Swansea University
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MASTER'S THESIS

Recycling heat into useful energy for green hydrogen production & Producing carbon nanotubes from clothing waste

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Abstract- This thesis investigates hydrogen production through electrolysis, explores heat recovery mechanisms and searches innovative methods to develop materials that enable technology to become more sustainable.

The latest forms of energy transport and storage are studied, alongside methods to improve the efficiency of the energy sector, as well as the advantages of hydrogen to support the energy industry.

To enable sustainable solutions, approaches are presented to enhance efficiencies while considering polluting impacts. The thesis delves in the study of hydrogen as an energy vector and storage method. It offers methods to produce hydrogen efficiently to promote green solutions with the aid of energy recovery systems. In addition, carbon nanotubes (CNTs) were researched, to take advantage of their unique physical properties and aid heat recovery technology.

This research aims to find methods to generate economical CNTs to increase their availability for energy engineering projects. To do so, experiments are carried out to generate CNTs sustainably from waste plastic. This effort aims to create new methods to recycle waste.

In essence, this thesis studies methods to tackle the increasingly demand for sustainable energy, while also proposing ways to reduce manmade pollution and incentivising a circular economy.

Methods for heat recovery and conversion have been suggested, and new CNT material produced from recycled materials has been synthesised and characterised.

Key findings demonstrate that electrolysis systems combined with heat recovery systems can improve an electrolyser's efficiency from 75% to as much as 83%. In addition, the CNTs synthesised from waste plastics proved to be a method to reuse waste while also producing CNTs with desirable structural properties. This finding therefore demonstrates that CNTs can be suitable to improve heat exchange systems while being produced sustainably.

Keywords: CNTs, energy storage, hydrogen, heat recovery systems, industry, sustainable economy

Declarations and Statements

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

Signed..[redacted]

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This thesis is the result of my own investigations, except where otherwise stated. Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

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I hereby give consent for my thesis, if accepted, to be available for photocopying and for interlibrary loan, and for the title and summary to be made available to outside organisations.

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The University's ethical procedures have been followed and, where appropriate, that ethical approval has been granted.

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Abbreviations	Definitions
3D	3 Dimensions
AC	Alternating current
AWE	Alkaline water electrolyser
CNF	Carbon nanofibers
CNH	Carbon nanohorns
CNTs	Carbon nanotubes
Co	Cobalt
COP	Coefficient of performance
CR	Compression ratio
CVD	Chemical vapour deposition
DC	Direct current
DIB	Dual-ion Batteries
EPS	Expanded polystyrene
ESOIe	Energy stored on investment
EU	European Union
eV	electronvolt
GO	Gaphene oxide
HOPG	Pyrolytic graphite
HP	Heat pumps
HTD	High temperature difference
IFM	Intermediate frequency mode
IMM	Inverted metamorphic multifuncion cells
KCS	Kalina cycle
kWh	Kilowatt hour
LCA	Life cycle assessments
LDPE	Low density polyethylene
Li	Lithium
Li-ion	Lithium ion
LIR	Liquid injector reactor
LTD	Low temperature difference
LWD	Long working distance
MOF	Organic framework materials
MWNT	Multiwall nanotube
NC	Nanocube
ND	Nanodiamonds
NGO	Non-governmental organisation
Ni/MH	Nickel metal hydride
NT	Nanotube
OFC	Organic flash cycle
ORC	Organic rankine cycle
PEG	Pyroelectric generators
PEM	Proton exchange membrane
PET	Polyethylene terephthalate
PFC	Power flash cycle
PHE	Plate heat exchangers

PV	Photovoltaic
Q	Heat exchange
RBM	Radial breathing modes
SEM	Scanning electron microscope
SiO_2	Silicon dioxide
SMR	Steam methane reforming
SSBs	Solid state batteries
SWNT	Single wall nanotube
T_C	Constant temperature
T_h	high temperature
T_l	Low temperature
TEG	Thermoelectric generator
TGA	Thermogravimetric analysis
USA	United States of America
W	Net work
ZT	Thermoelectric figure of merit
ZWI	Zero Waste Index

1. REVIEW ON ENERGY STORAGE AND CIRCULAR ECONOMY INNOVATIONS

1.1. Introduction

This chapter studies the applications of hydrogen technology as a method to store energy. To obtain an integral picture of the available methods to aid energy storage, a review is completed of the most popular technologies being used to manage the increase of energy demand. Therefore, various processes are studied to improve energy management, including batteries, hydrogen, and nanomaterials. Moreover, to find sustainable solutions to improve energy storage systems, this chapter studies methods to produce new materials from waste, including high performance nanomaterials.

Multiple methods are suggested to reuse waste and reduce global mining, by incentivising recycling and a circular economy. The importance of new materials is presented and examples of technology that benefit from them are shown through the chapter. Particularly the physical and chemical properties that nanomaterials offer.

Since the origin of communities, people have searched for better methods to control energy and matter. From making fire and metals to computerising buildings and fusing matter, humanity has not stopped developing ways to manipulate the environment. Now the world faces new challenges due to the increasing scale at which humans are manufacturing and consuming. This now makes us responsible for the alteration of the environment globally, which will not only affect the environment, but also our next generation's health and prosperity. Meeting the increasing demands of energy and materials while reducing the carbon footprint can only be achieved reimagining current technology. Here, efficiency and circular economies are key to avoid an exponential increase in material and energy waste.

This thesis does a study on the materials and the energy that is currently being wasted. It suggests alternative methods to obtain, transport and store energy with less inefficiencies. This would decrease the demand of electricity and our carbon footprint. In addition, this chapter indicates how consumed materials have key properties that can be capitalised but are wasted instead [1].

1.2. Energy waste

It has been proven that the increase in CO_2 and other greenhouse gas production of humans has caused an effect on the ratio of gases in the atmosphere, causing global warming [2]. Therefore, reducing CO_2 production is an urgency. It is the only way to sustain the world's ecosystem as well and humanity's growth. To do so, an analysis must be done to find the main CO_2 emitters.

From universal data, it is known that over 33% of all CO_2 emissions is caused by electricity production [3]. This is of no surprise when we think of the increase in global reliance on power sources for society's commodities as well as productions of any kind. Therefore, tackling this CO_2 source will have a big impact to the sustainability of the atmosphere.

The foremost reason why electricity causes large amounts of CO_2 is the usage of coal and gas. The world's supply of electricity is made 41% from coal and 22% from gas. Countries like China and India intend to annually increase their energy consumption by over 2% and 5% respectively to reach their production plans [4]. This development cannot be stopped; therefore, alternatives must be analysed to generate energy more efficiently, to reduce the energy production rate.

1.2.1. *Encouraging new sources of energy*

The production of electricity must change categorically to avoid environmental damages which will cause economic, political, and humanitarian crisis worldwide. To do so, renewable energies must be the main productors of electrical energy. As renewable energies do not burn hydrocarbons, they provide a source of energy which doesn't directly emit greenhouse gases, while they also provide energy from sources that are not finite [5].

In an ideal world the solution would simply be to substitute current non-renewable methods of electrical production with eco-friendly ones. However, renewable sources have a capped efficiency with current technology. Major obstacles in these systems don't allow renewable energy to be the main source. For this reason, new systems must be brainstormed to tackle this issue. Solar panels for example have a limit in their efficiency, as more than 50% of the applied energy on a photovoltaic (PV) cell is lost, either due to thermalization, or due to photons not being able to be absorbed [6]. For PVs to reach overall efficiencies higher than 30%, new approaches must be designed. For example, to absorb different wavelengths in the electromagnetic spectrum, more layers can be applied. Currently some semiconductors are used to absorb most of the energy from the excited electron.

Research in new materials allow more ideas to be put into practice. For example, being able to absorb more light into the PV is now possible thanks to new materials on the front layer which restrict light from deflecting [6]. Other examples in this field are nanomaterials and new semiconductor materials which are improving further the efficiency of parts of the cells. Improving the semiconductors' conductivity by decreasing the energy gap required to release an electron would improve the photovoltaic panel [6].

