscript{p-p} and 50 mA at a frequency of 50 Hz. The plasma gases used were N\textsubscript{2}, synthetic air (80% N\textsubscript{2}, 20% O\textsubscript{2}) and Ar (99.998% purity) in dry or humid conditions. For the humid conditions, the inlet gas relative humidity was RH = 75\% ± 2\% (H\textsubscript{2}O = 2.3 ± 0.3 \%), at T = 24°C, measured with a HTD-625 thermo-hygrometer. The total flow was 5 L min\textsuperscript{-1} passing through bubblers filled with n-dodecane or odourless kerosene and water (for the humidity investigation), to create a vapour of initial concentration 90 and 300 ppm dodecane and odourless kerosene respectively. Plasma gas temperatures were obtained applying a K-type thermocouple at a 1.5 cm distance between the probe and the electrode and in a 4 cm position along the electrode axis as shown in Figure 4.2a. On-line FTIR spectroscopy (Shimadzu 8300) with a long path IR cell (5 m) at resolution 1 cm\textsuperscript{-1} was used for the identification and concentration determination of the gaseous products. Every measurement is an average of ten scannings and is repeated five times to obtain the uncertainty in values < 2\%. Optical emission spectroscopy measurements occurred as depicted in Figure 4.2b. The position of the
multi-mode quartz optical fibre allowed the integration of 4 cm diameter optical field along the GAD downstream plume. The optical fibre was connected to a CCD Princeton Instrument 320PI spectrograph with a 2400, 600 or 1500 g/mm grating (0.03, 0.13 and 0.52 nm resolution) and wavelength in the range 200-800 nm.

**Figure 4.1** Schematic diagram of experimental configuration: 1) mass flow controller, 2) bubbler with odourless kerosene or dodecane, 3) bubbler with water, 4) bypass for experiments with no water, 5) AC gliding arc reactor, 6) gas FTIR sample inlet, 7) optical emission spectrometer

**Figure 4.2** a) Position of the K-type thermocouple probe to collect gas temperatures (red dot) and electrodes dimensions. b) Position of the multi-mode quartz fibre during the OES measurements in gliding arc discharge. The half angle of the maximum cone of light that can enter the fibre is 21.7° resulting in an optical field diameter of 4 cm along the plasma plume.
The results obtained from the oil conversion were expressed as follows:

\[
\% \text{ Degradation} = \frac{C_i - C_o}{C_i} \times 100
\]

\text{Equation 4.1}

where, \(C_i\) and \(C_o\) are the input and output odourless kerosene or dodecane concentrations, respectively.

\[
\% \text{ Product Selectivity} = \frac{C_{\text{product}}}{C_{12H_{26}^{converted}}} \times 100
\]

\text{Equation 4.2}

\[
\% \text{ IC Selectivity} = \frac{(C_{\text{HCN}} + C_{\text{CO}} + C_{\text{CO}_2})}{C_{12H_{26}^{converted}}} \times 100
\]

\text{Equation 4.3}

\[
\% \text{ OC Selectivity} = \frac{(C_{\text{CH}_4} \cdot C_{\text{C}_2\text{H}_4} \cdot C_{\text{C}_2\text{H}_2})}{C_{12H_{26}^{converted}}} \times 100
\]

\text{Equation 4.4}

where \text{IC Selectivity} is the selectivity of dodecane conversion to inorganic carbon as HCN, CO and CO\(_2\) and \text{OC} is the selectivity to organic carbon of CH\(_4\), C\(_2\)H\(_4\) and C\(_2\)H\(_2\). Existence of C\(_2\)H\(_6\) could not be determined by FTIR, as its absorption frequencies overlap with those of C\(_{12}\)H\(_{26}\). However, based on the carbon balance calculations, if any C\(_2\)H\(_6\) forms, it cannot only have low selectivity (> 5%).

**4.3 Results and Discussion**

**4.3.1 OES diagnostics of the GAD under different gas compositions and comparison with end-products formation**

In this work dodecane degradation using GAD was applied in different gas streams of argon, nitrogen and air, in both dry and humid conditions. Changing the gas composition causes observable changes in the plasma plume characteristics like colour, length, and carbon deposition. OES was used as a diagnostic tool to identify and study the behaviour of the reactive excited species which are correlated with these changes.

The emission spectra collected under argon plasma with different admixtures are given in Figure 4.3 and interpretation was done using the NIST Atomic Spectra Database and literature [12, 13]. Table 4.1 summarises the intermediate excited species that were identified in these conditions, in addition to the end-products identified in the reaction gas outlet by FTIR spectroscopy.
**Figure 4.3** Optical emission spectra of a) Ar GAD plasma with b) 90 ppm dodecane admixture c) 2.3% H₂O admixture and d) both H₂O/dodecane admixture. Spectral resolution is 0.13 nm and the intensity has been scaled to account for different exposure times used.

*Other oxygenated products are observed, such as aldehydes or ketones (RCHO, RCO) but cannot be specified*

**Table 4.1** Summary of the intermediate species observed by OES and the end-products observed by FTIR. Relative intensities are characterised as strong (s), medium (m) or weak (w). The input power of the reactor is the maximum achievable in each case and photographs are given indicating the difference in colour.
The emission spectrum of the argon gliding arc discharge is mainly composed of neutral argon lines (Ar I) in the red to near infrared spectral region 690–850 nm belonging to transitions from the $3p^54p$ to $3p^54s$ configuration with ionisation energies between 13.08 - 13.33 eV depending on the transition. The $3p^54s$ configuration belongs to the excited argon metastable state (Ar$_m^*$), as explained before in chapter 1.8. Much weaker emission is seen in the violet between 410 - 430 nm including transitions from the Ar I $3p^55p$ to $3p^54s$ configuration or the singly ionised argon atoms Ar II with higher ionisation energies at 14.7 eV and 19.6 - 24.3 eV respectively. The weak band at 315 nm corresponds to the OH $A \rightarrow X$ emission due to water impurities existing in the feed gas (< 2 ppm). The admixture of dodecane creates strong chemiluminescence in the green-blue region due to the dominant emission of the C$_2$ d $\rightarrow$ a Swan system and CH $A \rightarrow X$, CH $B \rightarrow X$ system, while the intensity of the argon lines is decreased. This decrease could be due to competitive electron impact reactions that lead to dodecane dissociation and argon excitation, but also to the quenching reactions of argon metastables with dodecane. A weak Balmer H$_\alpha$ emission at 656 nm is also observed in the argon/dodecane plasma. The addition of humidity to the argon plasma causes dissociation of the water to create OH, H and O radicals, either from electron impact of energy transfer reactions as shown in R 4.1 and R 4.2. In the emission spectrum, OH $A \rightarrow X$ is the dominant emission and in addition to the Ar lines, the Balmer series H$_\beta$ ($4d \rightarrow 2p$) and H$_\alpha$ ($3p \rightarrow 2s$) emissions and singlet O I ($2s^22p^33p \rightarrow 2s^22p^33s$) line emissions are observed at 486, 656 nm and 777, 844 nm respectively. The dodecane admixture in humid argon has caused a significant decrease in the OH $A \rightarrow X$ emission relative to the Ar I lines intensity, while at the same time only very weak emission of C$_2$ Swan group and CH $A \rightarrow X$, CH $B \rightarrow X$ emission is observed, compared to the dry argon dodecane plasma spectrum. This indicates that in the humid argon dodecane plasma, the OH radicals play an important role in the oxidation of the hydrocarbon.

R 4.1 \[ e + H_2O \rightarrow OH + H + e \]

R 4.2 \[ Ar^* + H_2O \rightarrow OH + H + Ar \]

The emission spectra collected from the N$_2$ plasma with the different admixtures used are shown in Figure 4.4. Table 4.2 compares the intermediate excited species and the end-products that were identified.
Figure 4.4 Optical emission spectra in the range of 300-410 nm of a) N$_2$ GAD plasma with b) 90 ppm dodecane admixture c) 2.3% H$_2$O admixture and d) both H$_2$O/dodecane admixture. Spectral resolution is 0.13 nm and the intensity has been scaled in account for different exposure time used.

Table 4.2 Summary of the intermediate species observed by OES and the end-products observed by FTIR. Relative intensities are characterised as strong (s), medium (m) or weak (w). The input power of the reactor is the maximum achievable in each case and photographs are given indicating the difference in colour.
The emission spectrum of the dry nitrogen gliding arc discharge is dominated by the characteristic second positive system of neutral molecular \( \text{N}_2 \rightarrow \text{B} \) in the UV which is commonly formed in discharges by the primary steps of direct electron impact excitation of \( \text{N}_2(X) \) to \( \text{N}_2(C) \) or to \( \text{N}_2(A) \) and stepwise excitation to \( \text{N}_2(B, C) \). This was also observed in the packed bed dielectric barrier discharge in chapter 3.3.1. The \( \text{N}_2(A) \) metastables are considered to play a key role in promoting plasma chemical reactions since they are the first electronically excited \( \text{N}_2 \) metastable with an energy threshold of 6.2 eV and with a lifetime close to 2 s [14]. Weak emission from the first negative ionic \( \text{N}_2^+ \rightarrow X \) system is also observed in the violet. The \( \text{N}_2^+ \rightarrow X \) ionisation energy is 18.7 eV and it is characteristic in plasmas with high electron temperature, indicating the non-equilibrium character. The admixture of dodecane dramatically changes the plasma chemistry in the gliding arc discharge and thus the emitted spectrum. In this case, \( \text{N}_2 \rightarrow \text{B} \) is not observed, as the nitrogen metastables may quench with dodecane to initiate the decomposition. Very strong chemiluminescence of the CN \( B \rightarrow X \) system is also observed in the violet, correlative with the formation of HCN as the major end-product observed in FTIR. Emission of \( C_2 a \rightarrow d \) is also observed at \( \sim 516 \) nm but the CH \( A, B \rightarrow X \) system is not observed. When water is added to the nitrogen plasma, the intensity of the \( \text{N}_2 \rightarrow \text{B} \) is decreased and dissociation of water can occur either by electron impact (R 4.1) or by energy transfer reactions as shown to reactions R.4.3 and R4.4 leading to OH, and subsequently H, O radicals.

\[
\begin{align*}
\text{R 4.3} & \quad \text{N}_2(A) + \text{H}_2\text{O} \rightarrow \text{N}_2(X) + \text{OH} + \text{H} \quad [15] \\
\text{R 4.4} & \quad \text{N}(^2\text{D}) + \text{H}_2\text{O} \rightarrow \text{NH} + \text{OH} \quad [15] \\
\text{R4.5} & \quad \text{OH} + \text{e} \rightarrow \text{O} + \text{H} + \text{e}
\end{align*}
\]

It is interesting to note that in the humid nitrogen plasma the dominant emission belongs to the NH \( A \rightarrow X \) system and the OH \( A \rightarrow X \) system is also observed in the UV but no H or O emission is observed. Excited NO\(^*\) as intermediate cannot be seen due to the transmittance of the Pyrex vessel used. The fact that no NH\(_3\) but instead \( \text{NO} > \text{HNO}_2 > \text{N}_2\text{O} \) are formed as end-products seen by FTIR, indicates that NH\(^*\) is most likely an intermediate correlated with reaction R 4.4, rather than the reaction products. The NH radical which could be then oxidised towards NO according to
reactions R 4.6, R 4.7 and R 4.8. NO can be formed by N and O or OH radical recombination, and NO can also react with OH to produce HNO₂ as shown in the reactions below. However, the oxidative environment is not sufficient to form further oxidation to NO₂.

\[
\begin{align*}
R 4.6 & \quad \text{NH} + \text{OH} \rightarrow \text{H} + \text{HNO} \quad k_{300} = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [16] \\
R 4.7 & \quad \text{HNO} + \text{O} \rightarrow \text{OH} + \text{NO} \quad k_{300} = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [17] \\
R 4.8 & \quad \text{NH} + \text{O} \rightarrow \text{NO} + \text{H} \quad k_{300} = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [16] \\
R 4.9 & \quad \text{N} + \text{OH} \rightarrow \text{NO} + \text{H} \quad k_{300} = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [18] \\
R 4.10 & \quad \text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M} \quad k_{300} = 7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [19] \\
R 4.11 & \quad \text{NO} + \text{OH} \rightarrow \text{HNO}_2 \quad k_{300} = 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [20]
\end{align*}
\]

The addition of 90 ppm dodecane to the N₂/H₂O plasma does not cause a significant change to the emission spectrum where again the dominant emission belongs mainly to the NH \( \text{A} \rightarrow \text{X} \) system and then to the N₂ \( \text{C} \rightarrow \text{B} \) system. The intensity of the OH \( \text{A} \rightarrow \text{X} \) emission in this case appears slightly decreased as OH and O radicals react with dodecane to give CO, CO₂ and oxygenated end-products. In contrast to the dry nitrogen-dodecane admixture, in the case of the humid nitrogen-dodecane admixture only weak peaks of CN \( \text{B} \rightarrow \text{X} \) and C₂ \( \text{a} \rightarrow \text{d} \) systems are observed, and gaseous HCN and C₂H₄, C₂H₂ hydrocarbons as end-products are measured in low concentrations. In the humid nitrogen plasma with dodecane, NH₃ is observed but no HNO₂, as reactions R 4.6, R 4.7 and R 4.11 may be suppressed by alternative faster reactions of OH and O reactions with dodecane and subsequent hydrocarbon fragments.

The emission spectra of different admixtures of an air gliding arc discharge are given in Figure 4.5 and Table 4.3 summarises the intermediate excited species and gaseous end-products observed in each case.

In the air gliding arc plasma, the emission spectrum is also dominated by the N₂ \( \text{C} \rightarrow \text{B} \) system in the UV range, and the N₂⁺ \( \text{B} \rightarrow \text{X} \) system is also observed in the violet. Emission of oxygen atomic O I is observed in the red caused mainly by electron impact dissociation of molecular oxygen. Other smaller peaks observed in the red region are caused by second diffraction order of N₂ \( \text{C} \rightarrow \text{B} \) and N₂⁺ \( \text{B} \rightarrow \text{X} \).
Figure 4.5 Optical emission spectra of a) Air GAD plasma with b) 90 ppm dodecane admixture c) 2.3% H₂O admixture and d) both H₂O/dodecane admixture. Spectral resolution is 0.13 nm and the intensity has been scaled in account for different exposure time used.

*Other oxygenated products are observed, such as aldehydes or ketones (RCHO, RCO) but cannot be specified.

Table 4.3 Summary of the intermediate excited species and the end-products observed in air plasma admixtures. Relative intensities are characterised as strong(s), medium (m) or weak (w). There were no observable differences in colour in the different admixtures in the air plasma.
It is interesting to note that the intensity of the $\text{N}_2 \, C \rightarrow B$ in the air plasma is about 10 times weaker compared to the dry nitrogen discharge indicating the decreased relative concentration of nitrogen metastables. This is expected, as firstly the plasma electron energy can more favourably go into electron impact reactions with oxygen reducing the overall $\text{N}_2^*$ metastables and secondly, nitrogen metastables can be quenched by oxygen to form nitrogen oxides as end-products such as NO, NO$_2$ and N$_2$O. However, the intensity of the $\text{N}_2^+ \, B \rightarrow X \, (0,0)$ band head appears similar to the case of nitrogen discharge and thus the ratio $\text{N}_2 \, C \rightarrow B \, (0,0) / \text{N}_2^+ \, A \rightarrow X \, (0,0)$ in air (Table 4.3) is smaller than in nitrogen discharge (Table 4.2), suggesting that the relative concentration of the nitrogen metastables is mainly decreased due to the reactions with oxygen to form NOx, and less affected by the competitive electron impact processes with oxygen. When adding dodecane to the air plasma, the emission of $\text{N}_2 \, C \rightarrow B$ and $\text{N}_2^+ \, B \rightarrow X$ intensity is not significantly affected. This could be an indication that the nitrogen metastables that give rapid reactions to NOx, may not play an important role in dodecane radical initiation reactions as electron impact of dodecane does, in the relatively dense gliding arc discharge ($n_e \sim 10^{13}$ cm$^{-3}$ [8]). In contrast, as described and suggested earlier in Chapter 3.3.3, nitrogen metastables in the air plasma could play an important role in the radical initiation reactions of dodecane degradation in a less dense plasma such as the BaTiO$_3$ packed bed discharge ($n_e \sim 10^9$ cm$^{-3}$ [21]). The O I emission appears to be decreased in the air/dodecane admixture, as oxygen atoms react with dodecane to remove H and form OH radicals and the OH $A \rightarrow X$ system is also observed in the UV range. In the humid air plasma, dissociation of water creates extra OH and O radicals, where OH $A \rightarrow X$ is the dominant emission and O I emission appears increased. Similar to the humid nitrogen spectrum described before, $\text{N}_2 \, C \rightarrow B$ is decreased as nitrogen metastables may also contribute to the water dissociation and NH radicals could also form, according to Reaction 4.4 given before. The emission spectrum when dodecane is added to humid air appears similar to that for humid air, only in this case the intensity of the $\text{N}_2 \, C \rightarrow B$ band and O I line are decreased indicating their reaction with the hydrocarbon.