Another way of incentivising renewables is applying efforts to generate PVs to be economically feasible for industries and households. House PVs decrease the demand on the power grid, and even occasionally supports the grid when an electrical surplus is produced.

In addition to the inefficient production of renewable energy, the generated electricity must be stored for a reliable electrical supply. Electrical storage is also inefficient, particularly under extreme climates and frequent charging cycles. Therefore, another key factor to improve renewable production of PVs is improving the energy management of the electrical output. This is why technology like hydrogen as an energy storage enables renewable energy production.

On an interesting note, observations have been caried out on bacteria and algae showing a photon-to-charge conversion efficiency close to 100% under certain conditions [7]. The fact that nature can convert solar energy into productive energy so efficiently shows that there is room for improvement, but more research must be incentivised.

1.2.2. *Managing energy efficiently*

As mentioned before, the rapid growth of population as well as its standard of living is generating unprecedented energy demands. To avoid an increase in rate of production, efficient methods to avoid energy waste must be implemented at large scale. For example, in conventional coal power plants, less than 50% of energy is transformed to electricity. This means that over 50% of energy is wasted in heat. Evidently, this leads to global warming and environmental disorder [1]. For this reason, heat recovery systems are gaining importance due to the massive losses in heat in most mechanical or chemical processes [8]. In coal power plants, being able to recover energy waste with double cycles have already shown to improve efficiency significantly [1].

Thermal inefficiencies also affect energy storage systems. Storing energy efficiently is key to supply the population with cleaner energy. However, these storages also face other restraints. For example, batteries must store energy for long periods of time in non-optimal environments. They must also be able to provide a stable charging cycle efficiency after many uses. There are currently several methods to store energy, but they withstand several challenges.

Batteries are a key element on the grid. They are needed to constantly generate stable supplies of electricity. In addition, batteries are key to electrify systems such as transport and heating, which subsequently can lead to zero emissions systems once power sources become renewable. However, to rely on only electricity as the main power source, batteries must be further developed to be more cost effective, have a larger lifespan and generate less environmental hazards after its use.

1.2.2.1. Stationary batteries

Stationary batteries are the biggest energy storages used by industries that do not require light batteries. For these industries, the key value to optimise is the cost per unit of energy ($/kWh) [9]. To obtain an optimal value, elements must first be analysed and compared by cost and safety.

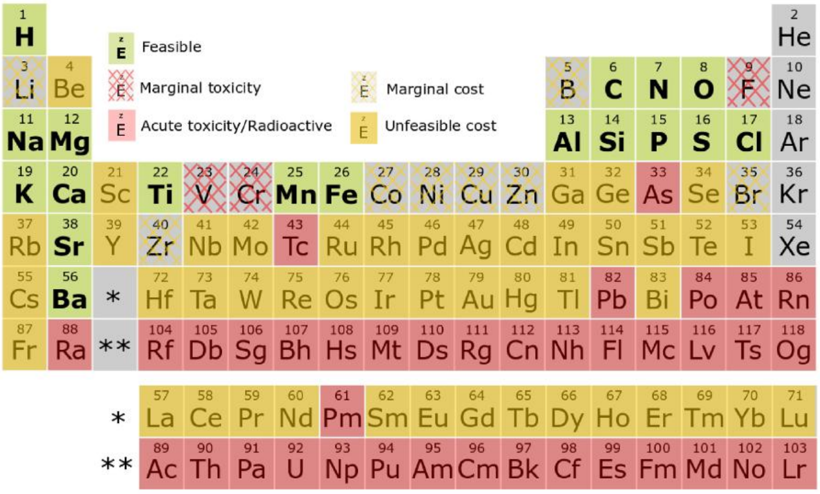


Figure 1 The periodic table for cheap and safe materials to be used in batteries. [10]

Dual-ion batteries (DIBs) are an example of alternative technology to alkali metal ion batteries, with environmentally benign materials as well as being inexpensive. They possess a unique working mechanism where ions intercalate simultaneously between anodes. DIBs do this with carbon-based anodes and PF_6^- to move away from Lithium usage [11].

Each battery has a different set of advantages and disadvantages for a desired voltage and lifespan, therefore knowing when to use each is key to maximise efficiency. Commercial Li-ion batteries for example, have a limited energy density which in stationary systems isn't necessarily a problem. On the other hand, they have a highly efficient reversibility, and its cycles are stable. This is achieved by using graphite and $LiCoO_2$ as electrodes [12]. As it can be seen in Figure 1, Co has marginal costs due to its availability. Therefore, using this element is a constraint to the environment and to the cost of the battery.

Substituting materials are a solution to replace scarce elements. To achieve similar performances, cheaper and benign elements have been analysed to synthesise new materials. That is the case of the substitution of Cobalt in $LiCoO_2$ with iron and phosphorus, forming $LiFePO_4$. Similarly, as many variants of DIBs involve Li, it is important to find replacements to avoid overmining this metal. Metal ions like Al^{3+}, K^+, Na^+ and Ca^{2+} are emerging substitutions that provide safety, durability, and environmental sustainability.

Moreover, developing the production of kWh increases the cost of stationary batteries. Therefore, a different approach to increase performance could be to ease mass manufacturing and lifespan of batteries. As weight increase is not a main problem, it can be sacrificed to improve other parameters. This means that physical systems added to increase efficiency provides more advantages than disadvantages. This idea is analysed in depth in the following chapters for the generation of green hydrogen.

To store chemical energy in the form of hydrogen, metal hydrides provide the most volumetric energy density. This is useful in applications where space is restricted, and weight is not an inconvenience. Metal hydrides offer high volumetric density because it contains materials that adsorb hydrogen particles close together. This means that high pressure and low temperatures are not needed to compress hydrogen like H_2 tanks [13].

The two main disadvantages of metal hydrides are the additional time required to charge hydrogen, and the energy required to remove the bonds between the hydrogen and the metal. Here, new materials and systems are improving the efficiency of metal hydrides.

For instance, nanomaterials like CNTs improve thermodynamic processes, like the desorption kinetics, which accelerates hydrogen discharge rates. CNTs also improve the thermal stability of the storage parts and even have the capacity to adsorb hydrogen in case of structural imperfections [14]. This avoids hydrogen embrittlement, which occurs when hydrogen, due to its small size, penetrates some materials and fractures them [15].

In addition, to tackle the energy requirement to release hydrogen, heat management is used. This is another example of systems which benefit overall efficiency which decreases energy waste. The system consists of recovering the waste heat from exothermal reactions and releasing in under highly endothermal reaction, to avoid drastic temperature changes. Here, high performance materials like CNTs have been used for high thermal conductivity. These systems essentially eliminate the need for additional energy requirements [16].

1.2.2.2. Mobile batteries

In sectors like the aeronautical industry the constraints of current mobile batteries are easily detected. The reasons why aircrafts cannot yet become electric is due to the weight, expense, and hazards of batteries.

The energy density per price unit of batteries calculated as $\left(\frac{\frac{\$}{kWh}}{kg}\right)$ provides an appropriate method to analyse the key variants to improve [10]. To achieve a good value, each component in a battery must be analysed, them being the anode and cathode, the current collectors where these may sit on, the electrolyte to transport ions and a separator for safety and durability.

The main options to improve those parts are the replacement of materials and the addition of high-performance materials to generate smaller batteries with equal performance.

Solid-state batteries (SSBs) are a great example of a material replacement solution. The modification of the electrolyte structure consists in changing the electrolyte from liquid to solid, transferring ions at a higher rate ($> 1\ \mathrm{mS} \cdot \mathrm{cm}^{-1}$ for halide electrolytes [17]). This allows for faster charging and discharging, as well as longer lifespans. Additionally, they can be made in a variety of shapes and sizes, making them more versatile than traditional batteries.

The main reason why SSBs are safer is because the electrolyte does not leak when fractured. However, having a solid electrolyte can result to the battery achieving higher temperatures, which provides a highly flammable environment if materials around the battery are susceptible to high temperatures [18]. In addition, the pack must seal the battery from the ambient environment as SSBs can produce toxic H_2S if the exterior encounters the inside of the battery. Therefore, to be able to implement this technology, isolating and temperature control systems must be applied. This can be done with appropriate battery packs and heat capturing devices.

As previously shown in $\left(\frac{\frac{\$}{kWh}}{kg}\right)$, the price variant is key. SSBs have not yet been able to be mass produced at competitive prices. This is due to the manufacturing process required and price of solid electrolytes. The main constraints are the chemistry between solids instead of solid-liquid and the manufacturing of thin products.

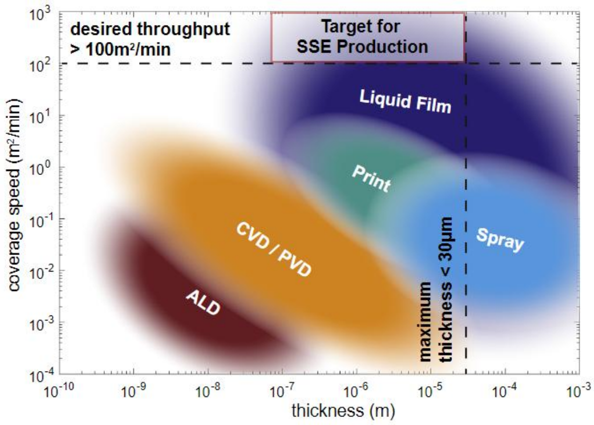


Figure 2 Manufacturing techniques comparing speed of production and thickness of the product [19]

SSBs electrodes and electrolytes must be thin (less than 30 mm) and produced at high throughput (over 100 m^2/min). As shown in figure 2, manufacturing processes are limited. Current manufacturing processes like vapour phase deposition, can provide thin films in a roll-to-roll configuration in a non-efficient manner.

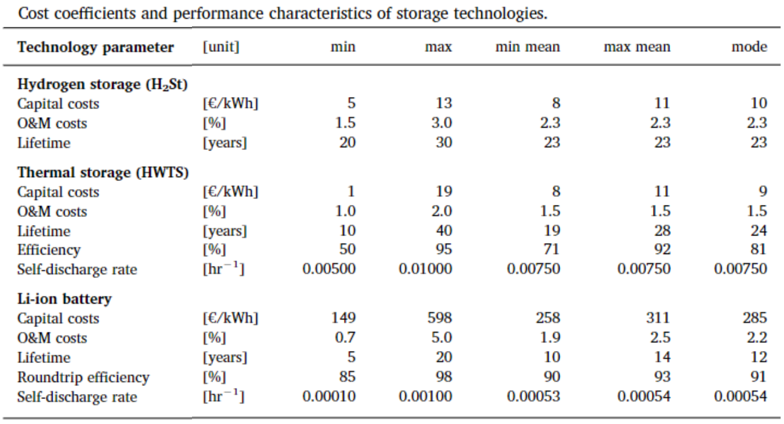
Curtain coating is a new form of wet coating where an electrolyte and cathode slurry are pumped into a roll-to-roll process in conjunction with drying units, creating a solid-state electrolyte composite [19]. Introducing new processes that are compatible with existing ones is important as offering new processes with existing infrastructure accelerate the development of SSBs.

Other essential research to aid mobile batteries is the addition of high-performing and ultralight materials. Nanomaterials like CNTs have shown to increase the electrical and mechanical properties of positive electrodes in Ni/MH rechargeable batteries, also increasing the cycle stability, discharge voltage and specific capacity [20]. Carbon nanofibers (CNF) and carbon nanotubes (CNT) have also been studied to replace entirely current collectors. As metal is eliminated, the 5 basic layers of collectors are reduced to 3, by merging the current collector with the active layer of the electrode. In addition, carbon-based layers allow manufacturers to 3D-print most components, which would avoid the mechanical lay-down of foils [21].

1.2.2.3. Hydrogen Storage

An interesting approach to store excess energy is hydrogen, a gas that stores high levels of energy due to its high energy density per molecule and unit of weight. Hydrogen storage proves to be more efficient than batteries in many applications, due to the low maintenance cost and material price of the storage system [22].

Table 1 Cost coefficients and performance of storage technologies. [22]



Cost coefficients and performance characteristics of storage technologies.

Technology parameter	[unit]	min	max	min mean	max mean	mode
Hydrogen storage (H_2St)						
Capital costs	[€/kWh]	5	13	8	11	10
O&M costs	[%]	1.5	3.0	2.3	2.3	2.3
Lifetime	[years]	20	30	23	23	23
Thermal storage (HWTS)						
Capital costs	[€/kWh]	1	19	8	11	9
O&M costs	[%]	1.0	2.0	1.5	1.5	1.5
Lifetime	[years]	10	40	19	28	24
Efficiency	[%]	50	95	71	92	81
Self-discharge rate	[hr^{-1}]	0.00500	0.01000	0.00750	0.00750	0.00750
Li-ion battery						
Capital costs	[€/kWh]	149	598	258	311	285
O&M costs	[%]	0.7	5.0	1.9	2.5	2.2
Lifetime	[years]	5	20	10	14	12
Roundtrip efficiency	[%]	85	98	90	93	91
Self-discharge rate	[hr^{-1}]	0.00010	0.00100	0.00053	0.00054	0.00054

Table 1 shows some of the advantages of hydrogen compared with thermal storage and Li-ion batteries, which are currently one of the most used battery types [23]. Table 1 however, shows how Li-ion batteries are much costlier than hydrogen storage. Crucial values like the low price per kWh and the longevity of the system shows hydrogen storage technology to be more advantageous and should be incentivised to be used in bigger scales than current ones, as it provides an alternative to projects where batteries' constraints outweigh their benefits.

An important variable studied by Petkov & Gabrielli [22] is the uniformity of performance across each time of day through a year of a hydrogen storage system vs its competitors. This can be seen in Figure 3.

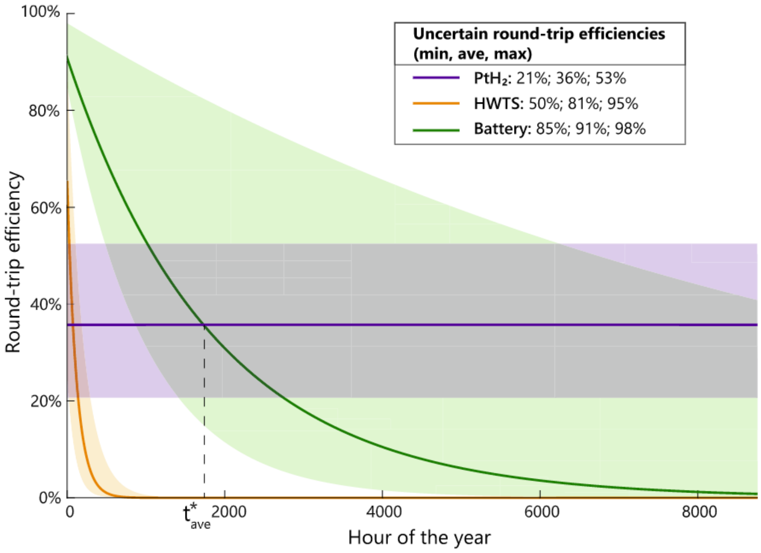


Figure 3 Efficiencies and self-discharge of Hot Water sensible Thermal Storage (HWTS), battery and PtH2 storage as function of time. Average values are indicated by solid lines and ranges by shaded areas [22].