The emission spectra of the different gliding arc plasma systems have been used to obtain rotational and vibrational temperatures from characteristic band heads as shown in Table 4.4 where they are compared with the gas temperature and input
The gas temperature ($T_{\text{gas}}$) was measured using a K-type thermocouple, while rotational ($T_r$) and vibrational temperatures ($T_v$) were obtained by fitting experimental vibrational bands with their simulated spectra calculated by using Specair 2.2, assuming Boltzmann distribution [22]. The rotational temperature governs the width of each band, while the vibrational temperature determines the band intensity ratios. The bands used were OH $A\rightarrow X$, $C_2 a \rightarrow d$ and $N_2 C\rightarrow B$ as appropriate in each case. They were selected by the criteria of sufficient intensity and no overlapping.

<table>
<thead>
<tr>
<th>GAD Gas</th>
<th>Ar</th>
<th>Ar/C$<em>{12}$H$</em>{26}$</th>
<th>Ar/H$_2$O</th>
<th>Ar/H$<em>2$O/C$</em>{12}$H$_{26}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/ W</td>
<td>110</td>
<td>110</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>$T_{\text{gas}}/K$</td>
<td>335 ± 5</td>
<td>340 ± 5</td>
<td>370 ± 5</td>
<td>375 ± 5</td>
</tr>
<tr>
<td>OES species</td>
<td>OH $A\rightarrow X$</td>
<td>$C_2 a \rightarrow d$</td>
<td>OH $A\rightarrow X$</td>
<td>OH $A\rightarrow X$</td>
</tr>
<tr>
<td>$T_r/ K$</td>
<td>900 ± 50</td>
<td>1400 ± 100</td>
<td>2800 ± 100</td>
<td>2900 ± 100</td>
</tr>
<tr>
<td>$T_v/ K$</td>
<td>2700 ± 50</td>
<td>3200 ± 100</td>
<td>3900 ± 100</td>
<td>4100 ± 100</td>
</tr>
<tr>
<td>GAD Gas</td>
<td>N$_2$</td>
<td>N$<em>2$/ C$</em>{12}$H$_{26}$</td>
<td>N$_2$/ H$_2$O</td>
<td>N$<em>2$/H$<em>2$O/ C$</em>{12}$H$</em>{26}$</td>
</tr>
<tr>
<td>P/ W</td>
<td>190</td>
<td>190</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>$T_{\text{gas}}/K$</td>
<td>475 ± 5</td>
<td>480 ± 5</td>
<td>575 ± 5</td>
<td>575 ± 5</td>
</tr>
<tr>
<td>OES species</td>
<td>N$_2$ $C\rightarrow B$</td>
<td>N$_2$ $C\rightarrow B$</td>
<td>N$_2$ $C\rightarrow B$</td>
<td>N$_2$ $C\rightarrow B$</td>
</tr>
<tr>
<td>$T_r/ K$</td>
<td>3000 ± 100</td>
<td>2700 ± 100</td>
<td>3400 ± 100</td>
<td>2500 ± 100</td>
</tr>
<tr>
<td>$T_v/ K$</td>
<td>4300 ± 100</td>
<td>4200 ± 150</td>
<td>4400 ± 100</td>
<td>4000 ± 100</td>
</tr>
<tr>
<td>GAD Gas</td>
<td>Air</td>
<td>Air/ C$<em>{12}$H$</em>{26}$</td>
<td>Air/ H$_2$O</td>
<td>Air/ H$<em>2$O / C$</em>{12}$H$_{26}$</td>
</tr>
<tr>
<td>P/ W</td>
<td>200</td>
<td>200</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>$T_{\text{gas}}/K$</td>
<td>575 ± 5</td>
<td>575 ± 5</td>
<td>575 ± 5</td>
<td>575 ± 5</td>
</tr>
<tr>
<td>OES species</td>
<td>N$_2$ $C\rightarrow B$</td>
<td>N$_2$ $C\rightarrow B$</td>
<td>N$_2$ $C\rightarrow B$</td>
<td>N$_2$ $C\rightarrow B$</td>
</tr>
<tr>
<td>$T_r/ K$</td>
<td>2000 ± 100</td>
<td>2300 ± 100</td>
<td>2450 ± 50</td>
<td>2700 ± 250</td>
</tr>
<tr>
<td>$T_v/ K$</td>
<td>4300 ± 100</td>
<td>4500 ± 200</td>
<td>4000 ± 250</td>
<td>4000 ± 250</td>
</tr>
</tbody>
</table>

Table 4.4 Temperatures profile of different gas composition gliding arc plasma. The gas temperature ($T_{\text{gas}}$) was obtained by a thermocouple and rotational and vibrational temperatures were obtained by fitting simulation spectra using Specair 2.2 [22]

As seen in Table 4.4, the temperature profile in the gliding arc discharge shows elevated rotational and vibrational temperatures in the different gas mixtures in the
range of 1300 - 3400 K and 3100 - 4700 K respectively. The only exception is in case of argon plasma, where the temperatures of the OH $A \rightarrow X$ band was found to be lower, $T_r = 900 \pm 50$ and $T_v = 2400 \pm 50$. The difference between the $T_r$ and $T_v$ temperatures with $T_v > T_r$ is indicative of the non-equilibrium character of the discharge, however it is rather small compared to other “cold” plasma systems, such as DBDs [23, 24]. This is not surprising for a “hotter” plasma as a gliding arc discharge combining both quasi-equilibrium and non-equilibrium physical characteristics. Czernichowski et al [8] have studied this FENETRe phenomenon (Fast Equilibrium to Non-Equilibrium Transition) in the GAD, by obtaining spectroscopic measurements of the $N_2$ $C\rightarrow B$ band along the electrode axis using two different models. The temperatures they obtained fall within two ranges of high temperatures $T_r = 2300 - 4000$ K, $T_v = 3100 - 4000$ K and lower temperatures $T_r = 800 - 2100$ K , $T_v = 2000 – 2700$ K, showing the quasi-equilibrium and non-equilibrium zone. However, other researchers have found higher temperatures in the non-equilibrium zone downstream of the discharge such as $T_r = 3700 - 4500$ K and $T_v = 4700 - 5500$ K [11] , and $T_r = 2900 - 3500$ K and $T_v = 4000 - 4500$ K [25]. It is generally believed that the rotational temperature in non-equilibrium plasmas is close to the translational gas temperature if the intermolecular rotation-translation relaxation time is much shorter than the radiative lifetime of the exited state, allowing thermalisation of the rotational population [26]. In our case, the rotational temperatures are much higher than the gas temperatures obtained by the thermocouple 330-380 K, 470-580 K and 570-580 K in argon, nitrogen and air plasma respectively, and cannot be considered close to the translational temperature. Bruggeman et al [27] have discussed that non-Boltzmann behaviour can happen due to the different production processes of the excited species such as, electron impact or metastable collisions, and it is more likely in non-homogeneous discharges such as arcs. We only find that the temperature for rotation is close to that for translation in case of the argon plasma which is found using OH $A \rightarrow X$ as $Tr = 900\pm50$ K. In this case, OH is produced by the feed argon gas humidity impurities. Its relatively low concentration could minimise collisions with Ar* and favour direct electron impact excitation to OH* which can then lead to lower rotational energies and display Boltzmann behaviour. However, due to the non-homogeneous and quasi-equilibrium character of the gliding arc discharge, the thermocouple values are taken as more precise for obtaining the gas temperature.
4.3.2 Gas effect on the GAD odourless vapour oil degradation and products

In this section, the GAD degradation of odourless kerosene and dodecane in the vapour phase will be discussed using the different plasma gases, N\textsubscript{2}, air and Ar in dry and humid conditions. The degradation efficiency and end-product distribution is determined as a function of the maximum input power achievable in each case. As mentioned before, odourless kerosene (OK) cannot be used for accurate quantitative analysis, thus only dodecane was used, instead. However, in order to check if dodecane can be used as a surrogate for OK, the GAD treatment of both dodecane and OK has been performed.

A comparison between the maximum degradation achieved for OK and dodecane with the different gases at maximum input power in each case is shown in Figure 4.6. Both dodecane and OK show similar degradation efficiencies for the same gas and the same end-products have been identified, showing that dodecane can be considered a good simulant.

![Figure 4.6](image)

**Figure 4.6** The degradation efficiency of both dodecane and odourless kerosene under gliding arc discharge in argon, nitrogen and air, with maximum input power achieved in each case.

The maximum conversions observed in air plasma are 43 % and 47% for dodecane and kerosene, respectively, at a maximum input power of $P_{\text{max (air)}} = 200$ W. Plasma
in N$_2$ was less efficient for both oils at 32 % and 37 % respectively for $P_{\text{max}}$(N$_2$) = 185 W. The maximum input power achieved in the Ar gliding arc plasma was only $P_{\text{max}}$(Ar) = 105 W and resulted in poorer conversion of 12 and 14 %, respectively. This observation is in contrast with Yan et al’s work on GAD for the decomposition of hexane (C$_6$H$_{14}$) comparing also the effect of Ar, N$_2$ and air plasma [28]. They observed higher decomposition efficiency of the hydrocarbon in an argon plasma rather than nitrogen plasma, however, as no plasma power parameters are given clear conclusions cannot be drawn.

The dodecane degradation products observed under the different gas GAD plasma are shown in Figure 4.7 and the product selectivity for each case is given in Figure 4.8.

![Figure 4.7 FTIR absorption spectra of dodecane degradation products in Ar, N$_2$ and air GAD with input power $P_{\text{max}}$(Ar) = 105 W, $P_{\text{max}}$(N$_2$) = 185 W, $P_{\text{max}}$(air) = 200 W. The initial concentration of dodecane is 90 ppm in all cases. The resolution is 1 cm$^{-1}$.](image)

In the non-oxidative, dry argon gliding arc plasma, electron impact and Ar* reactions with dodecane lead to methane, ethylene and acetylene with a selectivity C$_2$H$_2$ > CH$_4$ > C$_2$H$_4$, while there is also low selectivity to CO formation due to the < 2 ppm oxygen impurities in the feed gas. Similarly in the dry nitrogen plasma, dodecane
degradation gives a good selectivity to organic hydrocarbons, but the dominant product formation is HCN and the overall sequence in selectivity is HCN > C₂H₄ > C₂H₂ > CH₄ and NH₃ and CO are also observed. In the case of air, low selectivity occurs towards the specified organic hydrocarbon products since the generation of the reactive O and OH radicals oxidise dodecane and the subsequent fragments to CO and CO₂. The rapid reaction of nitrogen metastables N₂* and N* or N atoms with O and O₂ leads to the characteristic formation of NO and NO₂, but no N₂O is observed. Additionally, HNO₂ is formed by the reaction of OH with NO, but no HNO₃ is observed.

![Graph showing selectivity of dodecane degradation products in argon, nitrogen, and air.]

**Figure 4.8** Dodecane degradation product selectivity in argon, nitrogen and air in maximum input power achieved in each case P_{max}(Ar) = 110 W, P_{max}(N₂) = 190 W, P_{max}(air) = 200 W.

It must be noted that the formation of other nitrogenated or oxygenated organic intermediates such as RNH₂, RCN, ROH, RCHO, R₁R₂CO is possible, but they could not be identified by FTIR. In addition, soot formation is observed during argon and nitrogen treatment. Qualitative analysis of the soot by x-ray diffraction (XRD) has shown that it is formed of amorphous carbon with Fe impurities derived from the stainless steel electrodes used.
Water vapour is important in plasma processing as it can be a major source of OH and HO₂ radicals which may accelerate the oxidation reactions. In this work, the effect of humid argon, nitrogen and air as carrier gases is investigated and compared to the dry conditions. The water concentration was 2.3 ± 0.3 % (RH = 75 ± 2 %, T = 24 °C) in each case. When water is injected into the plasma gas, it can also affect the physical characteristics of the discharge as electron energy goes into water dissociation to produce the OH, O radicals, confirmed by OES. That makes the discharge more stable and stronger, resulting also in an increased power. This effect has been also observed by Yu et al. [29]. Figure 4.9 and 4.10 show the effect of humidity on dodecane degradation and end-products selectivity and Table 4.4 summarises the end-products concentration in each case, including as well the NH₃, N₂O, NO, NO₂ and HNO₂ emissions in each case.

**Figure 4.9** Effect of humidity on the argon, nitrogen and air gliding arc discharge degradation of dodecane with the maximum input power achieved in each case. Initial concentration of dodecane is 90 ppm and H₂O = 2.3 ± 0.3 (RH = 75 ± 2%, t = 24°C).
Figure 4.10 Influence of humidity in the end-products products selectivity of GAD
dodecane degradation to the inorganic (IC) and the organic products (OC) as
observed in each case.

In the non-oxidative environment of the argon and nitrogen plasma, the humidity
significantly enhances the degradation from 12 % to 42 % and 31 % to 51 %,
respectively. In both cases compared with the dry conditions, the selectivity towards
the organic products is very much decreased, as the O and OH leads to CO, CO₂ and
other oxygenated products such as aldehydes or ketones (RCHO, RCO) which were
qualitatively identified. In addition, humid nitrogen produces nitrogen oxides such as
N₂O and NO from the reactions of the nitrogen metastables N₂⁺ with the OH and O
radicals. Surprisingly, in the case of air, the humid admixture causes no significant
effect on either the degradation which remains about 43 %, or the products
selectivity. A suggested explanation could be that O atom and secondary OH radicals
in dry air create a sufficiently oxidative environment for the dodecane degradation
that addition of water does not enhance. This could be due to the competitive
electron impact reactions between O₂ and H₂O as their threshold energies for the
electron impact dissociation are close to each other as shown below.

\[
R 4.12 \quad O_2 + e \rightarrow O + O + e \quad 5.6 \text{ eV}
\]

\[
R 4.13 \quad H_2O + e \rightarrow H + OH + e \quad 5.1 \text{ eV}
\]
The reaction R 4.13 with the lower threshold energy could be favoured, decreasing the relative concentration of O. This could also agree with decrease in emission of O I between dry and humid air observed in OES and described in the section 4.3.1. On the other hand, the increased relative concentration of OH could react not only with dodecane but also with NO to form HNO₂. As we observe in Table 4.5, humidity slightly decreases the amount of NO and NO₂ in the air plasma, while HNO₂ is increased. Looking at the reactions below, the reaction rate constant of the OH with NO is higher than OH with C₁₂H₂₆. In addition, one has to bare in mind that the relative concentrations of OH and NO are much higher, so the collision probability is increased.

\[
R\ 4.14\ \ \ \ \text{OH} + \text{NO} \rightarrow \text{HNO}_2 \quad k_{300} = 3.2 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \ [20]
\]

\[
R\ 4.15\ \ \ \ \text{OH} + \text{C}_{12}\text{H}_{26} \rightarrow \text{products} + \text{H}_2 \quad k_{300} = 1.32 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \ [30]
\]

<table>
<thead>
<tr>
<th>Product/ ppm</th>
<th>Ar/C₁₂</th>
<th>Ar/H₂O/C₁₂</th>
<th>N₂/C₁₂</th>
<th>N₂/H₂O/C₁₂</th>
<th>N₂/H₂O</th>
<th>Air/C₁₂</th>
<th>Air/H₂O/C₁₂</th>
<th>Air/H₂O/C₁₂</th>
</tr>
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<tbody>
<tr>
<td>CH₄</td>
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<td>37.0</td>
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<td>60.5</td>
<td>-</td>
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<tr>
<td>C₂H₄</td>
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<td>-</td>
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<td>-</td>
<td>39.8</td>
<td>-</td>
<td>91.7</td>
<td>105.4</td>
</tr>
<tr>
<td>N₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
<td>3.8</td>
<td>3.8</td>
<td>2.9</td>
<td>2.4</td>
</tr>
<tr>
<td>NO</td>
<td>-</td>
<td>-</td>
<td>337.3</td>
<td>228.5</td>
<td>1180.2</td>
<td>-</td>
<td>873.1</td>
<td>906.2</td>
</tr>
<tr>
<td>NO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1860.1</td>
<td>1980.5</td>
<td>1579.1</td>
<td>1669.2</td>
</tr>
<tr>
<td>HNO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>68.5</td>
<td>-</td>
<td>-</td>
<td>138.36</td>
<td>527.2</td>
</tr>
</tbody>
</table>

Table 4.5 The end-products concentration in the different admixtures of gliding arc NO, NO₂, N₂O and HNO₂ formation in gliding arc discharge. Uncertainty is < 2%
4.3.3 The oxygen effect on dodecane GAD degradation in \( N_2/O_2 \) mixtures and end-products formation

The influence of oxygen concentration in the \( N_2-O_2 \) mixture gliding arc plasma treatment of dodecane has been studied in order to identify potential optimal conditions. It is generally believed that increasing oxygen can enhance volatile organic compounds degradation by promoting complete oxidation to \( CO_2 \). However, there are cases where the optimal conditions have been found for only small concentrations of oxygen, such as 3 \% \( O_2 \) in case of dichloromethane in a packed bed discharge [31, 32], or best destruction rates have been noted in the absence of oxygen in dry nitrogen packed bed plasma of methane [33] and butane [34]. Our work on the \( O_2 \) % variation in \( N_2-O_2 \) mixtures in the packed bed discharge as described in chapter 3 showed no effect to the degradation of dodecane for \( O_2 \) concentration up to 40 \%, where only the NOx production was increased. In this work, the oxygen concentration steps were 0, 2, 4, 6, 8, 10, 15 and 20 \% vol. and the influence on the dodecane degradation efficiency is depicted in Figure 4.11.