Figure 3 indicates the stability that hydrogen provides to power supplies, as its efficiency to store energy does not decrease through the year, unlike thermal storage systems and batteries. This property allows hydrogen to be practical for back-up power supplies, power generation for remote locations, stand-alone power stations, distributed generation for buildings and cogeneration (in which excess thermal energy resulting from the production of electricity is used to provide the thermal agent) [24].

However, to obtain efficient and clean energy green hydrogen must be generated. To do so, more research must be put in the production of green hydrogen to find methods to generate the maximum quantity of hydrogen with the least amount of energy. Like in renewable developments previously mentioned, green hydrogen research can find inspiration in systems that harness excess energy and reinstate it back into the system. Further research in this field is done in following chapters, analysing the viability of systems capable of harnessing wasted energy, and reusing it to generate H_2.

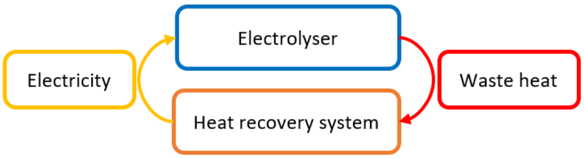


Figure 4 BFD Diagram of heat recovery system.

1.2.2.3.1. Nanomaterials for Hydrogen transportation

The transportation of H_2 has some difficulties due to the small size of the molecule and the need to pressurise it or liquefy it [24]. While this constraint still puts H_2 at a higher energy efficiency than fuels in many applications, it causes some doubts when H_2 is considered instead of common electrical batteries.

Nanomaterials in this field are becoming key to fix this issue in various ways. Ammonia is a common molecule which contains hydrogen. Its bigger size makes it easier to be handled and carried than pure H_2. However, each extra step in energy transport decreases the efficiency of the energy transfer. Thanks to new nanomaterials this process can efficiently transform ammonia into N_2 and H_2. To achieve this, CeO_2 is impregnated on nanotubes (NT) and nanocubes (NC) to act as a catalyst to increase surface area and facilitate the process [25]. This is just one example of nanomaterials supporting hydrogen technology. This thesis will research how to generate nanoparticles efficiently to aid hydrogen technology and incentivise these chemical processes.

1.2.3. *Industrial energy usage*

Energy usage by industries is a huge portion of the world's energy demand. Therefore, finding effective methods to lower the energy needed, to manufacture and process products, will have a huge impact on the total energy usage [26].

Studying a highly industrialised country like the USA, it is possible to quantify the demand of industries' energy consumption.

There are 3 main uses for fossil fuels and renewable energies; heat in industrial sites, steam generation to produce electricity and feedstock to create plastics and chemicals [27]. Ironically, many chemical processes are exothermal therefore useful heat is wasted in many chemical processes. Being able to recycle the energy by-product and use it instead of fossil fuels can reduce the industrial energy demand as well as being economically beneficial. More research is completed in the following chapter of this thesis to find methods to recover the waste energy of industries like the previously mentioned, to reduce their energy consumption.

Another industry that benefits from sustainable solutions is the mining industry. Most of the extraction of raw materials are inefficient and unsustainable. Even in developed countries like the USA, processes to extract some metals require an adequate environment and a feasible geological site. That is the case of Lithium extraction, where the purification process takes place in brines, left in the desert to evaporate undesired water. To avoid this process, many chemical processes must be applied like roasting, calcination, leaching and multiple filtrations [28].

1.2.3.1. Usage of nanomaterials for more energy efficient industrial processes

Interestingly, new nanomaterial compounds can replace some chemical processes. For example, novel metal organic framework materials (MOF) have been developed by *EnergyX* to extract Lithium. They consist of membranes with nanochannels which act as filters to extract Lithium atoms. MOFs are nanoporous materials with homogenous structures. These membranes filter out similar ions to Li^+ which would otherwise take many chemical steps to separate.

Chemical discoveries in the nanomaterial sector are proving to be a major catalyst to allow new technology to become a reality. Therefore, this thesis hopes to encourage more research in this area and hopes that cross-disciplinary research increases between the chemical and mechanical fields.

1.3.Global waste

The key to manage global waste is a circular economy that considers and finds use in all material's afterlife. According to the European Commission, being able to achieve such economy shows to have positive repercussions environmentally and economically. In the EU, a circular economy will save €600 billion, reduce 450 million tons of carbon emissions and create 580,000 jobs by 2030 [29].

1.3.1. *Methods to reuse waste*

New methods must be analysed and improved as waste has been growing rapidly with the increase in population. According to NGOs like *The World Counts*, it is estimated that waste generation will be almost doubled by 2050 and tripled by 2100 [30]. Bearing in mind most of the waste in all countries is left in landfills, it is crucial to find ways to reuse materials.

The ZWI is the measurement of waste management performance by accounting for the potential amount of virgin material of the world in waste. Studies measure it to be 0.12, meaning only 12% of the total virgin material has a waste management system [31].

1.3.1.1. Recycling processes

The main alternative to obtain precious materials is to dismantle products that have already used them.

A great example is batteries, a product that is increasingly popular due to the electrification of systems like transport. Virgin materials inside of them cause damaging repercussions to the countries where they're sourced. It has been proven that finding mines of desired elements do not reflect an improvement in the country where they are found [32].

This is the case of Lithium, a metal searched and extracted by corporations in developing countries, which rely on poorly structured governments to increase profit. Therefore, it is crucial that the recycling industry expand by increasing the amount of recycling plants worldwide as an alternative to industries that promote mafias and damage the ecosystem of the country.

However, the demand of Lithium for electric vehicles and batteries will create in less than 15 years must be met. By 2035 all produced vehicles in Europe will be electric and with this change, the disposal of electric machinery must evolve. Modern waste management, although it provides low profit, eliminates most of the problems associated with mining while also decreasing the traffic of transatlantic transportation.

This thesis aims to generate carbon-based nanomaterials (CNTs) from waster plastic. That CNT production would be an example of a material that disincentivises mining and long distance transportation, as the source of material can be local waste.

1.3.1.2. New designs

Modifying designs intelligently allows an easier dismantling of machinery. This eases their recyclability and reusability of parts. Doing so will incentivise a circular economy.

For recyclers to obtain an economic advantage, researchers must provide the technical provision and guidance to dismantle products. The key goals of each design must be the selection of materials, simplicity of its parts and time taken to release each material.

These parameters are being increasingly used but still face some issues. One is the decrease in recycling efficiency caused by materials like heavy metals. Another is loss in profit for companies. Being able to achieve replaceable parts in complex machines allows materials to circulate and be used for longer. This, however, decreases the profit of the producers.

However, some companies like *Fairphone* have started to design their product with these concepts. Their product has a modular design, where each component can be replaced and fixed. This generates less electric waste and increases the lifespan of the product [33]. Modular designs also allow innovation to reach society at a faster pace without the need to dispose the product and all its *still-functioning* components.

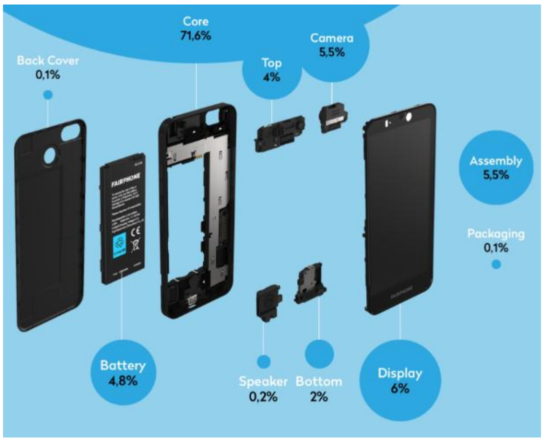


Figure 5 Modular smartphone design depicting the CO_2 emission percentage of each component [33]

New designs can also be applied in the creation of composites. Understanding the recyclability of the chosen materials will later allow an easier recycling process. This is done for example by finding similar materials for the matrix and the fibre reinforcement of the composite. For example, polymers that can work as matrix and reinforcement should be encouraged. Substituting inorganic fibres with organic ones, like low density polyethylene (LDPE), can provide another pathway to reuse plastic waste. These composites can also offer good properties as the adherence between fibres and the matrix of similar materials is stronger and therefore more durable. Using the same material also speeds up the dismantling process which, as mentioned before, creates an economical advantage for the recyclers [34]. To be able to match the properties of glass fibre reinforcements, polymer nanocomposites can be added such as CNTs [35].

One of the reasons why CNTs can improve the physical properties of composites is its elastic modulus reaching terapascal values [36]. These high values are achieved thanks to the correlation between fracture stress and diameter.

$$\boldsymbol{R} = \frac{dE}{2\sigma_f} \quad (1.1)$$

where R is the radius, E Young modulus and σ_f stress at fracture.

Carbon nanotubes logically have one of the smallest possible radii, being therefore strong and flexible [36]. However, to be able to substitute completely non-eco-friendly materials, nanomaterials must be produced in bigger scales. Through later chapters this issue is analysed, and new methods to produce them are suggested.

Being able to substitute carbon-based materials with precious metals therefore discourages overmining limited materials. Therefore, carbon-based nanomaterials can be regarded as eco-friendly because they are generated from common elements (carbon and hydrogen). However, it is required to burn carbon at high temperatures to synthesise such structures. Therefore, to generate more eco-friendly materials, the carbon source should be reconsidered, for example, by reusing the carbon-based materials which have already been produced and disposed, like plastics.

As shown, being able to replace materials can only be achieved by researching new ways to improve the efficiency of eco-friendly materials. Doing so, materials like heavy metals or natural materials will not be overmined, which as well as improving recycling, can have massive ecological benefits in developing countries where these materials have been sourced in an unsustainable manner.

1.3.1.3. Reshaping waste

A great method to create a circular economy is to reshape common waste for new purposes. Taking plastic waste as an example, only 9 to 19% is currently recycled globally [30, 37]. Remaking the same materials is good but not enough as the quality of the plastic deteriorates per cycle [38]. Creating new uses for these materials is therefore an imperative. This is currently done, for example, by adding plastic waste as fibres in a concrete matrix to improve its physical properties. Another innovative method is done in construction, reshaping plastic has proven to be useful to replace natural materials like timber as railway sleepers, benches, fencing or floor m larger lifespans for plastic materials.

(a) Recycled plastic railway sleepers (b) Recycled plastic benches

(c) Recycled plastic decking (d) Recycled plastic fencing

Figure 6 Modifying shape of used plastics [30]

Analysing the properties of each plastic like the toughness of PET plastic or the flexibility of LDPE creates new purposes to disposed waste.

Table 2 Properties of plastics [39]

Physical properties and possible construction application of recycled plastic types.

Plastic composition	Physical properties	Possible construction application
HDPE	Rigid	Plastic lumber, table, chairs
LDPE	Flexible	Bricks and blocks
PP	Hard and flexible	Aggregates in asphalt mixture
PS	Hard and brittle	Insulation material
PET	Hard and flexible	Fibres in cementitious composites
PC	Hard and rigid	Aggregates in cementitious composites

Table 2 shows some of the most common plastics reused and their potential applications according to their properties.

Some restraints must be tackled to promote the reshaping of waste plastic. The varying composition of plastic waste must be resolved either by finding better ways to sort waste or by finding a chemical process that evens the quality of the plastic waste. Secondly, the density must be altered for some uses like replacing materials with high toughness and elasticity. Increasing density can also facilitate transport of plastic waste. Another issue to resolve is the low surface energy of plastic waste. If composites are made from polymers, increasing the surface energy will allow better mechanical bonding and overall performance [40].

1.3.1.4.Creating new chemical structures

Chemists in recent years have investigated the possibility to reshape the chemical structure of used chemicals such as oils, fats and used plastics to create polymers without the need to use virgin sources like crude oil. through that research, laboratories have found new properties in carbohydrates and fats, such as the possibility to create biodegradable plastics from them [41].

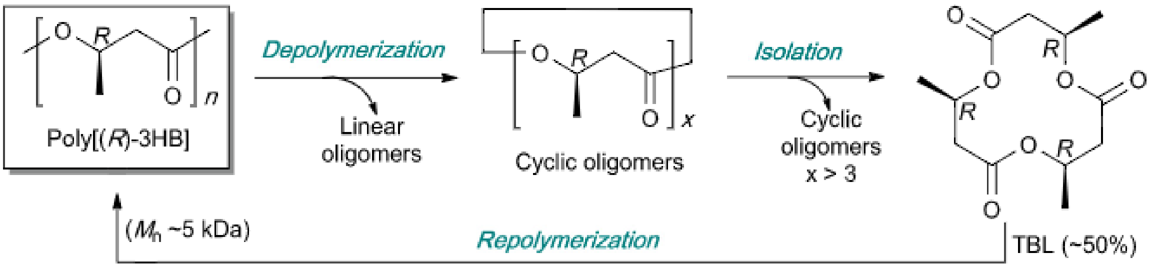


Figure 7 Chemical Recycling of P3HB via Depolymerization of Poly[(R)-3HB] to Cyclic Oligomers and Polymerization of the Cyclic Trimer to Low-Molecular-Weight Oligomers [41]

Figure 7 shows an example of how depolymerization provides building blocks to create high quality polymers, resembling the qualities of a plastic formed from virgin materials. This can potentially create infinitely recyclable plastics with competent properties, compared to plastics produced from raw materials. Considering that by 2050, plastics will be approximately 20% of oil consumption, this process can heavily cut the global crude oil usage.

Similarly, used polymers contain desirable elements which, through chemical processes like pyrolysis, these elements can be extracted and restructured into new chemicals. At high temperatures, portions of solids, liquids and gases are synthesised to then be transformed into useful products. Liquids can be used directly as fuel gases when smaller carbon chains are produced, which can become the building blocks of new structures.

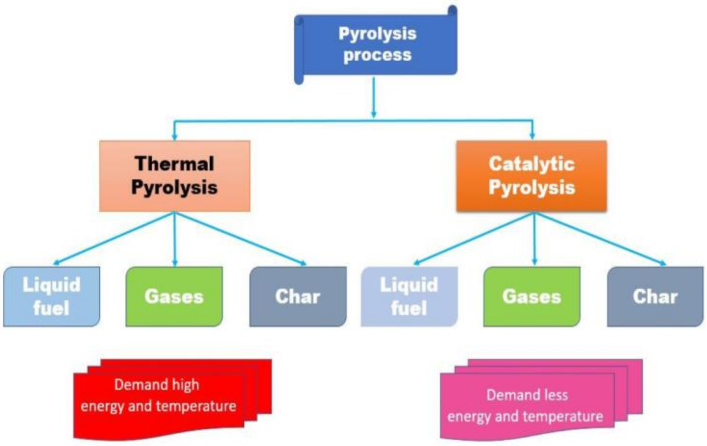


Figure 8 Classification of pyrolysis [37]

Catalytic pyrolysis has a low energy demand thanks to catalysts. This process provides a higher quality of oils due to the breakdown of longer carbon chains. To ensure a catalyst is effective the surface area, pore size, volume, and acidity of the catalyst must be optimal.

Thermal pyrolysis requires high energy inputs and a high temperature. This process is less environmentally sustainable but is required when the reactants have inorganic compounds. This process also generates a product with higher density and viscosity [37].

However, thermal pyrolysis has an interesting utility. Using carbon-based compounds, it is possible to generate high performing materials with a modification of the pyrolysis process. Adding catalysts to thermal pyrolysis has proven to create carbon nanotubes and other carbon-based nanoparticles. These are materials which can aid the energy sector, as well as providing another life to disposed plastic waste.