![Figure 4.11](image_url)

**Figure 4.11** Oxygen concentration effect on 90 ppm dodecane plasma degradation in \( N_2-O_2 \) mixture GAD, at maximum input power \( P_{in} = 190-200 \) W and \( Q = 5 \) L min\(^{-1}\)
As observed, adding small amounts of oxygen up to 10-15 % does not change significantly the degradation efficiency which seems rather stable at ~32 % degradation similar to that in the absence of oxygen. However, an increase is noticed when higher doses of oxygen are used, with the maximum degradation efficiency noted in case of air 20% O₂, at ~41%. This enhancement is in agreement with the work of other researchers looking at the influence of oxygen concentration on the gliding arc treatment of butane [35], hexane [28] and heptane [36]. However, it might be the nature of dodecane as a longer chain saturated hydrocarbon molecule that might need higher doses of O₂ for a better oxidation.

Figure 4.12 and Figure 4.13 show the end-products distribution as a function of the oxygen concentration variation in the N₂-O₂ gliding arc treatment of dodecane. It can be seen that in the absence of oxygen major products formed are HCN > CH₄ > C₂H₄ > C₂H₂ and also lower concentrations of NH₃. When adding only 2% O₂ and more the plasma-chemical mechanism suddenly changes, decreasing dramatically the HCN, CH₄, C₂H₄ and C₂H₂ products concentration and giving rise to oxidation reactions forming CO, CO₂ and nitrogen oxides. No further production of NH₃ is observed in the presence of oxygen and no CH₄ for ≥ 4% O₂.

![Graph showing oxygen concentration effect on end-products formation](image)

**Figure 4.12** Oxygen concentration effect on the end-products formation for 90 ppm dodecane plasma degradation in N₂-O₂ mixture GAD plasma, at maximum input power $P_{in} = 190-200$ W and $Q = 2$ L min⁻¹
Figure 4.13 The NO\textsubscript{x}, HNO\textsubscript{2} and N\textsubscript{2}O distribution as a function of increasing oxygen concentration in the GAD plasma, with or without the addition of 90 ppm dodecane at maximum input power $P_{in} = 190-200$ W and $Q = 5$ L min$^{-1}$.

The concentrations of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} remain stable and low for all O\textsubscript{2} additions, however a slight rise of HCN is seen again at O\textsubscript{2} > 10% which may come from the reactions of NO with hydrocarbon fragments as shown in reaction R 4.16 [37] and R 4.17. The latter reaction has been studied in combustion systems for high temperatures [38] and the calculated rate constant is very slow, thus it is considered negligible. The increasing oxygen concentration in the N\textsubscript{2}-O\textsubscript{2} plasma is promoting the oxidation steps, as we see the ratio CO\textsubscript{2}/CO is constantly increasing.

\begin{align*}
\text{R 4.16} & \quad \text{NO} + \text{CH} \rightarrow \text{HCN} + \text{O} \quad k_{300} = 1.37 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} [37] \\
\text{R 4.17} & \quad \text{NO} + \text{CH}_3 \rightarrow \text{HCN} + \text{O} \quad k_{1000} = 4.98 \times 10^{-16} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} [38]
\end{align*}

In Figure 4.13 the NO\textsubscript{x} and N\textsubscript{2}O distribution for the 0-20% oxygen concentration in the N\textsubscript{2}-O\textsubscript{2} gliding arc discharge is compared in absence and presence of dodecane where HNO\textsubscript{2} also forms. In both cases, we see NO and NO\textsubscript{2} whose concentrations increase with increasing oxygen concentration, following a similar trend. However, the addition of dodecane to the plasma affects the NO\textsubscript{x} production by decreasing the
NO concentration and increasing NO\textsubscript{2}. The decrease of NO can be assigned both to the reaction with OH to form HNO\textsubscript{2} (R 4.14), but also to the reaction with peroxy radicals as intermediate hydrocarbon oxidation products which promotes its oxidation to NO\textsubscript{2} [39-42].

\[ \text{ROO} + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]  

It is also interesting to note that the concentration of NO\textsubscript{2} becomes greater than that for NO at 15\% O\textsubscript{2} in absence of the hydrocarbon but at \( \geq \) of 8\% when dodecane is added indicating the promotion of NO to NO\textsubscript{2} by reaction R 4.18. Low concentrations of N\textsubscript{2}O are observed both with or without dodecane, which are slightly increased with increasing oxygen concentration following the same trend. The lower N\textsubscript{2}O concentration in presence of dodecane is expected due to competitive reactions of N\textsubscript{2}\textsuperscript{*} and O with dodecane.

**4.3.4 The plasma-chemical degradation of vapour dodecane in the gliding arc discharge, comparison with BaTiO\textsubscript{3} packed bed discharge treatment.**

The principal processes of the destruction of gaseous pollutants in plasma include primary charge or energy transfer reactions (\(10^{-8}\) s) and secondary radical impact reactions (\(\leq 10^{-3}\) s) to cause dissociation of the pollutants [43]. Usually, due to their larger timescale, radical reactions are considered more for the decomposition mechanism. However primary reactions are important for their initiation. The plasma-chemical degradation of dodecane vapour has been discussed earlier for the nitrogen and air BaTiO\textsubscript{3} packed bed discharge. In this section, the degradation mechanism will be discussed for the case of dry and humid argon, nitrogen and air gliding arc discharge and any differences will be emphasised.

It has to be noted that the physical characteristics of the BaTiO\textsubscript{3} packed bed discharge and gliding arc discharge are very different. The first one is considered to be generally homogeneous and the occurrence of the microdischarges creates high mean electron energies \( \sim 4-5\) eV, but low electron densities at \( \sim 10^8\) cm\textsuperscript{-3} [21], while the “quenched” gliding arc discharge has a less homogeneous character, with a lower mean electron energy \( \sim 1\) eV, but the electron density is much higher at \(\sim 10^{13}\) cm\textsuperscript{-3} [8]. In addition, the energy deposited in the packed bed discharge was SIE\textsubscript{max} = 42 J.
L$^{-1}$, while in case of gliding arc discharge and using the assumption that the discharge power is approximately equal to the input power used, the energy density was $\text{SIE}_{\text{max}} = 1200 - 2400$ J L$^{-1}$. As discussed in chapter 3.3.4, electron impact reactions with dodecane were not considered significant in the packed bed discharge, however it would be inaccurate to ignore them in the higher electron density discharge of gliding arc.

In the argon GAD, the primary electron impact reactions generate excited argon species such as Ar (4$p$), Ar (5$p$) and argon metastables Ar$_m$(4$s$), and in less extend excited singly ionised Ar$^{+*}$, as also observed in our OES observations by the emission of Ar I and Ar II. Reactions are given below:

Electron impact excitation

\begin{equation}
R 4.19 \quad e + Ar \rightarrow e + Ar_m^* Ar^* \text{ or } Ar^{+*} \quad \Delta E = 11.5 - 11.7, 13.08 - 13.33 \text{ or } 14.7 \text{ eV}
\end{equation}

Electron impact ion excitation

\begin{equation}
R 4.20 \quad e + Ar^+ \rightarrow e + Ar^{+*} \quad \Delta E = 19.6 - 24.3 \text{ eV}
\end{equation}

The argon metastables considered to be the dominant reactive species (see chapter 1.8) while excited argon ions can be neglected as their relative concentration is expected to be very low, due to the high ionisation energy required. Thus, the main decomposition paths of dodecane in the argon GAD is considered to be by electron impact dissociation or by Ar$^*$ energy transfer reactions, followed by homolytic scission of the C-C or C-H bond. The electron impact dissociation is believed to more likely happen indirectly, by electron impact ionisation followed by dissociative recombination $[44]$:

\begin{equation}
R 4.21 \quad e + C_{12}H_{26} \rightarrow C_{12}H_{26}^+ + 2e
\end{equation}

\begin{equation}
e + C_{12}H_{26}^+ \rightarrow C_{12}H_{25} + H, \text{ or } \rightarrow R_1 + R_2
\end{equation}

\begin{equation}
R 4.22 \quad Ar^* + C_{12}H_{26} \rightarrow C_{12}H_{26}^* + Ar
\end{equation}

\begin{equation}\rightarrow C_{12}H_{25} + H, \text{ or } \rightarrow R_1 + R_2
\end{equation}

where, $R_1, R_2$ are the alkyl radicals derived from the C-C homolytic scission in the different possible carbon atom positions.
It was discussed earlier in chapter 3.3.4 that the cleavage of C-H and C-C bond is more thermodynamically favoured at the C₄ carbon forming subsequent alkyl radicals. Chain radical reactions with simultaneous β-scission C₂H₄ elimination and methyl fragments breakdown, can then lead to the final C₂H₄, C₂H₂ and CH₄ products, as shown in Figure 4.14.

In humid argon conditions, water dissociation by electron impact reactions can happen both directly and indirectly by dissociative electron attachment [45], but also by Ar* energy transfer reactions [46] to generate OH, O and H radicals. These radicals can not only contribute to the initiation step of the radical degradation mechanism by H-abstraction reactions but also react rapidly with the different alkyl fragments to create oxygenated intermediates and finally CO and CO₂, increasing the overall decomposition rate. A summary of these processes is given in Figure 4.14.

**Figure 4.14** Schematic summary of plasma-chemical decomposition of dodecane in dry and humid Ar gliding arc discharge

It is interesting to note that when water is added to the argon-dodecane plasma processing, the selectivity to C₂H₄, C₂H₂ hydrocarbons is decreased in favour of oxygenated products formation, whilst the selectivity to CH₄ is increased. This suggests that we should consider the recombination reaction R 4.23 as being more significant in humid conditions, due to the higher concentration of H radicals coming from dissociation of water. In this case, reaction R 4.23 is favoured over the competitive reaction R 4.24, and it is suggested that pathway A in Figure 4.14 is
more likely than pathway B for the formation of CO and CO$_2$ oxidation products. Indeed, kinetics of O, OH reaction with other alkyl fragments heavier than methyl support this argument, as shown in reactions R 4.23- R 4.26:

R 4.23 \[ \text{CH}_3 + \text{H} \rightarrow \text{CH}_4 \quad k_{300} = 3.21 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [47] \]

R 4.24 \[ \text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H} \quad k_{300} = 1.30 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [48] \]

R 4.25 \[ \text{C}_4\text{H}_9 + \text{H} \rightarrow \text{C}_4\text{H}_{10} \quad k_{300} = 4.26 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [47] \]

R 4.26 \[ \text{C}_4\text{H}_9 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{C}_3\text{H}_7 \quad k_{300} = 1.59 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [49] \]

The nitrogen plasma dodecane degradation has been discussed earlier in the case of packed bed discharge. In the dry N$_2$ GAD, the mean electron energy of ~1 eV gives a higher probability to create vibrationally excited nitrogen N$_2$ and in a less extent N radicals. This is different in N$_2$ packed bed discharge, where the higher mean electron energy of 4-5 eV creates a higher probability of N radical generation due to the higher energy for dissociation [50]. Thus, in GAD, N$_2^*$ charge transfer and electron impact reactions are more likely to play a significant role in the initial dodecane breakdown, while H-abstraction by N radicals could be considered to be less important. The fact that between the end-products in GAD, there are high concentrations of HCN and hydrocarbons but low concentrations of NH$_3$, while in PB plasma the formation of ammonia is more significant, shows an extra indication to support this suggestion. In humid N$_2$ GAD, the generation of OH, O radical create an oxidative environment which enhances the dodecane degradation and leads to the formation of CO and CO$_2$ and low concentrations of HCN and NH$_3$. The N$_2$/H$_2$O GAD reactions are summarised in Figure 4.15.
In the air GAD plasma, the dodecane degradation mechanism is mainly initiated by \( \text{N}_2^* \) (and to a lesser extent \( \text{N}^* \)) metastables through energy transfer reactions, by O (and secondary OH) radicals through H-abstraction and through electron impact reactions. After the initiation step, radical reactions occur with O, OH radicals promoting oxidation of the hydrocarbon to CO, CO\(_2\) products. As described earlier, in the case of \( \text{N}_2 \) and air PB plasma, the degradation rates of dodecane were similar. In fact, increasing the oxygen content in the \( \text{N}_2\)-O\(_2\) mixture between 0-40% in PB discharge did not improve the degradation efficiency but instead increased the NO, NO\(_2\) formation. This effect was assigned to a potential suppression of the degradation radical initiation, due to \( \text{N}_2^* \), \( \text{N}^* \) and O radical recombination reactions leading to NOx. This is different to what we observe in case of GAD dodecane treatment, where the air plasma provides higher degradation efficiency compared to nitrogen and variation of 0 - 20% O\(_2\) in \( \text{N}_2\)-O\(_2\) mixture shows an increase taking place for 10% and more. The NOx distribution also differs, where in pure air GAD NO\(_2\)/NO > 1 and the addition of dodecane even increases that ratio, indicating the oxidation chemistry. So the question is why air plasma oxidation is more favoured in the gliding arc discharge rather the packed bed discharge?
One reason can be related to the electron density and input energy dissipated in the discharge in each case. As mentioned earlier, the electron impact radical initiation reactions should not be neglected in the case of the GAD as higher electron energy density plasma compared to PB plasma. Thus, if in the air packed bed plasma the radical initiation is suppressed by the rapid \( \text{N}_2^* \), \( \text{N}^* \) reactions with \( \text{O} \) to form \( \text{NO}_x \), in air GAD electron impact reactions could create radicals than then could promote oxidation reactions with \( \text{O} \), \( \text{OH} \) radicals. This can also explain the \( \text{NO}_x \) distribution in the air GAD where the formation of peroxy radicals such as \( \text{HOO}^* \), \( \text{ROO}^* \) promote the oxidation ratio \( \text{NO}_2/\text{NO} > 1 \) [41, 42].

In the humid air GAD plasma, the dissociation of water creates \( \text{OH} \) and \( \text{O} \) radicals that can also participate in the radical initiation step of dodecane degradation. However as discussed earlier, humidity has caused no improvement to the overall degradation but instead has increased significantly the \( \text{HNO}_2 \) formation. A summary of the dry and humid air reactions are given in Figure 4.16.

**Figure 4.16** Schematic summary of plasma-chemical decomposition of dodecane in dry and humid gliding arc discharge
4.4 Summary & Conclusions

The gliding arc discharge has been used as a source of low temperature plasma for the treatment of oil in the vapour phase, in order to investigate the gas chemistry and identify optimal conditions, before the plasma-liquid treatment. The effect of different gas compositions such as dry or humid Ar, N₂ and air plasma, or the variation of 0-20 % oxygen to N₂-O₂ mixture plasma gas has been studied.

A comparison between the treatment of the target oils such as odourless kerosene and n-dodecane in Ar, N₂ and air GAD showed similar degradation efficiency and end-product formation. Thus, n-dodecane was chosen as a simulant for further experiments in order to perform quantitative analysis.