This method is called spray pyrolysis or in other cases, injection chemical vapour deposition (injection-CVD) [42]. Here, thermal pyrolysis cuts the sprayed carbon chains while the catalyst provides a surface and a lower energy path for the small carbon particles to deposit and bond again in a modified structure.

Reconstructing carbon molecules for recycling has another advantage. As commented on this chapter, hydrogen is a useful gas for the energy industry. Its main constraint is its production. This process has hydrogen gas as a by-product, providing another source [43].

This process will be experimentally tested in the third chapter, putting waste plastic (polyester) under CVD to generate carbon nanotubes.

1.3.2. *Life Cycle Engineering*

All the factors mentioned in this chapter are key to tackle environmental issues. This sector has been given the name of “Life cycle engineering” and is becoming an important branch of engineering as companies and governments start to invest to tackle these issues. This sector undertakes activities that include the application of technological and scientific principles to manufacturing products with the goal of conserving resources, protecting the environment, encouraging economic progress, keeping in mind social concerns, and the need for sustainability, while optimizing the product life cycle and minimizing pollution and waste [44].

Life cycle assessments (LCAs) are a great tool to analyse and subsequently compare various technologies, processes, or product’s pieces. These are key to obtain a thoughtful indication of the best ecological option for any given product. LCAs prove that no answer is the only option to the ecological crisis. Rather, most solutions are viable under the right circumstances. Therefore, a combination of new emergent technology will be key to tackle the climate crisis by being able to reach all ecological harms.

1.4. Conclusion

Through this chapter energy waste and material waste are analysed. Each type of waste was studied to understand where the constraints exist in the process of production. Once these bottlenecks and inefficiencies were identified, a series of solutions were reviewed.

The main methods to recycle plastic were studied, including reusing, reshaping and chemical recycling. In addition, the chapter reviewed how new designs are considering the end life of the product. This makes industries consider what materials will be used and how easy their product will be dismantled.

The designs, therefore, require new materials to substitute rare metals, which cause unsustainable mining and promotes materials that can be reused, such as carbon-based parts.

Hydrogen was studied with special interest as it is a growing technology that is proving to assist the energy sector. The chapter showed how it offers solutions to the limitations of present energy storage methods. It is however necessary to generate green hydrogen for these solutions to be sustainable and ecological. To achieve this, hydrogen production must become more efficient. This will be explored further in the following chapter.

An introduction about the role of new nanomaterials was studied to show how they can facilitate energy storage. They have proved to assist batteries, metal hydrides for hydrogen storage, hydrogen transport or lithium mining.

In addition, the chapter showed how nanomaterials can be produced with material waste, with chemical recycling and pyrolysis. This process can therefore generate carbon-based parts for new sustainable designs with remarkable physical properties to improve the efficiency of a wide variety of technology. The last chapter of this thesis explores experimentally methods to produce carbon nanotubes to support new sustainable designs.

With the information gathered by this chapter, the following chapters focus to improve the technology detected that has the greatest potential to aid a sustainable energy industry. Therefore, hydrogen electrolysis is studied further with the aim to lower the electrical requirement to generate green hydrogen.

2. RECOVERING HEAT ENERGY FOR GREEN HYDROGEN PRODUCTION

2.1. Introduction

Following the exploration into the energy system in chapter 1 this chapter explores methods of efficient hydrogen production as was highlighted previously. A study to find the optimum method to increase the efficiency of low temperature difference (LTD) hydrogen electrolysers, by recovering its dissipated heat into useful energy. Thermoelectric generators (TEG), heat pumps, Stirling Engines and thermodynamic cycles were studied to find the best combination or single machinery to reinject electricity back into the system. The chapter explores each of these technologies before recommending and highlighting areas for further concentrated efforts.

2.1.1. *Background literature review*

Hydrogen (H_2) fuel is a growing energy vector due to its ability to store and transport energy. In addition, unlike fossil fuels, hydrogen is present in a massive amount of chemicals making it vastly abundant if it can be extracted. H_2 can be extracted using renewable sources; therefore, it has the potential to supply and store energy sustainably.

However, low efficiencies in hydrogen production causes a lack of economic viability in the energy sector, as utilizing H_2 requires many steps that waste energy, from creating and transporting to generating electrical power [45]. This currently makes H_2 unable to compete in price and convenience.

Achieving an increase in economic viability in H_2 is hugely beneficial as it offers advantages in the long term for consumers which other technologies cannot. For example, it's a solution to store excess energy efficiently from unstable renewable sources. H_2 can also store energy for a long period of time without discharging on cold environments, unlike electrical batteries, who suffer under extreme weather conditions. In addition, the storage does not lose its energy capacity from charge cycles like an electrical battery. H_2 has also shown to be more cost effective than batteries, in terms of operating cost, comparing the energy it can store and the energy required to build the system (Energy Stored on Investment ratio, $ESOI_e$ ratio) [46]. $ESOI_e$ is a comparative value, used to rank what electrical storage system is more efficient to build and maintain.

Looking at the transportation sector, H_2 in fuel cells already offer a higher energy efficiency compared to petrol or diesel engines [47]. In addition, the energy density of H_2 fuel cells is much higher than electric batteries and can potentially contain less harmful materials [45]. Moreover, its only by-product is water once electricity has been produced in a fuel cell. This can be of interest to industries as well as being a non-pollutant to cities.

There are many reasons why it is crucial to give more attention to H_2 technology. It functions as an energy storage with lower polluting life cycles to its alternatives, and it has the potential to be carbon neutral. This clean Hydrogen is called “Green Hydrogen”. Currently, most H_2 production is labelled as “blue” or “grey” as its production unfortunately requires the burning of gases. The most economical method is steam-methane reforming (SMR). This process generates carbon monoxide and hydrogen as by-products [48]. To avoid this, green hydrogen is extracted from water through electrolysis, which to this day is approximately 60-70% efficient [45, 49] (65% for alkali electrolysis, currently used in Swansea University laboratories [50, 51]). To be able to push hydrogen production to become green, it’s imperative that its efficiency must be increased. This will lower costs and make this green technology competitive.

As the loss in efficiency is mainly due to heat losses in the process, this project looks at how to recycle the heat, radiated from the electrolyte tank, back into the hydrogen production process, decreasing overall energy losses.

After background research on methods to recycle heat losses of H_2 production systems, a comparison is performed to design a heat recovery system for the alkaline water electrolyser (AWE) currently being developed by Swansea University with a low temperature gradient.

2.2. Electrolyser’s efficiency review

A study on the electrolysis’ efficiency, or rather its efficiency losses, was made to search key components to improve. This was also done to understand all the variables that must be considered to try to improve the electrolyser.

Logically, the less power (P) required to perform a set amount of electrolysis the better the efficiency. So, looking at Ohms Law ($P = VI$), decreasing voltage (V) needed for electrolysis will make the system more efficient. Decreasing resistance will also allow voltage to decrease to generate hydrogen. This can be done for example increasing the electrolyte temperature [52]. The theoretically minimum voltage required for electrolysis is 1.23V [53]. Currently over a 1.5V input is required, showing room for improvement.

The efficiency of an electrolyser is given by the formula:

$$\eta_{Total} = \frac{H_{H_2} + Q_{waste}}{E_{in}} \qquad (2.1)\ [54]$$

Where H_{H2} is the energy that produced H_2 gas, Q_{waste} is the losses in heat and resistance, and E_{in} is the energy put into the system through electricity.

The energy losses are known to be majorly due to heat dissipated from resistances and electrodes. This energy therefore is recoverable. The remaining irrecoverable energy (like resistance and minimal heat requirements) accounts for approximately 25% of the wasted energy [54]. If the productive energy is known, the waste energy can be calculated, 75% of which can then be reused. To know how much energy directly created H_2, the produced mass of H_2 must be known, for example, by capturing the volume produced. Then, using the following formula, the productive kWh can be calculated:

$$E_{Productive} = mass_{H2} * LHV \text{ (2.2) [54]}$$

Where LHV is the lower heating value per kg of H_2 (kWh/kg), in other words, the chemical energy content of H_2. [54]. If around 75% of the unused energy can be reused, the total efficiency of an electrolyser can be deduced to be 18-20%, assuming an electrolyser has an efficiency of 75-80%. Depending on the heat recovery system the percentage of energy recovered will change. In other words, out of the potential 20% improvement, only a fraction will be recovered. This chapter therefore looks at methods to recover the maximum amount of reusable energy.

The tank for water storage currently has a temperature limit of approximately 70ºC. An excess of power will increase temperature of tank and degrade the acrylic walls of the container and polluting the water. Being able to extract the heat away from the system would allow an increase in the power input of electrolysis, increasing the rate of electrolysis.

However, electrolysis becomes more efficient at higher temperatures, as under that condition water goes through direct thermal water splitting, at approximately 2000ºC [55]. When water reaches those temperatures, it "naturally" breaks down into H_2 and O_2. It is worth noting that both activation and ohmic losses decrease with a higher temperature [56]. In addition, O_2 cannot dissolve as easily in hotter water, therefore less contamination will occur through the electrolyser, and O_2 collection will be higher. Therefore, changing the materials used in the system to hold a higher temperature can contribute to improving the efficiency of the system. Perhaps using plastics with semi-crystalline properties instead of amorphous plastics like acrylic.

However, for simple electrolyser systems, having constantly such high temperatures is expensive and requires complex maintenance. Therefore, a simple heat recovery system is a solution in some cases.

Table 3 Electrolyser's parameters that achieve highest performance at 84% efficiency. [50, 51]

Voltage per cell (V)	1.76
Current density (mA/cm^2)	400
Power per cell (kW)	21.12
Highest Temperature (ºC)	65-70
Surface area of cell (cm^2)	300

2.2.1. *Electrolyser's parameters*

The purpose of this study is to lower the voltage required to generate hydrogen to as close the minimum theoretical voltage able to produce hydrogen from electrolysis (1.23V).

The material chosen to transfer the desired heat will compromise the energy recycled. For this reason, the tank must be greatly insulated where no heat exchange is desired. These materials could be aerogel thermal insulator material, expanded polystyrene (EPS) or mineral wool [57]. On the other hand, the surface where heat transfer is desired must have a high thermal conductivity coefficient while being waterproof. A metal like aluminium is a sensible option with a conductivity value of 247 W/mK. The heat output of the tank is then given by the formula:

$$Q = \frac{\alpha A dT}{L} \text{ [57]} \quad (2.3)$$

where Q is heat exchange, α is heat conductivity coefficient, A and L are the area and thickness of the position where heat is being exchanged (respectively), and dT is change in temperature.

Therefore, when the face of the tank is 0.4m with 0.25cm thickness, such as the tank owned by Swansea University laboratories, Q=3,604kW. This is the energy available to capture, currently being wasted as heat. It is a significant quantity, confirming that a recovery system could assist with the electrical power supply to generate electrolysis.

2.2.2. *Using a renewable source*

As previously mentioned, the goal of generating sustainable electricity, it is required to generate Green Hydrogen.

Solar energy has been studied in the past to generate hydrogen and increase the temperature of electrolysis to improve its efficiency.

A high temperature gradient provides a higher efficiency in a heat capturing method implemented. In this situation, a heat capturing system would be used to generate electricity for electrolysis and to control the temperature.

However, this system is only useful if the heat capturing method proves to be more efficient than a solar panel. It would also be dependent on hot and sunny days making the system unreliable [58].

It is known that renewable sources provide fluctuating power. Inputs of fluctuating currents into an electrolyser can potentially modify the voltage of the electrolyser, the temperature, gas pressure, gas purity, or amount of generated gas over time. Durability of the entire system is ensured by avoiding changes of those parameters [59]. Therefore, it is important to maintain the variables as steady as possible. This can potentially be achieved with heat recovery systems, as they can provide the energy surplus in periods of low current.

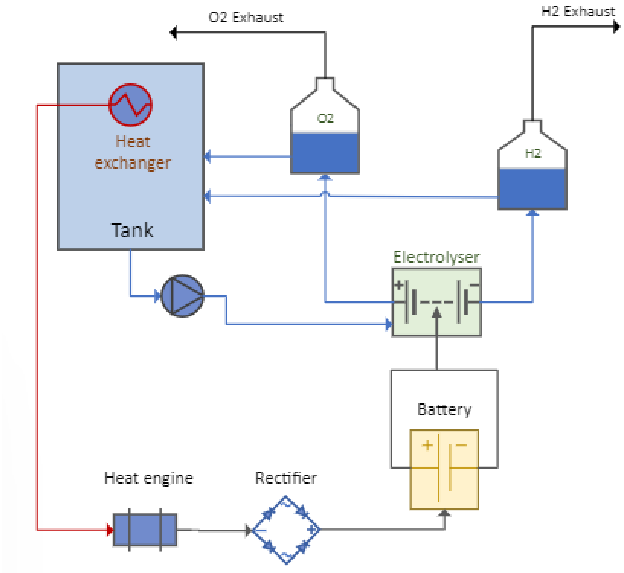


Figure 9 Diagram of potential heat recovery system.

Figure 9 shows the system design proposed to recover the heat released by the tank and utilise it to feed the electrolyser. There are various types of heat engines that allow heat to generate electricity. Those methods are analysed through this chapter.

2.3. Heat capturing methods

There are many technologies capable of absorbing energy, which will be analysed. Properties like the Piezoelectric effect, where materials have the property to be charged through applied mechanical stress, or the pyroelectric effect, where materials such as crystals or ceramics have the property to release electrons relying only on temperature changes over time. From this property pyroelectric generators (PEG) are created, which can absorb the heat emitted by an electrolyser to produce some of the electricity needed to start the electrolysis process [60]. However, PEG only produces a voltage while being under a temperature change. Therefore, it would have to be placed accordingly under that environment.

2.3.1. *The Thermoelectric Generator*

A thermoelectric generator (TEG) on the other hand, works under constant temperature gradient or constant heat flow [61]. However, these are still under development and produce electricity at approximately 4-9% efficiency [62]. TEGs work thanks to the Seebeck effect, which consists of using conductors, connected in series, with different thermal conductivities to produce an imbalance in electrons when heat is applied, creating a voltage [61]. To achieve this effect, paths of varying semiconductors are placed as shown in Figure 10, where ‘N’ and ‘P’ are semiconductors with different thermal conductivity. The pattern is repeated to obtain an increased voltage.

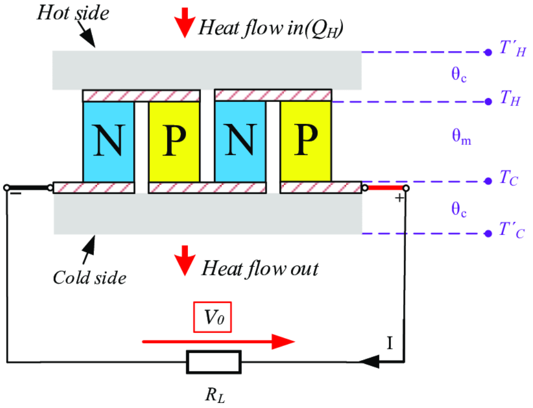


Figure 10 Diagram of TEG [61]

The semiconductors must have high electrical conductivity and low thermal conductivity. Materials with both of those properties are scarce, making TEGs expensive. However, utilising TEGs allow the system to be simple and without moving parts. This can be beneficial to some electrolysers and fuel cells. More research will allow this technology to be widely used due to its simplicity. Some of the newest research focuses for example on the modification of the cross-sectional area of the semiconductors. This new research delves with the idea of changing the constant cross-sectional area (cuboid shaped material) to hexahedrons, which provide a variable cross-sectional area. This was found to facilitate the power output of TEGs. [63]. Other research has been focusing on the Heat Exchanger structure, analysing how the performance difference when hot and cold sources are applied in a different flow direction or cross-sectional area. Improvements in the stress distribution, compactness of the TEG and adding heat insulation measurements have also showed to increase their efficiency [64].