Changing the plasma gas composition causes observable changes to the gliding arc plasma characteristics and thus the plasma-chemical dodecane degradation and end-products formation. OES diagnostics at different conditions show a strong correlation between the intermediate excited species and the end-products. The rotational and vibrational temperature from the different species shows the non-equilibrium degree of the discharge. However, rotational temperature values in most cases are high (\( T_r = 1300 – 3500 \) K) and cannot be used to obtain the translational gas temperature. In case of dry argon plasma, the rotational temperature of OH\(^*\) is lower \( T_r = 900 \pm 50 \) K. However, thermocouple measurements are taken as more reliable values for the gas temperatures which are 330 - 380 K, 470 - 580 K and 570 - 580 K in the different argon, nitrogen and air admixtures respectively.

In dry conditions, the maximum dodecane degradation achieved was 41% with the air plasma. The variation of oxygen concentration before 0-20 % in the N₂-O₂ mixture showed a degradation increase for O₂ >10% with optimal conditions in case of air (20% O₂). The increasing oxygen concentration promotes oxidation and increases the ratios of CO₂/CO and NO₂/NO. However there is a significant amount of NOx production.

Humidity increases significantly the degradation efficiency in the Ar and N₂ GAD by about 70% and 40%, respectively, but not in case of air plasma. Humid nitrogen gives the best degradation efficiency with an overall of 51% degradation. However humid argon gives better selectivity towards CO, CO₂ and better energy efficiency. Table 4.6 compares the energy efficiency in PB and GAD plasma.
<table>
<thead>
<tr>
<th>Plasma</th>
<th>Power (W)</th>
<th>Flow (L/min)</th>
<th>SIE (JL⁻¹)</th>
<th>C_{12}H_{26} treated (ppm)</th>
<th>E (mg C_{12}H_{26} kJ⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ PB</td>
<td>P_d = 1.4</td>
<td>2</td>
<td>42</td>
<td>14.3</td>
<td>2.37</td>
</tr>
<tr>
<td>Air PB</td>
<td>P_d = 1.4</td>
<td>2</td>
<td>42</td>
<td>15.6</td>
<td>2.58</td>
</tr>
<tr>
<td>N₂ PB</td>
<td>P_{in} = 200</td>
<td>2</td>
<td>6000</td>
<td>14.3</td>
<td>0.016</td>
</tr>
<tr>
<td>Air PB</td>
<td>P_{in} = 200</td>
<td>2</td>
<td>6000</td>
<td>15.6</td>
<td>0.018</td>
</tr>
<tr>
<td>Ar GAD</td>
<td>P_{in} = 110</td>
<td>5</td>
<td>1320</td>
<td>9.9</td>
<td>0.052</td>
</tr>
<tr>
<td>Ar/H₂O GAD</td>
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<td>5</td>
<td>1440</td>
<td>38.7</td>
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</tr>
<tr>
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<td>P_{in} = 190</td>
<td>5</td>
<td>2280</td>
<td>27.9</td>
<td>0.080</td>
</tr>
<tr>
<td>N₂/H₂O GAD</td>
<td>P_{in} = 200</td>
<td>5</td>
<td>2400</td>
<td>45.9</td>
<td>0.133</td>
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<td>5</td>
<td>2400</td>
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<tr>
<td>Air/H₂O GAD</td>
<td>P_{in} = 210</td>
<td>5</td>
<td>2520</td>
<td>36.0</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Table 4.6 Comparison of dodecane degradation ability between BaTiO₃ packed bed plasma (PB) and gliding arc discharge plasma (GAD) used in this work, where P_{in} and P_d is the input and discharge power respectively.

The dodecane plasma processing is controlled by the radical initiation mechanism in each case. In the non-oxidative environment of the Ar and N₂ GAD, Ar* and N₂* energy transfer reactions, together with the electron impact dissociation reactions initiate the breakdown of dodecane and by stepwise β-scission can lead to high selectivity for C₂H₄ and C₂H₂ and in addition HCN in case of nitrogen, with correlated C₂* and CN* dominant emissions in each case.

Humidity in Ar and N₂ GAD produces OH, O radicals confirmed by OES. They are believed to play a significant role in dodecane processing, by contributing to the radical initiation through H-abstraction reactions and creating an oxidative environment, reacting with dodecane fragments. Thus, the C₂H₄, C₂H₂ or HCN selectivity is decreased in favour of CO, CO₂ products. The fact that CH₄ selectivity is not affected by humidity indicates that methyl radical may be more favourable to H recombination rather than O reaction and suggests that the CO, CO₂ could mainly result from heavier alkoxy or peroxy radicals.

There is a significant difference between the PB and the GAD plasma treatment of dodecane, due to their different physical characteristics. GAD might have a lower
mean electron energy compared to PB, but it has higher electron density and gives higher electron power dissipated in the discharge. This gives higher degradation efficiency compared to PB discharge, but it appears more energy demanding (Table 4.6). However, the reactor was designed for the plasma-liquid waste treatment and higher power is needed to treat concentrated organics.

For future plasma-liquid treatment, humid argon and humid nitrogen conditions look favourable in terms of degradation efficiency and avoiding the excess NOx formation.

4.5 References


Chapter 5

5. Argon Dielectric Barrier Discharge degradation of n-dodecane in the liquid phase

5.1 Introduction

This chapter investigates the argon DBD plasma treatment of n-dodecane as a first approach to the plasma-liquid treatment of oil waste. This work was carried out in the Applied Electrostatics Laboratory in Toyohashi University of Technology in Japan, as a joint-research project with Prof. Akira Mizuno, under a two months fellowship supported by Japanese Society for Promotion of Science (JSPS).

Electrical discharges in gas-liquid or liquid environments have been studied for a number of years. DBD discharges have been also studied in this field mainly in water environments in applications such as wastewater treatment [1, 2] and biomedical applications [3, 4]. More recently, DBD discharges in contact with oils have been also found in applications of surface cleaning [5] or oil upgrading and reforming [6-8]. When DBD plasma configurations are used for liquid treatment, the liquid could be considered as one of the dielectrics, as illustrated below in Figure 5.1. In our case liquid n-dodecane works as the dielectric.

![Figure 5.1 Schematic of a dielectric barrier discharge configuration where one electrode is covered by a dielectric and microdischarges are formed in the discharge gap [9].](image)

A series of experiments on argon DBD degradation of n-dodecane have been performed, as a part of a preliminary research on non-thermal methods for the
degradation of oil waste. Argon plasma gas was chosen in order to avoid the undesirable \(\text{NO}_x\) formation found in air mixtures plasmas. Moreover, previous work has shown it can provide good energy efficiency (Chapter 4). The methods investigated can be categorised as given below:

i) The effect of HV electrode position in gas or liquid environment

Experiments were performed using the DBD reactor with the HV electrode placed inside or outside the oil in order to investigate how two different electrode positions can affect the target liquid treatment as the plasma characteristics are expected to be different. In the first case, the electrode placed inside the oil and argon gas was bubbling through the liquid to facilitate the discharge “inside” the liquid. It is expected that bubbles will enhance the breakdown, increase the reaction surface area and create intense mixing in order to allow the reactive species to diffuse into the bulk liquid. In the second case, the HV electrode was placed outside the oil in order to create an argon discharge “in contact” with the target liquid. The aforementioned two methods create discharges with different characteristics, so different results are also expected.

ii) The effect of humidity to the oil degradation

Water vapour is an important factor in plasma processing as it can be a major source of \(\text{OH}\) and \(\text{HO}_2\) radicals which may accelerate the oxidation reactions. In this work, the effect of humidity is investigated in the argon DBD plasma “inside” and “in contact” with the target oil.

iii) The effect of temperature to the oil degradation

A temperature increase is expected to enhance the oil degradation by promoting endothermic reactions and change the product selectivities. Moreover, it may enhance the generation of \(\text{OH}\) radicals under humid conditions. In addition, it would be interesting to determine if the heating influences the electrical discharge characteristics.
5.2 Experimental set-up

Experiments were performed using argon atmospheric pressure DBD plasma for the treatment of liquid n-dodecane and two main experimental configurations were used as illustrated in Figure 5.2. The DBD reactor consisted of a 0.5 L quartz glass vessel, a HV stainless steel mesh plate electrode (d = 3 cm) and an aluminium foil plate (d = 3 cm) as the ground electrode attached on the bottom of the glass vessel (dielectric) preserving an electrode gap of 6 mm. The first experimental set-up uses the HV electrode surrounded by the oil. Argon gas is supplied by a capillary glass tube also submerged in the oil to create bubbles, in order to generate the discharge “inside” the liquid (Figure 5.2.a). The second configuration uses the HV electrode above the oil in an argon gas atmosphere, to create an argon discharge “in contact” with the oil.

Figure 5.2 (A) DBD oil treatment with gas bubbling through the liquid and HV electrode submerged (B) DBD oil treatment “in contact”. 1) Flow controller, 2) humidity generation, 4) AC HV stainless steel electrode, 5) aluminium foil ground electrode, 6) gas outlet for FTIR analysis, 7) PC FTIR control.
The power supply consisted of a Trek HV 20/20C amplifier, and an Agilent 33210 10 MHz generator to produce sinusoidal waveforms of maximum $V_{p-p} = \pm 20$ kV and $I_{p-p} = \pm 20$ mA at frequency of 1 kHz across the discharge gap. The applied voltage was measured by an oscilloscope (Tektronix TDS 2014) using a high voltage probe. When current was allowed to pass across a capacitor ($C = 0.1 \ \mu F$), the charge could be collected and the oscilloscope could plot the charge-to-voltage $Q-U$ Lissajous figures which were used to calculate the discharge power [10] (see also Chapter 3 and Appendix II). Ar (99.998%) was used as the carrier gas passing through the DBD reactor containing liquid n-dodecane (99%) and the flow was stable at 0.5 L min$^{-1}$. For the humid conditions, argon was passed through a water bubbler, creating humidity of $H_2O \sim 3 \ %$ ($T = 25 ^\circ C$). For the investigation of the temperature effect, the reactor was placed in a Sibata Lab Ltd oven heater where temperature was set to 100$^\circ$C. In-line FTIR spectroscopy (BioRad 4000 Excalibur Series) at a resolution of 1 cm$^{-1}$ set with a long path IR cell (Infrared Analysis Inc, 6 m) was used for the identification and concentration determination of the gaseous products. After the plasma treatment of dodecane, there was no obvious change in the liquid colour which usually indicates the formation of liquid end-products and so no liquid analysis was performed at this short period of experimental time.

5.3 Results and Discussion

5.3.1. The effect of HV electrode position on argon DBD treatment of liquid n-dodecane, in dry or humid conditions

When the HV electrode was submerged in the oil without any bubbles feed, the ignition of DBD was not possible at a voltage $\leq 40$ kV and a 1 kHz frequency. This is not surprising as generally, discharges in liquids are harder to generate in comparison with gas discharges [11], and also n-dodecane is considered as an insulator (dielectric liquid) that could act as a second barrier to the dielectric barrier discharge formation (Figure 5.1). When Ar bubbles are introduced to the reactor, as shown in Figure 5.2.a, breakdown first occurred at 7.3 kV at 1 kHz frequency. When the HV electrode is put above the oil with the electron-oil gap at 1 mm, the electrode gap at 6 mm and with an argon gas flow above the liquid (Figure 5.2b), breakdown first occurs at 10 kV. These two different configurations create different discharge
characteristics. Some photographs of the different discharges are shown in Figure 5.3a and b.

![Figure 5.3 Ar DBD A) inside the n-dodecane with bubble feed, B) in contact with n-dodecane, where a = 6 mm is the electrode gap and b = 10 mm, c = 4 mm the oil height in each case respectively](image)

In Figure 5.3a, one can observe the formation of microdischarges between the two electrodes, but the plasma emission seems more intense next to the bubbler, where the bubbles first form. It is possible that breakdown occurs inside the Ar bubble and then interacts with the oil. Gershman et al. [12] and Sato and Yasuoka [13] have investigated pulsed electrical discharges in single bubbles in water and they have observed discharges occurring inside the bubble or on the surface between the bubble and the water. Bruggeman et al. have also shown that streamers preferentially form along the bubble surface when the bubble is immersed in a high dielectric liquid such as water [14, 15].

The Lissajous figures $Q-U$ method was used to calculate the discharge power ($P_d$) where charge is collected across a capacitor and the integration of $Q-U$ plot area represents the discharge power (see Appendix II for further details). Figure 5.4 shows the Lissajous figures obtained during the Ar DBD treatment of dodecane with bubbles feed (A) and Ar DBD “in contact” treatment of dodecane (B). Despite the fact that the same input voltage was used to generate both plasmas ($V_{in \text{p-p}} = 24 \text{ kV}$) their energy is dissipated differently, thus creating different discharge characteristics. The discharge (B) has a higher power of 2.9 W in comparison to 1.42 W in case (A). This suggests that the discharge (B) is more stable and consequently more powerful. The argon bubble feed in case (A) may hinder the formation of a homogeneous and stable discharge.
Figure 5.4 Lissajous Figures in case of A) the Ar DBD treatment of dodecane with bubbles feed and B) Ar DBD “in contact” treatment of dodecane, under the same applied electrical field, $V_{in-p} = 24$ kV, $f = 1$ kHz and the same electrode gap = 6 mm. 

X is the discharge voltage ($U$) expressed in kV and Y is the charge ($Q$) expressed in nC though capacitor of $C = 100$ nF.

Furthermore, the Lissajous figures (Figure 5.4) have different shapes for the two different discharge configurations. In case (A) the Lissajous figure forms an ellipsoidal, indicative of diffused discharge and proposed by many researchers to be a characteristic of surface discharge [16, 17]. This could be an indication that the discharge occurs along the bubbles surface creating a more uniform charge transport through the liquid. In case (B) of the “in contact” Ar plasma treatment of the oil, the Lissajous figure tends to form a parallelogram, a characteristic of a volume non-uniform filamentary discharge [18, 19].

5.3.2 The influence of humidity and temperature in the DBD treatment of liquid $n$-dodecane with the assistance of Ar bubbles

The DBD reactor with the HV electrode submerged in the oil was placed inside a furnace and a gas flow of $Q = 0.5$ Lmin$^{-1}$ through a glass capillary nozzle created the bubbles feed in the oil. The experiments were performed in dry and humid conditions at temperatures of 25 °C and 100 °C. In all cases the applied voltage was set at a maximum of $V_{in-p} = 40$ kV at frequency of 1 kHz. The humidity and temperature effect on the electrical characteristics is shown in the Lissajous figures recorded in each case as illustrated in Figure 5.5 below.
Figure 5.5 Lissajous figures s for (A) dry argon DBD at 25 °C, (B) humid argon DBD at 25 °C, (C) Dry argon DBD at 100 °C and (D) humid argon DBD at 100 °C. In all cases the maximum applied voltage was used ($V_{in-p-p} = 40$ kV) at $f = 1$ kHz.

The maximum discharge power ($P_d$) achieved is different in all cases. For both dry and humid conditions, the increase of temperature at 100 °C gives a rise to the discharge power from 1.4 to 4.3 W and from 0.2 to 17.6 W for the dry and humid conditions, respectively. In addition, the shape of the Lissajous figure slightly changes from an ellipsoidal to a more parallelogram-like form. This suggests that increased temperature may favour the formation of a filamentary discharge. In the humidity experiments in the case of 25 °C temperature, a negative influence on power is observed. The humidified argon bubbles weaken the discharge formation and result in an energy drop from 1.4 W to 0.2 W. Moreover, the charge appears more diffused (Figure 5.5-B). It may be that water vapour requires higher dissipated power for the breakdown, hindering the formation of a stable discharge. Increasing the temperature favours the formation of a stronger filamentary discharge, with a discharge power at 17.6 W (Figure 5.5-D).
Figure 5.6 shows the effect of humidity and temperature on the gaseous products formed during the Ar bubble DBD treatment of liquid dodecane, as a function of the specific input energy (SIE) achieved in each case. Table 5.1 shows the total concentration of the gaseous products detected and the respective products selectivity in each case. The degradation efficiency will be expressed in terms of the quantity of total gaseous products formation.

### Figure 5.6 Effect of humidity and temperature on the detected gaseous-products concentration in the Ar bubbles DBD plasma treatment of n-dodecane

<table>
<thead>
<tr>
<th>Condition</th>
<th>Total products (ppm)</th>
<th>CH₄ %</th>
<th>C₂H₄ %</th>
<th>C₂H₂ %</th>
<th>CO₂ %</th>
<th>CO %</th>
<th>SEI (J L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/H₂O 25°C</td>
<td>144.0</td>
<td>11.5</td>
<td>38.7</td>
<td>31.7</td>
<td>5.0</td>
<td>13.1</td>
<td>24.0</td>
</tr>
<tr>
<td>Ar 25°C</td>
<td>42.4</td>
<td>42.3</td>
<td>41.1</td>
<td>16.5</td>
<td>0.0</td>
<td>0.0</td>
<td>170.4</td>
</tr>
<tr>
<td>Ar 100°C</td>
<td>299.2</td>
<td>5.9</td>
<td>78.0</td>
<td>16.2</td>
<td>0.0</td>
<td>0.0</td>
<td>483.6</td>
</tr>
<tr>
<td>Ar/H₂O 100°C</td>
<td>1229.0</td>
<td>5.1</td>
<td>76.2</td>
<td>18.1</td>
<td>0.2</td>
<td>0.4</td>
<td>2109.6</td>
</tr>
</tbody>
</table>

### Table 5.1 Effect of humidity and temperature on the total gaseous end-products concentration and respective selectivity in each case. Uncertainty in values is less than 3%.

The major gaseous end-products which occur from the argon dodecane plasma degradation are CH₄, C₂H₄, C₂H₂ in dry conditions plus CO, CO₂ in humid conditions, while C₁₂H₂₆ is formed from vaporisation. In dry conditions, heating significantly improves the plasma degradation of oil. At 25 °C in dry argon, the
degradation is poor. However, when humidity is added the degradation is improved by a factor of 3, while the energy dissipated in plasma is decreased by a factor of 7. This is a significant effect as the overall process efficiency is improved by a factor of 21. At 100 °C temperature, the humid argon plasma leads to the discharge of highest power and also the best degradation yield in this case. Regarding the temperature effect in humid conditions, the degradation has increased eightfold, giving a good selectivity to C₂H₄ of 76.4%. However, the energy dissipated in humid argon plasma is also increased by a factor of 4. Overall, the humid argon plasma at 25 °C appears to be the most energy efficient degradation of dodecane leading also to a better selectivity of CO, CO₂ products.

5.3.3 The influence of humidity and temperature in the Ar DBD “in contact” treatment of liquid n-dodecane

In this case, the HV electrode in the DBD reactor has a 2 mm gap distance with the oil surface and argon gas \( (Q = 0.5 \text{ L min}^{-1}) \) flows in between to create an “in contact” plasma treatment. In all cases, the applied voltage was set at a maximum of \( V_{in,p-p} = 40 \text{ kV} \) at a frequency of 1 kHz. The reactor was placed inside a furnace for the temperature effect experiments at 25 °C and 100 °C. The humid conditions in this case were created by using an emulsion of oil and water. A ratio of water/oil = 0.1 was chosen for the emulsion and Figure 5.7 shows the effect of humidity on the discharge colour. The bright blue filaments that appear only in some parts of the discharge might be formed in the point where water droplets are positioned in the emulsion. The blue emission could be correlated with high concentration of excited CH, C₂ radicals that are formed from the dodecane dissociation and emit light in the blue region, as also observed previously in case of Ar/H₂O gliding arc discharge in Chapter 4.
Figure 5.7 Photographs taken during argon DBD “in contact” treatment of dodecane in a) dry conditions and b) humid conditions of water/oil = 0.1 emulsion.

The effect of humidity and temperature on the Lissajous figures measured in each case is shown in Figure 5.8.

Figure 5.8 Lissajous figures for (A) dry argon DBD at 25°C, (B) humid argon DBD at 25°C, (C) dry argon DBD at 100°C and (D) humid argon DBD at 100°C. In all cases the maximum applied voltage was used ($V_{\text{in,p-p}} = 40$ kV) at $f = 1$ kHz.

Overall, the argon DBD discharge “in contact” with the oil appears stronger compared to the one when argon bubbles are used (Figure 5.8). When argon plasma is humidified at 25°C, the discharge power does not change significantly, however, the $Q-U$ plot tends to form a more discrete parallelogram. This suggests that the
addition of water to the oil enhances the filamentary discharge. By increasing the temperature at 100 °C, the discharge power increases in both dry and humid conditions. However, in humid conditions, the discharge forms slightly weaker discharge than in dry argon plasma and the \( Q-U \) plot forms a more “almond-like” shape.

The influence of humidity and temperature concentration of the gaseous products during the Ar DBD “in contact” treatment of liquid dodecane is shown in Figure 5.9 as a function of the specific input energy (SIE) achieved in each case. Table 5.2 summarises the total products concentration and respective products selectivity in each case.

![Figure 5.9](image)

**Figure 5.9** Effect of humidity and temperature on gaseous-products concentration in the Ar DBD “in contact” treatment of n-dodecane

<table>
<thead>
<tr>
<th>Condition</th>
<th>Total products (ppm)</th>
<th>CH(_4) %</th>
<th>C(_2)H(_4) %</th>
<th>C(_2)H(_2) %</th>
<th>CO(_2) %</th>
<th>CO %</th>
<th>SEI (J L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar 25 °C</td>
<td>377.16</td>
<td>11.4</td>
<td>50.0</td>
<td>39.4</td>
<td>0.0</td>
<td>0.0</td>
<td>1516.8</td>
</tr>
<tr>
<td>Ar/H(_2)O 25 °C</td>
<td>242.31</td>
<td>14.4</td>
<td>56.3</td>
<td>15.7</td>
<td>2.0</td>
<td>11.6</td>
<td>1644</td>
</tr>
<tr>
<td>Ar/H(_2)O 100 °C</td>
<td>513.26</td>
<td>8.3</td>
<td>77.6</td>
<td>13.1</td>
<td>0.3</td>
<td>0.8</td>
<td>1803.6</td>
</tr>
<tr>
<td>Ar 100 °C</td>
<td>766.38</td>
<td>5.8</td>
<td>78.6</td>
<td>15.6</td>
<td>0.0</td>
<td>0.0</td>
<td>2228.4</td>
</tr>
</tbody>
</table>

**Table 5.2** Effect of humidity and temperature on the total end-products concentration and respective selectivity in each case. Uncertainty in values is less than 3%.
In all cases, the DBD “in contact” treatment of dodecane leads to degradation products in the same sequence \( C_2H_4 > C_2H_2 > CH_4 > CO > CO_2 \), where CO, CO\(_2\) is seen only in humid conditions. The DBD treatment of the oil/water emulsion at 25 °C gives poorer degradation than dry argon plasma and also appears to be slightly more energy efficient. When the temperature is increased at 100 °C, the plasma treatment of the oil mixed with water is enhanced. Surprisingly, the addition of water does not promote oxidation to CO, CO\(_2\), but increases the selectivity of C\(_2\)H\(_4\) instead at about 78%. The best treatment performance is noted in case of dry argon plasma-oil treatment at 100 °C which also gives a high selectivity of 79% to C\(_2\)H\(_4\).

### 5.4 Summary and Conclusions

Two different DBD plasma reactor configurations were used with argon gas in dry or humid conditions. The first reactor set up includes the HV electrode submerged inside the oil and plasma was generated with the assistance of argon bubbles feed. The second reactor uses the HV electrode above the oil surface to create an “in contact” plasma treatment of the oil. The humidity addition and temperature increase at 100 °C were studied in terms of their influence to the dodecane degradation.

The two different DBD configurations create discharges with different characteristics. When the HV electrode was submerged in dodecane, the bubbles feed was necessary to generate plasma inside the liquid. The breakdown in this case occurs in the gas inside the bubbles or at the bubble gas-liquid interface. However, this configuration created rather weak discharges that it could be due to the viscosity affect that hindered the formation of a stable discharge. Increasing the temperature at 100 °C decreases the viscosity and increases the volatility which favoured a higher power discharge and enhanced the dodecane degradation. Humidified argon at 100 °C present the best degradation efficiency in this case, however, it does not create a sufficiently oxidative environment to lead to high yields of CO, CO\(_2\). By using the Ar DBD plasma “in contact” with dodecane, more energy is dissipated in the discharge giving a more distinct filamentary character. Humidity does not improve the oil degradation and the best degradation rate is noted in case of dry argon at 100 °C, as a consequence of the highest power discharge formed in this case.
In all cases the product selectivity follow the sequence of $\text{C}_2\text{H}_4 > \text{C}_2\text{H}_2 > \text{CH}_4 > \text{CO} > \text{CO}_2$. Moreover, humid argon bubbles plasma presents the best energy efficiency in the dodecane treatment. However, further work is needed to improve the degradation rate and should be also expanded in the liquid. The next chapter will study the use of gliding arc discharge as more powerful plasma for the plasma-liquid treatment of dodecane.

### 5.5 References


[17] J. Kriegseis, Möller, Benjamin, Grundmann, Sven, Tropea, Cameron, "Capacitance and power consumption quantification of dielectric barrier


Chapter 6

6 The plasma-liquid treatment of n-dodecane using gliding arc discharge

6.1 Introduction

The scope of the plasma-liquid interactions is vast including a complex mechanism between gas and interfacial chemistry and subsequently the chemistry in the bulk liquid. A schematic summary of the plasma-liquid mechanism is given in Figure 6.1.

![Figure 6.1 The scope of plasma-liquid interactions](image)

The gaseous plasma containing reactive species such as electrons, ions, radicals and photons initially reacts with the liquid interface. Reaction can take place either as a gas-surface process leading mainly to gaseous products, or reactions can be initiated by diffusion and convection mechanisms in the bulk liquid. Mariotti et al. have discussed possible electron-liquid reactions in a plasma-liquid system for nanoparticles synthesis [1]. The electrons and charged particles in the gas phase have an isolated behaviour and their reactions are distinguished from reactions in the liquid phase. Electrons can penetrate into the plasma-liquid interface and solvent effects can diffuse the electrons initiating reactions in the bulk liquid. The solvation effect is not very well understood, but it is thought to be dependent on the electron kinetic energy [2]. Regarding the radicals behaviour, several researchers has proven the dissolution of reactive species to the bulk liquid, for example, OH, HO₂ radicals and NOₓ species formed in the plasma phase can react with liquid water to form H₂O₂ [3], HNO₂ and HNO₂ [4, 5], respectively.
Earlier in this thesis, the gliding arc plasma treatment of dodecane in the gaseous phase has been discussed, unravelling the plasma-chemical degradation mechanism under different gas compositions such as dry and humid nitrogen, argon and air. In terms of the degradation efficiency, humid nitrogen and humid argon are favoured, avoiding at the same time the NO\textsubscript{x} formation occurring in the air plasma. Extending this work, this chapter presents the study of gliding arc plasma treatment of liquid dodecane. The selected plasma gases are nitrogen and argon in both dry and humid conditions, in order to test their influence on the liquid dodecane degradation efficiency, but also to study the plasma-liquid mechanism looking at both gaseous and liquid chemistry with reference to the earlier gas phase experiments.

6.2 Experimental set-up

The gliding arc discharge (GAD) has been used for the treatment of liquid n-dodecane (C\textsubscript{12}H\textsubscript{26}, supplied by Alfa Aesar \(\geq 99\%\)) using two different approaches of batch and recycling treatment. The main GAD reactor that has been used and described earlier for the treatment of gaseous dodecane (Chapter 4) has been used for the treatment of liquid dodecane in this case, with some essential modifications to fit the experimental conditions.

For the batch treatment, the plasma gases used were N\textsubscript{2} and Ar (BOC 99.998\%) in dry or humid conditions. For the humid conditions, the inlet gas relative humidity was RH = 75\% ± 2\% (H\textsubscript{2}O = 2.3 ± 0.3 \%), at \(T = 24^\circ\text{C}\), measured with a HTD-625 thermo-hygrometer. The GAD was running with a 5 L min\textsuperscript{-1} flow of the gas and 15 ml of dodecane was placed below the plasma plume, at a distance of 17 mm from the electrode with no direct contact of the plasma with the liquid. In order to facilitate the treatment and minimise the vaporisation, a homemade jacketed cell was used and water cooling of 22 °C was applied, as shown in Figure 6.2. The plasma-liquid treatment of dodecane was running for 60 min with the maximum input power achieved in each case (\(P(\text{N}_2) = 200\ W\), \(P(\text{Ar}) = 120\ W\), \(P(\text{N}_2/\text{H}_2\text{O}) = 220\ W\), \(P(\text{Ar}/\text{H}_2\text{O}) = 140\ W\)) and the gaseous end-products were measured in-line and in real-time by FTIR spectroscopy. Under the same conditions, spectroscopic studies using OES spectroscopy were used as diagnostics of the plasma and intermediate excited species behaviour.
Figure 6.2. a) Picture of the homemade water cooling jacketed cell used for the gliding arc batch treatment of n-dodecane, b) N\textsubscript{2} gliding arc discharge dodecane treatment using the cell

For the recycling oil plasma treatment, 60 ml of dodecane were placed initially in the reaction vessel and a peristaltic pump was applied to drive the oil into a metal nozzle and recycle it using a set flow of 120 ml min\textsuperscript{-1}. The nozzle was homemade and it was consisted of a copper tube (id = 1.7 mm) with a mesh plate attached in the outlet. The plasma gases used in this case were N\textsubscript{2} and Ar in humid conditions only (H\textsubscript{2}O = 2.3 ± 0.3 %), as used during the batch treatment. Gaseous product analysis was performed using in-line FTIR spectroscopy. No OES analysis was performed in this case. A schematic of the recycling treatment reactor set-up and pictures during the plasma treatment are given in Figure 6.3.

Figure 6.3. a) Schematic of the gliding arc reactor design for the recycling plasma-liquid treatment of dodecane and photographs taken during b) humid argon and c) humid nitrogen plasma recycling treatment of dodecane showing the direct injection of the oil to the plasma plume
In both the batch and recycling methods of plasma treatment of dodecane, liquid analysis was performed in order to identify potential by-products formed in the liquid phase. Batch treatment samples were collected post-treatment \((t = 60\) min) while samples during the recycling treatment were collected in time intervals of \(t = 5, 20, 30, 40, 50\) and \(60\) min. GC-MS analysis was performed in crude treated oil samples to quantify the level of by-products formed in reference to dodecane. In order to facilitate a more profound analysis, column chromatography was performed to collect non-polar and polar fractions which were subject to ATR IR and GC-MS liquid analysis. Identification of the different components seen in GC-MS was done with the assistance of the NIST EI mass spectral database and by complementary interpretation of both EI and CI MS.

### 6.3 Results and Discussion

#### 6.3.1 The influence of plasma gas composition on the GAD plasma-liquid dodecane degradation yield

The overall results of the plasma-liquid degradation of \(n\)-dodecane in dry or humid \(N_2\) or \(Ar\) plasma in both dry and humid conditions are summarised in Table 6.1. The \% oil volume removal is given as an indication of the degradation efficiency and it was calculating by measuring the initial volume of oil and the volume of oil after \(1\) h of treatment. GC-MS analysis was performed in the post treatment crude samples and using a peak ratio technique, the level of end-products as impurities mixed with untreated dodecane was estimated.

<table>
<thead>
<tr>
<th>GAD gas</th>
<th>Pin / W</th>
<th>% v/v oil removal after treatment</th>
<th>oil removed / ml</th>
<th>% liquid end-products after treatment</th>
<th>gaseous products concentration / ppm at (t = 60) min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>120</td>
<td>5.3</td>
<td>0.80</td>
<td>&lt; 0.21</td>
<td>211.5 ± 8.5</td>
</tr>
<tr>
<td>(N_2)</td>
<td>200</td>
<td>25.3</td>
<td>3.75</td>
<td>&lt; 0.08</td>
<td>932.4± 37.3</td>
</tr>
<tr>
<td>Ar/H(_2)O</td>
<td>140</td>
<td>13.4</td>
<td>2.01</td>
<td>&lt; 0.64</td>
<td>712.4 ± 28.5</td>
</tr>
<tr>
<td>(N_2/H(_2)O)</td>
<td>220</td>
<td>44.2</td>
<td>6.63</td>
<td>&lt; 0.20</td>
<td>1546.9 ± 61.9</td>
</tr>
</tbody>
</table>

**Table 6.1** Summary of different plasma gas used for the GAD plasma-liquid degradation of dodecane. Initial volume of \(C_{12}H_{26}\) was 15 ml. The total oil volume reduction is calculated after 1 hour of treatment. GC-MS analysis has been performed to quantify the amount of liquid by-products in the post-treatment samples.
In dry conditions, using the argon plasma gives a poor degradation with only 5.3% of the oil volume being decreased after 1 h of treatment. The yield is increased by a factor of ~ 5 when dry N₂ plasma is used and the total oil reduction is 25.3% in this case. When humidified gases are used, the degradation yield is enhanced for both N₂ and Ar, increasing both the concentration of gaseous products, but also the formation of liquid by-products in dodecane. Overall, the best dodecane degradation yield is observed for the case of N₂/H₂O plasma with total 44.2 % oil volume removal.

6.3.2 The gaseous analysis of the dodecane plasma-liquid batch treatment using Ar, N₂, Ar/H₂O or N₂/H₂O gliding arc discharge

Plasma gases such as N₂ or Ar in both dry and humid conditions have been studied for the plasma-liquid degradation of n-dodecane. Figure 6.4 shows the gaseous products distribution in the Ar GAD treatment of dodecane, as a function of treatment time.

**Figure 6.4** Gaseous products concentration in the Ar GAD treatment of a) liquid dodecane as a function of treatment time and in b) gaseous dodecane treatment (90 ppm)
The Ar plasma gives a poor degradation of liquid dodecane and a low concentration of gaseous products. The off-gas is rich in gaseous dodecane which is formed by evaporation caused by the temperature increase inside the reactor and the concentration of all the gases is stabilised after the first 10 min of the Ar plasma treatment. The observed products following the Ar plasma-liquid treatment of dodecane does not differ significantly from those observed in case of the Ar plasma treatment of gaseous dodecane. No new products are observed and the selectivity for the production of the hydrocarbons remains the same \( \text{CH}_4 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2 \), while the low concentration of CO is thought to be due to oxygen impurities in the feed gas.

However, it needs to be reminded here, that \( \text{C}_2\text{H}_6 \) and other lighter hydrocarbons are possibly also formed, although they cannot be seen due to overlapping limitations caused by the IR spectroscopy. The decomposition mechanism as described earlier in chapter 3, leads mainly to \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) radicals which can then form final products as shown in reactions R6.1-6.4. In fact, \( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \) products are expected to be formed in higher abundance from the unsaturated hydrocarbons of \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_2 \), as more thermodynamically-stable products. At low temperatures, alkyl radicals are more likely to recombine with H atoms (reactions R 6.1, 6.2) forming a new \( \sigma \) bond, rather to react with H in order to form alkenes and molecular hydrogen involving the formation of a new \( \pi \) bond (reaction R 6.3).

\[
\begin{align*}
R\ 6.1 \quad & \text{CH}_3 + H \rightarrow \text{CH}_4 \quad k_{300} = 3.21 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \ [6] \\
R\ 6.2 \quad & \text{C}_2\text{H}_5 + H \rightarrow \text{C}_2\text{H}_6 \quad k_{300} = 2.25 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \ [5] \\
R\ 6.3 \quad & \text{C}_2\text{H}_5 + H \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad k_{300} = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \ [7] \\
R\ 6.4 \quad & \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \quad \text{(no available kinetic data)}
\end{align*}
\]

However our system is different to a system close to thermodynamic equilibrium. Merlo-Sosa et al. [8] have studied the thermodynamic pyrolysis of gaseous dodecane in a RF plasma reactor using a mixture of Ar / He / \( \text{C}_{12}\text{H}_{26} \) and the composition of the different species in the equilibrium are shown in Figure 6.5. According to their results, the thermodynamic equilibrium reactions show the gas composition is rich in \( \text{H}_2 \), \( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \) below 500 K, but \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \) start forming only for temperatures higher than 500 K and 800 K, whereas in our case the gas temperature during Ar GAD plasma treatment of gaseous dodecane is measured \( T(\text{Ar})_{\text{gas}} = 340 \pm 5 \) K.
When humid argon plasma is used for the degradation of liquid dodecane, the yield is increased for a factor of ~ 3 compared with the dry argon plasma and that reflects also to the total concentration of gaseous products formed, as shown in Figure 6.6.

**Figure 6.5** Equilibrium Composition for the System Ar-He-C\textsubscript{12}H\textsubscript{26} in a RF plasma reactor at 101.3 kPa and H/C Ratio 2.16, taken from [8]

**Figure 6.6** Gaseous products concentration in the Ar/H\textsubscript{2}O GAD treatment (H\textsubscript{2}O = 2.3 ± 0.3 %) of a) liquid dodecane as a function of treatment time and in b) gaseous dodecane treatment (90 ppm)
The off-gas in this case is rich in dodecane, CO and CH₄. The dodecane concentration deriving from liquid dodecane evaporation is higher than that observed in case of dry Ar plasma. This could be related to a higher gas temperature in the reactor. The gas temperatures of the gaseous mixtures Ar/C₁₂H₂₆ and Ar/H₂O/C₁₂H₂₆ GAD plasma as measured by a thermocouple, have been given earlier in Chapter 4 as \( T_{\text{gas}} = 340 \pm 5 \text{ K} \) and \( T_{\text{gas}} = 375 \pm 5 \text{ K} \), respectively. This could affect both the evaporation, but also the diffusion of the reactants in the gas phase. All product concentrations in this case are stabilised after 25 min. The gaseous product selectivity is similar to these observed in the case of gaseous dodecane treatment following the overall sequence of CO > CH₄ > CO₂ > C₂H₄ > C₂H₂.

Optical diagnostics of Ar plasma admixtures were discussed earlier in Chapter 4. Optical measurements have been also obtained during the plasma-liquid treatment in both dry and humid conditions and Figure 6.7 presents the overall spectra in the different conditions for comparison.

**Figure 6.7** Optical emission spectra of a) dry Ar GAD plasma, b) dry Ar with 90 ppm dodecane admixture plasma, c) Ar plasma-liquid treatment of dodecane, d) humid argon plasma (H₂O = 2.3 ± 0.3%), e) Humid argon plasma with dodecane (90 ppm) and f) humid argon plasma-liquid treatment of dodecane. Spectral resolution is 0.13 nm and the intensity has been scaled for exposure time \( t = 10 \text{ ms} \) to account for the different exposure times used.
When a dry Ar plasma is used to treat liquid dodecane, the intensity of emission from C\textsubscript{2} and CH is increased by a factor of 2 compared to the treatment of gaseous dodecane. This is correlated with the gaseous products of C\textsubscript{2} hydrocarbons from liquid dodecane treatment, as their concentration is also double compared to the gaseous dodecane treatment. In humid conditions, the intensity of the OH (A→X) emission observed in humid argon plasma is decreased by a factor of 4 and a factor of 10 in case of the gaseous and liquid treatment of dodecane respectively. The decrease in the relative concentration of the OH (A→X) emission indicates that OH reacts with gaseous dodecane to form CO, CO\textsubscript{2} products. In case of the treatment of liquid dodecane, it is also possible that quenching reactions can occur in the liquid interface and OH radicals can diffuse to react with the bulk liquid.

Figure 6.8 shows the gaseous products concentration as a function of time during the N\textsubscript{2} GAD treatment at the liquid dodecane, compared with the concentration of gaseous products for gaseous dodecane treatment under the same conditions.

Figure 6.8 Gaseous products concentration in the N\textsubscript{2} GAD treatment of a) liquid dodecane as a function of treatment time and in b) gaseous dodecane treatment (90 ppm)

There are two main observations deriving from this figure. Firstly, there are differences in the gas chemistry between the Ar and N\textsubscript{2} plasma gas used for the plasma-liquid treatment. In case of Ar (Figure 6.4 earlier), the selectivity of the lighter hydrocarbons is CH\textsubscript{4} > C\textsubscript{2}H\textsubscript{4} > C\textsubscript{2}H\textsubscript{2} which changes to C\textsubscript{2}H\textsubscript{4} > C\textsubscript{2}H\textsubscript{2} > CH\textsubscript{4} in
case of N$_2$ plasma. This could be due to the generation of different reactive species in each case. As discussed earlier in Chapter 4, degradation of dodecane into the subsequent alkyl radicals in Ar plasma is based on electron impact and energy transfer reactions that can lead only to hydrocarbon end-products by recombination reactions. In N$_2$ plasma, reactions between N$_2$ metastables or N*, N radicals with dodecane and alkyl radicals in the discharge form finally HCN as the major product. The reason that CH$_4$ selectivity is lower in the N$_2$ plasma compared to the one observed in Ar plasma, is related to the fact that methyl radicals react much faster with N$_2^*$, N* and N to form HCN rather CH$_4$ by recombination with H atoms. Moreover, the increased reactivity and gaseous products concentration in case of N$_2$ plasma could be due to its elevated input power used resulting in a higher energy dissipated in the chemical reactions ($P$(N$_2$) = 200 W, $P$(Ar) = 120 W). This also leads to an elevated gas temperature in case of N$_2$ plasma that could favour the formation of unstable unsaturated hydrocarbons ($T$(N$_2$)$_{gas}$ = 480 ± 5 K, $T$(Ar)$_{gas}$ = 375 ± 5 K, Chapter 4).

A second interesting observation based on the experimental results described in Figure 6.8, is that the gas composition is different for the N$_2$ plasma treatment of gaseous and liquid dodecane. In the latter case, the total gas concentration has increased for a factor of ~ 4, but the composition is rich in HCN and the unsaturated hydrocarbons C$_2$H$_4$, C$_2$H$_2$ rather than HCN and CH$_4$ as seen in case of the N$_2$ gaseous dodecane treatment. One possible scenario is to consider only the gas phase reactions, where a higher concentration of gaseous dodecane exists in the gas caused by evaporation during the plasma-liquid treatment [C$_{12}$H$_{26}$] $\geq$ 150 ppm, instead of 90 ppm observed in case of the plasma treatment of gaseous dodecane. This could affect the density of the reactive species in the discharge and thus, the kinetics of the reactions towards the hydrocarbons as shown earlier in reactions R 6.1- 6.4. Another possible scenario is to consider that the gaseous products reactions selectivity has changed due to the plasma-liquid interactions and possible solvent effects.

Figure 6.9 shows the distribution of the gaseous products seen in case of N$_2$/H$_2$O GAD treatment of liquid and gaseous dodecane.
Figure 6.9 Gaseous products concentration in the N$_2$/H$_2$O GAD treatment (H$_2$O = 2.3 ± 0.3) of a) liquid dodecane as a function of treatment time and in b) gaseous dodecane treatment (90 ppm)

In these conditions, the degradation of liquid dodecane is enhanced as are also the overall concentrations of gaseous products. The off-gas is rich in CO and C$_2$H$_4$, while HCN is produced less in the oxidative environment formed by OH, O radicals in the humid discharge. The N$_2$/H$_2$O plasma treatment of gaseous or liquid dodecane forms the same products, however, the selectivity changes again from CH$_4$ > C$_2$H$_4$ > C$_2$H$_2$ to C$_2$H$_4$ > C$_2$H$_2$ > CH$_4$, as was also observed in case of dry N$_2$ plasma. This again shows that the gas chemistry is different and could be related to the plasma-liquid interactions. Furthermore, in case of the plasma-liquid treatment, smaller amounts of NO are formed compared to the gaseous dodecane treatment and in both cases no NO$_2$ or HNO$_2$ is observed. Moreover, it is interesting that the initial concentration of NO ~ 180 ppm is continuously decreasing until it stabilises at ~ 115 ppm at ≥ 15 min of treatment. This could be correlated to the behaviour of CO formation which is linearly increasing until it levels off at ~ 425 ppm after 20 min of treatment. During this time, competitive reactions of the OH, O and N radicals may occur with dodecane and the subsequent alkyl fragments diffused in the discharge, affecting the rate of CO, HCN and NO production, respectively. Moreover, a
possible scenario is that the reactions during treatment might be initially affected by diffusion mechanisms in the plasma-liquid interface, until they reach a steady state.

Optical emission spectra have been obtained during the N₂ plasma-liquid treatment of dodecane in both dry and humid conditions and they are compared with the spectra collected under the same conditions in the different gas admixtures plasma in Figure 6.10.

![Optical emission spectra](image)

**Figure 6.10** Optical emission spectra of a) dry N₂ GAD plasma, b) dry N₂ with 90 ppm dodecane admixture plasma, c) N₂ plasma-liquid treatment of dodecane, d) humid N₂ plasma (H₂O = 2.3 ± 0.3%), e) Humid N₂ plasma with dodecane (90 ppm) and f) humid N₂ plasma-liquid treatment of dodecane. Spectral resolution is 0.13 nm for 300-420 nm and 0.02 nm when different gratings were used in the range of 502-520 nm to enable the detection of C₂ line. In both cases the intensity has been scaled to account the different exposure times used.

The characteristic emission of the second positive N₂ C→B in the UV region commonly formed in N₂ discharges is not observed during the gaseous or liquid treatment of dodecane. In both cases, the spectra are dominated by the strong chemiluminescence of the CN B → X system observed in the violet, in correlation with the formation of HCN as the major end–product observed by FTIR. However,
no difference in the relative intensity of CN $B \rightarrow X$, but also of C$_2$ $a \rightarrow d$ is observed between the plasma-gas and liquid treatment.

The spectrum of the N$_2$/H$_2$O/C$_{12}$H$_{26}$ gaseous plasma has been discussed earlier in Chapter 4. What is remarkable is that in the corresponding spectrum in the plasma-liquid treatment the OH $A \rightarrow X$ emission is not observed for the same exposure time used. Quenching reactions with the liquid surface are likely to happen which could induce reactions in the liquid phase. Furthermore, in humid conditions C$_2$ $a \rightarrow d$ emission is only seen during the plasma-liquid treatment and the CN $B \rightarrow X$ intensity is increased, showing a possible relationship of their increased relative intensity to the increased concentration of HCN, C$_2$H$_4$ and C$_2$H$_2$ end-products in the gas phase.

6.3.3 The liquid analysis of the dodecane plasma-liquid batch treatment using Ar, N$_2$, Ar/H$_2$O or N$_2$/H$_2$O gliding arc discharge

Many researchers have studied the use of non-thermal plasma-liquid reforming of hydrocarbons oils for H$_2$ production including the use of corona discharge [9-13], dielectric barrier discharge [14-16] and gliding arc discharge [17, 18]. However, no attention has been given to the plasma-liquid interaction or the potential liquid chemistry taking place in the hydrocarbon oil. Some work can be found in literature related to plasma-liquid treatment of liquid hydrocarbons for product synthesis purposes, but low temperature and low pressure was used in order to minimise the vaporisation and gaseous phase reactions and the chemistry could be different compared to our warmer atmospheric pressure system [19-23].

In this section, analysis has been performed on the liquid samples collected after 60 min of plasma treatment of dodecane under Ar, N$_2$, Ar/H$_2$O or N$_2$/H$_2$O gliding arc plasma. It must be noted that soot was found in all liquid samples, even under the humid conditions experiments. XRD analysis of the soot formed during the gas phase experiments showed that it is amorphous carbon and no further analysis was performed in this case. Liquid samples of each case were analysed as crudes collected after treatment but also as polar fractions collected after column chromatography separation, by means of IR and GC-MS spectroscopy.
When IR spectroscopy was applied to analysis of the post-treatment crude samples, no liquid by-products could be identified. However, using a more sensitive technique such as GC-MS analysis, a better detection was achieved. Figure 6.11 presents the GC chromatograms of crude post treatment samples of each case, compared with the blank chromatogram of untreated dodecane.

![GC Chromatograms](image)

**Figure 6.11** Normalised GC chromatograms using of crude liquid samples in case of a no treatment, N\(_2\) plasma treatment, Ar plasma treatment, N\(_2\)/H\(_2\)O plasma treatment and Ar/H\(_2\)O plasma treatment of dodecane

The peak ratio analysis of the blank GC chromatogram showed that 0.83% impurities exist in dodecane before treatment. These are identified to be saturated alkanes such as decane (C\(_{10}\)H\(_{22}\)), undecane (C\(_{11}\)H\(_{24}\)), 1-methyl undecane (C\(_{12}\)H\(_{26}\)) and tridecane (C\(_{13}\)H\(_{28}\)). Peak ratio analysis of the sample after N\(_2\) plasma treatment shows that 0.08% liquid products are formed, after subtracting the blank impurities. These are identified as unsaturated hydrocarbons of decene (C\(_{10}\)H\(_{20}\)), undecene (C\(_{12}\)H\(_{22}\)), dodecene (C\(_{12}\)H\(_{24}\)), but also the formation of 1-hexadecanol (C\(_{16}\)H\(_{34}\)O) was observed. This is surprising for the case of dry N\(_2\), but we might suggest that it could be derived from low O\(_2\) or H\(_2\)O impurities existing in the feed gas (≤ 20 ppm), in the same way as low concentrations of CO are observed in the gas phase (Figure 6.8).
The analysis of the chromatogram of the Ar plasma-treated sample showed the formation of 0.21 % liquid products other than dodecane. Surprisingly, the products identified other than saturated hydrocarbons were mainly oxygenated products such as alcohols of decanol (C_{10}H_{22}O), isomers of dodecanol (C_{12}H_{26}O), isomers of C_{12}H_{24}O (could be dodecanone or dodecanal isomers), tridecanol (C_{13}H_{28}O) and hexadecanol (C_{16}H_{34}O). The same trend of products is also observed in case of Ar/H_{2}O plasma treatment but the concentration of liquid products other than dodecane is higher (0.64 %). In case of the N_{2}/H_{2}O plasma treatment of dodecane, the same oxygenated products are identified, however the abundance of the C_{12}H_{26}O alcohols is higher than the abundance of the C_{12}H_{24}O isomers and the concentration of the total liquid by-products in this case is lower at 0.2 %.

Polar fractions of the crude samples were collected after liquid column chromatography and subjected to IR analysis. In this case, absorption peaks of characteristic functional groups were detected as shown in Figure 6.12. In all cases, hexane solvent was used as background and was subtracted, as it was found to exist as impurity after separation.

![Figure 6.12 IR spectra of polar fractions of liquid samples after N_{2}, Ar, N_{2}/H_{2}O and Ar/H_{2}O plasma treatment of dodecane. Hexane spectrum was used as background](image-url)
The C-H stretching (~ 2800 cm\(^{-1}\)), and bending (~ 1380, 1430 cm\(^{-1}\)) modes are seen in all spectra. In the IR spectrum of N\(_2\) plasma-treated sample, the broad peak at ~ 3400 cm\(^{-1}\) belongs to the H-bonded O-H stretching mode and the peak of C-O stretching mode at ~ 1100 cm\(^{-1}\) is also detected, although they appear with very low intensity. Their observation indicates the existence of alcohols in the sample as was seen in the crude analysis, however no C=C bonds are detected relating to unsaturated hydrocarbons. It is possible that the latter ones could not be collected in the polar fraction due to their very low polarity compared with the oxygenated products. In case of the Ar treatment sample, O-H and C-O are also observed with higher intensity. Moreover, the carbonyl group stretching is also seen at ~ 1700 cm\(^{-1}\).

The spectrum of the N\(_2\)/H\(_2\)O plasma treated sample detects the same functional groups, however the shape of the broad peak at ~3400 cm\(^{-1}\) could be interpreted as an overlapping double band at the same region, characteristic of primary amines [24]. Moreover, a new peak at ~ 1260 cm\(^{-1}\) is detected, which could belong to unsaturated or cyclic C-O-C ether bonds [24]. The weak double band at ~ 1625 cm\(^{-1}\) and ~1550 cm\(^{-1}\) could be assigned to the aromatic ring C-H stretching, indicating low concentrations of aromatics. Similarly in the spectrum of Ar/H\(_2\)O treated sample, functional groups of OH, C-O, C=O and C-O-C are also observed. Additionally the double band at ~ 1625 cm\(^{-1}\), ~1550 cm\(^{-1}\) appears stronger in this case.

The polar fractions of the crude plasma post-treated samples were also subject to GC-MS analysis and the comparative chromatograms for each case are shown in Figure 6.13. In all cases, the formation of primary aliphatic alcohols is dominant and hexadecanol (C\(_{16}\)H\(_{34}\)O) especially is formed with the highest abundance. In the case of N\(_2\) plasma treatment, other alcohols identified are dodecanol (C\(_{12}\)H\(_{26}\)O), tridecanol (C\(_{13}\)H\(_{28}\)O) and tetradecanol (C\(_{14}\)H\(_{30}\)O), and also isomers of dodecanone (C\(_{12}\)H\(_{24}\)O). It must be noted these alcohols have very low abundance which might be the reason that they could not be identified in the crude analysis, with the exemption of C\(_{16}\)H\(_{34}\)O. Remarkably, the aromatic compound of triphenylmethanol (C\(_{19}\)H\(_{16}\)) has been also identified. It must be noted that the C\(_{10}-C_{12}\) aliphatic unsaturated hydrocarbons seen in the crude sample are most likely not contained in the polar fraction after separation. In case of Ar plasma treatment, in addition to the alcohols already mentioned before, pentadecanol (C\(_{15}\)H\(_{32}\)O) but also the aromatic alcohol 2,6-di-tert-butyl-4-methylphenol (C\(_{13}\)H\(_{24}\)O) is also identified. Furthermore, higher
Oxidation state products such as aldehydes or ketones seem to form in higher abundance in this case and among them nonanal (C\textsubscript{9}H\textsubscript{18}O) and decanal (C\textsubscript{10}H\textsubscript{20}O) are also observed. Several isomers of C\textsubscript{12}H\textsubscript{24}O have been observed among them 2-dodecanone and 4-dodecanone were identified.

**Figure 6.13** Normalised GC chromatograms of polar fractions of liquid samples after N\textsubscript{2}, Ar, N\textsubscript{2}/H\textsubscript{2}O and Ar/H\textsubscript{2}O plasma treatment of dodecane.

In case of the N\textsubscript{2}/H\textsubscript{2}O plasma treatment of dodecane, mainly aliphatic primary alcohols are formed, but surprisingly, the formation of a phthalate ester 6-methylheptyl2-(2-(heptyloxy)-2-oxoethyl)benzoate (C\textsubscript{24}H\textsubscript{38}O\textsubscript{4}) is also identified. It must be noted that phthalates are commonly considered as contaminants in routine GC-MS as they are used as plasticisers in the sample vials. However, the fact that the IR spectrum in this case presents evidence of aromatic rings and the =C-O-C bond, considered with the fact that no contamination is observed in repetitive blank samples, lead us to conclude that the phthalate is a liquid reaction by-product. In the analysis of Ar/H\textsubscript{2}O plasma treated sample shows that similar products are observed as in case of dry Ar, only in this case they are formed in much higher abundance. The isomeric products of C\textsubscript{12}H\textsubscript{24}O are the dominant products in this case. Their high abundance allows a better interpretation, showing that 2- dodecanone, 3- dodecanone and 4-dodecanone are all formed, as well as a cyclic ether, 2-isopentyl-5-
propylytetrahydrofuran. Moreover, aromatic alcohols such as triphenylmethanol (C\textsubscript{19}H\textsubscript{16}O) and 2,2,2-triphenylethanol (C\textsubscript{20}H\textsubscript{18}O) are also identified. A new ester of bis(3-ethylhexyl) adipate (C\textsubscript{22}H\textsubscript{42}O\textsubscript{4}) as well as the one seen in case of N\textsubscript{2}/H\textsubscript{2}O phthalate ester bis(6-methylheptyl) (C\textsubscript{24}H\textsubscript{38}O\textsubscript{4}) is also seen in low abundance.

6.3.4 Unravelling the liquid chemistry in the plasma-liquid treatment of dodecane

Our experiments and analysis have shown that the gliding arc plasma-liquid treatment of dodecane induces reactions in the liquid phase. This indicates that electron and reactive species formed in the discharge can be diffused in the liquid interface to initiate the decomposition of dodecane molecules. Stepwise fragmentation and radical reactions can then form light gaseous end-products, or heavier products, which latter ones are more likely to remain in the liquid phase. However, vaporisation phenomena cannot be neglected adding further complexity to the plasma-liquid interaction. The degree of vaporisation could be dependent on the gas temperature and energy provided to the discharge and it is possible to induce further reactions in the gas phase.

Results show that during the dry or humid N\textsubscript{2} plasma treatment of dodecane, the concentration of gaseous products is higher and the abundance of liquid products is lower compared to the Ar plasma conditions. During the dry or humid Ar plasma degradation of dodecane, the liquid chemistry is more active and can lead to higher oxidation products (aldehydes, ketones). This could be driven by their differences in input energy and temperature causing different degree of vaporisation and gas phase reactions.

A wide range of different end-products have been identified in the plasma post-treated dodecane. These fall into categories of alkanes, alkenes, aromatic hydrocarbons and different oxidation level products such as both aliphatic and aromatic alcohols, ethers, aldehydes, ketones and esters. Figure 6.13 summarises the major liquid products observed.
Electron impact reactions or hydrogen abstraction reactions from N, OH or O radicals formed in the discharge in different conditions can initiate the dodecane fragmentation leading to fragments varying from methyl radicals to undecyl radicals.

Recombination reactions between these radicals can lead to the formation of heavier alkanes as final products. In a dry N₂ or Ar plasma, a reducing environment rich in H atoms is expected and further hydrogen abstraction from alkyl radicals can lead to the formation of alkenes and molecular hydrogen, as shown in reaction R 6.5. Under humid conditions, the hydroxyl radical formed in the discharge by water dissociation can add to the alkyl radicals to form the respective alcohols (reaction R 6.6).

\[ \text{R 6.5} \]

\[
\begin{align*}
\text{C} & \text{C} + \text{H} \rightarrow \text{C} = \text{C} + \text{H}_2 \\
\end{align*}
\]

\[ \text{R 6.6} \]

\[
\begin{align*}
\text{C} & \text{C} + \text{OH} \rightarrow \text{C} - \text{C} - \text{OH} \\
\end{align*}
\]
Atomic oxygen also identified in humid conditions can add to alkyl radicals leading to alkoxy radicals which can then form alcohols if they are hydrogenated, aldehydes or ketones if dehydrogenated and ethers in they react further with another alkyl radical (reaction R 6.7).

\[
\begin{align*}
&\text{R}_1\text{CH-O}^- \quad \text{R}_1\text{CH-OR} \\
&\quad \text{H} \quad \text{R}_1\text{CH-OH} \\
&\quad \text{-H} \quad \text{R}_1\text{CH-R}_2
\end{align*}
\]

R 6.7

where \( \text{R}_1, \text{R}_2 \) could be alkyl radicals or hydrogen.

The formation of a cyclic ether like the hydrofuran shown in Figure 6.14, shows that intermediate products such as alcohols with a double bond in position 1,4 are possible, which can further react to form the cyclic ether as shown in reaction R 6.8.

\[
\begin{align*}
&\text{R-C=CH} \quad \text{R-C=CH} \quad \text{R-C=CH} \\
&\quad \text{OH} \quad \text{CO} \\
&\quad \text{R-C=CH} \\
&\quad \text{O} \quad \text{H} \\
&\quad \text{+H}
\end{align*}
\]

R 6.8

The formation of aromatic rings can occur after polymerisation reaction of acetylene, as shown in reaction R 6.9. However, no polyaromatics are observed which are commonly found in combustion systems [25].

\[
\begin{align*}
&\text{CH} \quad \text{C} \quad \text{CH} \\
&\quad \text{CH} \quad \text{H} \quad \text{H} \quad \text{H} \\
&\quad \text{CH} \quad \text{H} \\
&\quad \text{CH} \quad \text{H} \\
&\quad \text{H}
\end{align*}
\]

R6.9

Addition of \( \text{OH}, \text{O} \) radicals to benzene ring can form aromatic alcohols and subsequent oxidation can lead to the formation of benzoic acid or esters, which could be a precursor for the benzoate formation shown in Figure 6.14.
6.3.5 The gliding arc discharge treatment of recycling liquid dodecane under \( \text{Ar/H}_2\text{O} \) and \( \text{N}_2/\text{H}_2\text{O} \) plasma

The recycling dodecane plasma treatment has been investigated as a different approach in order to improve the degradation efficiency and \( \text{Ar/H}_2\text{O} \) and \( \text{N}_2/\text{H}_2\text{O} \) plasma were used. In this case, the injection of dodecane directly to the discharge area creates a direct plasma-liquid contact which is expected to increase the reaction surface and improve the degradation efficiency.

Table 6.2 compares the overall results in the plasma-liquid treatment of dodecane in the batch and recycling treatment method. In both \( \text{Ar/H}_2\text{O} \) and \( \text{N}_2/\text{H}_2\text{O} \) conditions, the recycling treatment has increased the total volume of oil treated by a factor of 4.9 and 4.2 respectively. Following this, both the gaseous and liquid products concentration is increased. The best degradation efficiency is noted in case of \( \text{N}_2/\text{H}_2\text{O} \) recycling treatment, where a total of 28.2 ml oil was removed after 1 h.

<table>
<thead>
<tr>
<th>GAD gas</th>
<th>Pin / W</th>
<th>oil removed / ml at t = 60 min</th>
<th>% liquid products treatment</th>
<th>end after gaseous products concentration / ppm at t = 60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch ( \text{Ar/H}_2\text{O} )</td>
<td>140</td>
<td>2.01</td>
<td>&lt; 0.64</td>
<td>712.4 ± 28.5</td>
</tr>
<tr>
<td>Batch ( \text{N}_2/\text{H}_2\text{O} )</td>
<td>220</td>
<td>6.63</td>
<td>&lt; 0.20</td>
<td>1546.9 ± 61.9</td>
</tr>
<tr>
<td>Recycling ( \text{Ar/H}_2\text{O} )</td>
<td>140</td>
<td>9.96</td>
<td>&lt; 1.1</td>
<td>960.3 ± 38.4</td>
</tr>
<tr>
<td>Recycling ( \text{N}_2/\text{H}_2\text{O} )</td>
<td>220</td>
<td>28.2</td>
<td>&lt; 0.5</td>
<td>5287.05 ± 206.2</td>
</tr>
</tbody>
</table>

Table 6.2 Summary of results of the GAD plasma-liquid degradation of dodecane using batch and recycling treatment. The total volume of oil removed is calculated after 1 hour of treatment. Initial volume of dodecane was 15 ml in the batch treatment and 60 ml in the recycling treatment. GC-MS analysis has been performed to quantify the amount of liquid by-products in the samples after the treatment.

A comparison of the gaseous end-products formation between the \( \text{Ar/H}_2\text{O} \) plasma batch and recycling plasma-liquid dodecane treatment is given in Figure 6.15. The degradation efficiency has been increased in the case of the recycling treatment, and the steady state concentration of CO, \( \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \) has been increased by a factor of \( \sim 2 \). Interestingly, the selectivity towards the end-products has also changed, and
instead of a CO/CH₄ rich off-gas during the batch treatment, the off-gas becomes rich in CO/C₂H₄ during the recycling and the concentration of C₂H₄ has increased by a factor of 15. Moreover, the concentration of gaseous dodecane is very low in the recycling treatment off-gas compared to that for the batch treatment. This is probably due to the direct reaction of plasma with dodecane which causes a faster degradation than that in the batch treatment.

Figure 6.15 Gaseous products comparison between Ar/H₂O GAD batch and recycling, Pin = 140W

Figure 6.15 shows the gaseous emissions from the dodecane plasma-liquid treatment in humid nitrogen comparing the batch with the recycling approach. The humid nitrogen plasma treatment of dodecane forms the same off-gases, however the composition of the off-gas changes. The degradation efficiency is again increased in the recycling treatment and the off-gas in this case is rich in C₂H₄/HCN rather than CO/C₂H₄ in the case of the batch treatment. Interestingly, the maximum concentration of C₂H₄ and HCN is increased by a factor of ~ 6 and ~ 10 respectively. Similar to Ar/H₂O plasma recycling treatment, the concentration of dodecane is again low indicating that recycling treatment causes a low degree of gasification and a faster degradation rate than the batch treatment.
Figure 6.16 Gaseous products comparison between N$_2$/H$_2$O GAD during 60 min of batch and recycling treatment, $P_{in} = 200$ W

During the recycling N$_2$/H$_2$O or Ar/H$_2$O plasma-liquid treatment of dodecane, liquid samples were collected at time intervals of 5, 20, 30, 40, 50 and 60 min, in order to characterise the by-product formation in the liquid during treatment time. In both conditions, the colour of the oil was turning gradually to yellow indicating the formation of liquid by-products. In addition, soot was also formed, in higher concentration in case of the N$_2$/H$_2$O treatment.

Figure 6.17 Crude samples of a) N$_2$/H$_2$O and b) Ar/H$_2$O plasma recycling treatment of dodecane at different treatment time up to 60 min
Moreover, it is interesting to note that the soot formation in case of N$_2$/H$_2$O increases significantly after 20 min, while in case of Ar/H$_2$O, no significant change is observed after the 10 min of treatment time. This could be correlated with the production rate of the gaseous products, where in Ar/H$_2$O they reach a steady state after 10 min, while in N$_2$/H$_2$O the concentration of HCN and C$_2$H$_4$ significantly increases after 20 min.

After filtration, the crude samples from 60 min of treatment were subjected to GC-MS analysis and using the peak ratio technique, the level of by-products mixed with untreated dodecane was estimated to be < 0.5 and < 1.1 % in case of N$_2$/H$_2$O and Ar/H$_2$O plasma, respectively. Figure 6.18 shows the respective chromatograms compared with the blank dodecane.

![Figure 6.18](image)

**Figure 6.18** Normalised GC chromatograms of liquid crude samples after N$_2$/H$_2$O and Ar/H$_2$O recycling plasma treatment of dodecane.

The liquid products identified in the crude samples after the N$_2$/H$_2$O plasma batch treatment of dodecane, are similar to those observed earlier in the case of the batch treatment. These are alkenes such as decene (C$_{10}$H$_{20}$), undecene (C$_{12}$H$_{22}$), alcohols such as tridecanol (C$_{13}$H$_{28}$O), tetradecanol (C$_{14}$H$_{30}$O), pentadecanol (C$_{15}$H$_{32}$O), hexadecanol (C$_{16}$H$_{34}$O) and triphehylmethanol (C$_{19}$H$_{16}$O). The aliphatic ester of bis(3-ethylhexyl) adipate (C$_{22}$H$_{42}$O$_4$) is also identified. These species are also seen in
case of the Ar/H$_2$O recycling treatment of dodecane, as well as some higher oxidation level products such as undecanal and isomers of C$_{12}$H$_{24}$O.

All the crude samples were subject to liquid column chromatography and polar fractions were collected for IR and GC-MS analysis. The IR spectra for each condition did not a significant difference, thus the samples at 60 min only are presented for comparison in Figure 6.19.

![Figure 6.19 IR spectra of polar fractions of liquid samples after N$_2$/H$_2$O and Ar/H$_2$O plasma recycling treatment of dodecane after 60 min](image)

The functional groups of the C-H stretching at ~ 2800 cm$^{-1}$ and bending at ~ 1380, 1430 cm$^{-1}$, C=O stretching at ~1730 cm$^{-1}$, and C-O stretching at ~1260, 1015 cm$^{-1}$ are detected in both spectra. The peak at ~1260 cm$^{-1}$ which lies at higher wavenumber and indicates a delocalised ether bond such as =C-O-C. In case of Ar/H$_2$O plasma sample spectrum, the polar functional groups have higher intensity compared to the one in case of the N$_2$/H$_2$O plasma. Moreover, only in case of Ar/H$_2$O, a weak band at 1595 cm$^{-1}$ indicates the existence of aromatic rings.

The liquid products identified by GC-MS in the samples taken at different time intervals did not change significantly, indicating that the treatment time had no major effect on the end-products formation. Figure 6.20 shows the polar fraction chromatograms of the 5, 30 and 60 min samples taken during the N$_2$/H$_2$O and Ar/H$_2$O GAD dodecane recycling treatment.
Figure 6.20 Normalised GC chromatograms of polar fractions of samples taken during the N\textsubscript{2}/H\textsubscript{2}O and Ar/H\textsubscript{2}O GAD recycling treatment of dodecane at 5, 30 and 60 min.

Major products formed in all cases are decanol, tetradecanol, pentadecanol, hexadecanol, the aliphatic ester of bis(3-ethylhexyl) adipate and the bis(6-methylheptyl) phthalate ester. In both N\textsubscript{2}/H\textsubscript{2}O and Ar/H\textsubscript{2}O plasma treatment at 5 min, alcohol products seem to have overall high abundance, while the products of esters seem to be more important in longer treatment time up to 60 min. This could indicate that light molecules formed initially in the treated dodecane can subsequently lead to heavier higher oxidation state molecules.

### 6.4 Summary and Conclusions

The plasma degradation of liquid dodecane has been studied using gliding arc discharge, as a batch and recycling treatment. Results show that there are differences between the gas chemistry during the plasma-liquid treatment of dodecane and the treatment of gaseous dodecane. The selectivity of the gaseous products can change, due to the plasma-liquid interactions. The reactive species formed in plasma can
diffuse into the liquid interface to initiate reactions which could mainly breakdown
dodecane to lighter gaseous products but also form heavier products remaining in the
bulk liquid. Cascaded liquid-based chemistry presents a scenario largely dominated
by molecular potentials and reaction activation energies. This differs from the gas-
phase chemistry in plasmas where the species and in particular charged species
behave as isolated entities and the reactions are mainly determined by their kinetic
energies.

In the case of batch treatment, Ar and N\textsubscript{2} have been studied as plasma gases in both
dry and humid conditions. Humidity increases the oil degradation for both Ar and N\textsubscript{2}
plasma by increasing the production rate of gaseous products and also the
concentration of the products in the liquid. The best degradation efficiency is noted
in the case of N\textsubscript{2}/H\textsubscript{2}O causing a 44.2 % reduction in the oil volume after 1 h of
treatment. The Ar/H\textsubscript{2}O plasma treatment of dodecane creates a slower rate of
gaseous-product formation, but a higher abundance of liquid end-products. It is
suggested that the higher energy dissipated in the N\textsubscript{2} plasma and the elevated gas
temperature can affect the degradation mechanism chemically, by increasing the
reactivity, but also physically, causing a higher degree of vaporisation.

A wide range of liquid products have been identified such as heavier saturated or
unsaturated hydrocarbons both aliphatic and aromatic, and oxidation products mainly
alcohols, but also aldehydes, ketones and esters. In the case of Ar plasma, the
abundance of aldehydes and ketones is higher than alcohols, in contrast to the N\textsubscript{2}
plasma liquid products, where alcohols abundance is higher. In the latter case, it is
possible that the oxidation reaction rates are decreased, due to slower diffusion rate
of the reactive species caused by dynamic vaporisation.

The recycling treatment of dodecane creates a direct plasma-liquid treatment, which
increases the reactivity and changes the selectivities of the gaseous products.
Compared to the batch treatment results, the degradation efficiency for both Ar/H\textsubscript{2}O
and N\textsubscript{2}/H\textsubscript{2}O plasma is increased by a factor of 4.2 and 4.9, respectively. Liquid
analysis of samples from different treatment times shows that similar products are
formed, with no significant change during the treatment time.

Overall, the study of gliding arc plasma-liquid treatment of dodecane shows
promising results for the application on organic liquid waste. Among Ar and N\textsubscript{2} in
both dry and humid conditions, humid N\textsubscript{2} plasma appears as the favoured condition which allows higher degradation rate and destroys a larger volume of oil, leaving lower concentration of residual end-products in the liquid. On the other hand, using dry or humid Ar plasma creates lower gasification and promotes the liquid chemistry. This would be interesting to be further explored for selective liquid treatment applications. In both cases, our results show that a potential recycling treatment would increase significantly the rate of the process.

### 6.5 References


Chapter 7

7. Thesis summary, conclusions and future work

7.1 Thesis summary and conclusions

This thesis has studied the low-temperature atmospheric pressure plasma as a potential technological application for the degradation of organic liquid waste found in nuclear industries. Odourless kerosene and dodecane have been used as simulants, as they are mostly found among spent solvents in nuclear industries. The study has been approached initially by investigating the degradation of oil in gas phase only, using a BaTiO$_3$ packed bed plasma reactor and a gliding arc discharge reactor. Kerosene has showed similar degradation behaviour to dodecane and the latter one was chosen as a surrogate to allow quantitative analysis. The dodecane plasma degradation efficiency and the distribution of end-gaseous products have been studied under these two reactors in different gas compositions. Overall, there are differences in dodecane degradation gas chemistry between the packed bed and the gliding arc plasma and postulated mechanisms are presented for each condition. Gliding arc discharge demonstrates higher degradation efficiency and it is mainly used for the plasma-liquid treatment.

The plasma-liquid dodecane treatment is firstly studied using argon dielectric barrier discharge. Using different reactor configuration, humidified plasma gas or increased operating temperature affects the discharge characteristics and thus the degradation efficiency. Using the DBD plasma “in contact” with dodecane, more energy is dissipated in the discharge giving a more distinct filamentary character. When DBD plasma is generated inside dodecane with the assistance of argon bubbles feed, discharge can occur in the gas inside the bubble or as a surface discharge in the bubble-liquid interface. Best degradation rate is shown in dry argon plasma “in contact” with dodecane at 100 °C. However, most energy efficient treatment occurs in case of humidified argon bubble plasma at 25 °C.

The study of the liquid dodecane degradation is expanded by using the gliding arc discharge, as a batch and recycling treatment. Nitrogen and argon plasma gases have been used in both dry and humid conditions for the batch treatment of dodecane.
Results show that there are differences between the gas chemistry during the plasma-liquid treatment of dodecane and the treatment of gaseous dodecane. The selectivity of the gaseous products can change, due to the plasma-liquid interactions. The reactive species formed in plasma can diffuse into the liquid interface to initiate reactions which could mainly breakdown dodecane to lighter gaseous products but also form heavier products remaining in the bulk liquid. Overall, humid N\textsubscript{2} plasma appears as the favoured condition which allows higher degradation rate and destroys a larger volume of oil, leaving lower concentration of residual end-products in the liquid. On the other hand, using dry or humid Ar plasma creates lower gasification and promotes the liquid chemistry. This could be useful if tailored for specific applications, for example in cases that minimum vaporisation is desirable to convert liquid waste into solid parts for transport and disposal. In both cases, our results show that a potential recycling treatment would increase significantly the rate of the process. Future work on these directions can contribute to the development of a promising technology for the organic waste treatment.

**7.2 Recommendations for future work**

The key factor to develop an efficient plasma-chemical process is to understand the mechanism, in order to be able to control, optimise and tailor the process. The plasma-liquid treatment of organics is a complicated mechanism that has been discussed in this thesis, but there are yet many discoveries to unravel. Optical emission spectroscopy is a strong plasma diagnostics tool that was used in this work and gave very interesting observations for the gliding arc plasma processing during gaseous or liquid treatment of dodecane. This work could be extended to space and time resolved spectroscopy, which would enable diagnostics of the intermediate excited species in different positions and during the treatment time. In addition, the advanced optical diagnostics such as laser-induced fluorescence (LIF) techniques would allow the calculation of densities of intermediate species which would add valuable information. The study of the plasma-liquid mechanism could be also enhanced by using further diagnostics in the liquid phase. Electron paramagnetic resonance (EPR) could be applied to detect the radicals in the liquid and give useful information for the chemistry in the liquid interface. Optimisation of the gas phase analysis is also needed to detect a full range of the gaseous end-products. In addition
to IR detection, a properly set-up GC system would also allow the identification of a wider range of hydrocarbons, as well as other gases including H₂, which would help to elucidate the waste destruction mechanism. This also opens research directions to potential optimisation of the plasma organic waste conversion towards high selectivities of H₂ or other valuable products, that would benefit the market.

Further work is also needed in terms of optimising the plasma-liquid waste treatment parameters in order to improve the efficiency of the destruction. This work has shown promising results under N₂/H₂O plasma conditions, however the influence of different gas compositions, could be also studied. Knowing that air is commonly supplied in industrial sites, it should be also investigated for the plasma-liquid processing. Preliminary experiments in this work has shown promising results, however difficulties in the analysis from the excess vaporisation and water production, did not allow a complete study and someone should consider this challenges in future research. Mixtures of Ar/O₂ plasma could be also tested, as it could improve the waste oxidation, avoiding at the same time the undesirable NOx formation occurring in air plasma.

This work has also shown that the recycling treatment has increased the efficiency of the plasma-liquid degradation, compared to the batch treatment. This work could be extended on investigating injection methods to further the efficiency of the process. Injecting the liquid from the top or optimising the injection nozzle to form aerosols could further increase the surface reaction area and thus, the degradation rate.
Energy Conversion Table

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<th>Hz</th>
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*Adapted from NIST Physical Measurement Laboratory [1].

Appendix II: Power measurement in a DBD plasma reactor

This text is adapted from Prof. Peter A. Gorry technical notes and also given in former group thesis of Dr. Helen J. Gallon [5]

Experimental set up

![Circuit for measuring the discharge power of a plasma reactor](image)

**Figure 1** Circuit for measuring the discharge power of a plasma reactor

Figure 1 shows a typical circuit layout of DBD reactor adapted from [1]. The power can be determined by measuring the high voltage $U(t)$ and either the current flowing through the resistor $R$, or the charge on capacitor $C$. A switch is used to select which method is used.

**Current method**

This is the simplest to understand and we follow here the formalism of Feng and Castle [2]. The instantaneous power in the reactor is simply given by

$$p(t) = U(t) \cdot i(t)$$

(1)

where $U(t)$ is the high voltage (HV) on the reactor and $i(t)$ is the current flowing through the reactor (and resistor $R$). The current $i(t)$ is simply found from
\[ i(t) = \frac{V_R(t)}{R} \]  

(2)

where \( V_R(t) \) is the voltage across \( R \).

The average power over a single cycle of the high voltage, period \( T \), is given by

\[
P = \frac{1}{T} \int_{t_0-T/2}^{t_0+T/2} P(t) dt = \frac{1}{T} \int_{t_0-T/2}^{t_0+T/2} U(t) \cdot i(t) dt = \frac{1}{T} \int_{t_0-T/2}^{t_0+T/2} \frac{U(t) \cdot V_R(t)}{R} dt
\]

(3)

where \( t_0 \) is the centre of the cycle.

The problem with this method is that the plasma itself is a series of microdischarges of short duration (typically \( \leq 2 \) ns) and the current waveform need to capture this information accurately. This in turn requires a very high bandwidth (and expensive) sampling oscilloscope [3].

![Figure 2 Reactor voltage, \( U(t) \), and current \( i(t) \).](image)

In practice, even with such an instrument, the overlap of spikes makes the use of Eqn 3 very difficult to perform accurately.
Lissajous method

This method was introduced by Manley [4] in 1943. In the absence of any way of accurately recording the microdischarge current spikes the alternative is to replace the probe resistor $R$ by a probe capacitor $C$. The capacitor accumulates a charge from the current flowing through the reactor and this can be determined by measuring the voltage on the capacitor $V_c$.

$$ q(t) = C \cdot V_c(t) $$

(4)

The advantage is that the charge is stored in the capacitor and does not require a fast transient digitiser to record it. The energy per cycle, $W$, can be found from Eqn 3 by multiplying by $T$.

$$ W = \int_{t_k-T/2}^{t_k+T/2} U(t) \cdot i(t) dt $$

(5)

The current flowing through the measuring capacitor, $C$, is given by

$$ i(t) = \frac{dq}{dt} = C \frac{dV_c}{dt} $$

(6)

hence we have

$$ q(t) = C \cdot V_c(t) $$

(7)

and the energy per cycle becomes

$$ W = \int_{t_k-T/2}^{t_k+T/2} U(t) \cdot C \cdot V_c(t) dt = \int_{t_k-T/2}^{t_k+T/2} U(t) \cdot dq(t) $$

(8)

If we record $U(t)$ and $q(t)$ as a series of $n$ regularly sampled points over one cycle we can approximate Eqn 8 by a summation, using trapezoidal integration, as

$$ W \approx \sum_{k=1}^{n} \left( \frac{U_{k+1} + U_k}{2} \right) (q_{k+1} - q_k) $$

(9)

We now simply have to multiply by the number of cycles per second to get the power in the reactor. So, if the voltage $U$ has a frequency, $f$, where $f = 1/T$, we have

$$ P = W \cdot f = f \sum_{k=1}^{n} \left( \frac{U_{k+1} + U_k}{2} \right) (q_{k+1} - q_k) $$

(10)
The integrals in Equations 8 and 10 represent the area of a U-q Lissajous figure.

\[ \frac{1}{C_T} = \frac{1}{C_g} + \frac{1}{C_d} \]  

(11)

During the discharge on period the current depend on the dielectric barrier capacitance alone, \( C_d \), and during the off period it depends on the total capacitance, \( C_T \). We have

\[ \frac{dq}{dU} = C_T = \frac{C_g C_d}{C_g + C_d} \] Discharge off

\[ \frac{dq}{dU} = C_d \] Discharge on

**References**


Appendix III: Publications and conferences

Publications


Conference Presentations


• Maria Prantsidou, J. Christopher Whitehead, “Non thermal plasma degradation of spent solvents and oils using a gliding arc discharge reactor”. RSC ChemCareers, Postgraduate Competition London, November 2011, poster

• Maria Prantsidou, J. Christopher Whitehead, "Non-thermal Plasma Degradation of Spent Oils", Annual meeting of Institute of Electrostatics Japan (IESJ), University of Science, Tokyo, Japan , Sept 2011, talk.


• Maria Prantsidou, J. Christopher Whitehead, "Non-thermal plasma destruction of oils in the vapour phase", 8th Technological plasma Workshop (TPW-8), Bristol UK, January 2011, poster.