To determine the viability of TEGs in an electrolyser system the following values can be calculated:

$$ZT = \frac{\alpha^2 \sigma T}{k} \quad [65] \quad (2.4)$$

where ZT is the thermoelectric figure of merit, α is the Seebeck coefficient, σ is electrical conductivity and k is thermal conductivity. For TEGs, it is recommended that ZT is greater than 1 but for an economically viable heat recovery system, the ZT must exceed 3 [65]. This figure can then be utilised to estimate the efficiency a thermoelectric generation in a determined environment with the following formula:

$$\eta_{\mathrm{TEG}} = \frac{\mathrm{T_H} - \mathrm{T_C}}{\mathrm{T_H}} * k \frac{(1+ZT)^{\left(\frac{1}{2}\right)} - 1}{(1+ZT)^{\left(\frac{1}{2}\right)} + (T_H/T_C)}, \quad [65] \quad (2.5)$$

This value can then be used to determine the added value of a TEG, considering its price and the efficiency requirements of the system.

To be able to maximise the efficiency of a TEG system for an electrolyser, the temperature gradient could be increased. A heat sink on the cold side of the TEG plate can increase the temperature gradient. A heat sink with a large surface area would be optimal as well as a fluid to absorb heat and evacuate it. As the electricity gained would be lost in a system with a fluid being pushed, alternative systems can be considered such as the manual replacement of a substance once heat has been absorbed, to maintain a high temperature gradient.

A layout of TEG spread through the top surface of the electrolyser requires the heat sink to be on top of the electrolyser. Heat's nature is to move upwards which would increase the rate of temperature increase on the cold plate. The heat gradient formed around the tank must be analysed to know the best placement of a heat recovery system. If the cold plate absorbs less amount of heat than on the top face of the tank, then the highest part of tank's side face will be the most efficient section.

The number of TEGs will determine how much power will come out of the system. The problem with TEGs working close together is the "parasitic power loss" which is avoided increasing the spacing of the TEGs. For example, according to a paper on *Modelling and optimization of low-temperature waste heat thermoelectric generator system*, an optimal spacing for the TEGs would be of approximately 1cm while applying a flow of water of 1L/s through the cold plate [66].

To be able to meet optimal parameters, TEGs need to adapt to the environment where they are installed. CNTs' high conductivity and flexibility have proved to make TEGs malleable and efficient in low temperature gradients. In addition, they are sustainable carbon structures that substitute rare metals [67]. CNTs are experimentally produced in the following chapter to find new methods to generate CNTs and improve TEGs. Producing economical CNTs enable TEGs use the nanomaterial and gain efficiency, which encourages electrolysers to implement heat capturing systems to gain productivity.

2.3.2. *Implementation of Heat Pumps in the heat recovery system*

Heat Pumps (HP) are a key component that can benefit systems that require a high temperature gradient or a thermal energy storage. They can improve the efficiency of most energy generators that work on applied heat like TEGs or heat engines. A heat pump works thanks to a thermodynamic cycle where heat is transferred into a fluid. The fluid is then compressed through a compressor which increases the temperature of the liquid. A heat sink then releases the increased heat, which according to literature can be approximately 4 times the energy input (electricity) to the heat pump, reaching a technical energy efficiency of up to 400% [68]. In other words, for every 1 J of electrical energy converted to mechanical work, a total of 4 J of heat is delivered into the environment—1 J from the electrical input and 3 J transferred from an external source. This system therefore requires a hot and cold reservoir. Lastly, an expansion valve decreases the temperature and velocity of the liquid which then restarts the heat absorption process.

To analyse if a heat pump is feasible in a system to harness the energy wasted it is important to understand the efficiency of the method to harness electricity. For example, with a heat pump in a TEG system, the energy stored can increase 3 to 4 times, but their 4-9% efficiency returns less electricity than the initially applied. On the other hand, a Stirling Engine with a heat pump can be feasible. This is because Stirling engines can reach up to 40% efficiency [69].

This efficiency gives the possibility to work with a heat pump to achieve a higher temperature gradient and therefore a higher electrical return. A heat pump can be considered after the efficiency of the selected system is calculated. If a heat pump doesn´t reach minimum efficiency threshold, the system would be intaking more energy than the energy released as heat, therefore making a heat pump useless as a method to generate a higher temperature gradient, for a more efficient energy recovery system.

To analyse the efficiency of the pump, the coefficient of performance (COP) is calculated as [70]:

$$\mathrm{COP_{HP}} = \frac{\mathrm{Heat\ input\ (Q_H)}}{\mathrm{Electricity(W_{in})}} \quad (2.6)$$

To ensure the heat pump is feasible a simple formula can be applied, the inverse value of the heat pump COP. If the inverse COP is smaller than the recovery system efficiency, then the heat pump can be implemented. If it is larger, the system would be using more energy than it provides.

$$\eta_{E\ recovery\ system} \geq \frac{1}{COP_{HP}} \quad (2.7)$$

2.3.3. *The Stirling engine*

This heat engine, invented in 1816, is a device with a closed, reversible, and regenerative thermodynamic cycle, with a cyclic expansion and compression with the assistance of a working fluid due to a temperature difference [71].

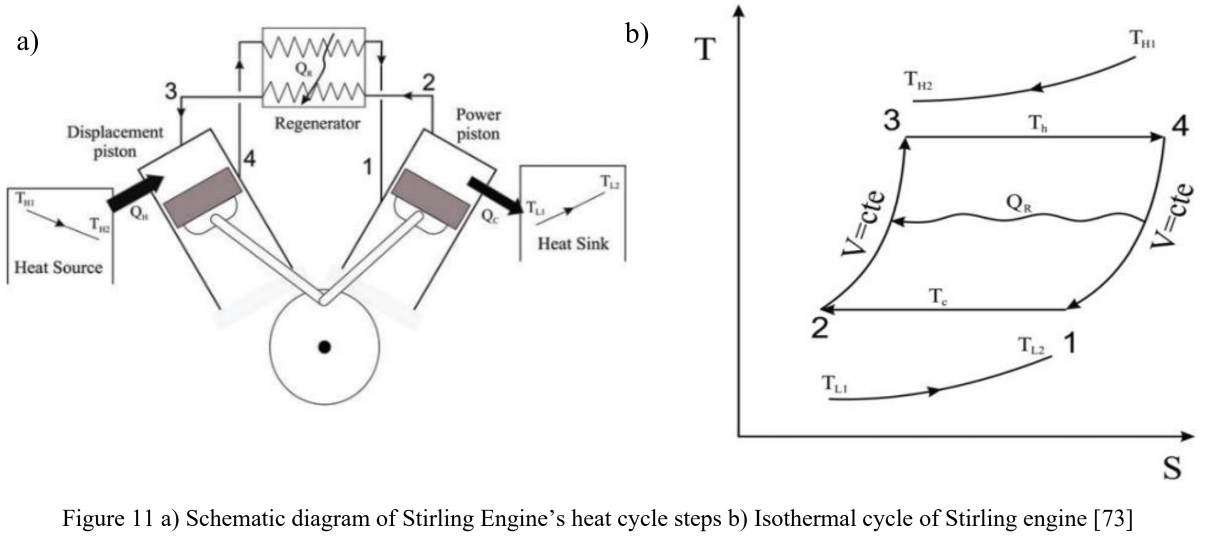


Figure 11 a) Schematic diagram of Stirling Engine’s heat cycle steps b) Isothermal cycle of Stirling engine [73]

A Stirling engine generates mechanical work which, with a generator, is then transformed to electricity. The engine achieves a higher efficiency than other alternatives, reaching 40% heat-to-work energy conversion [65]. They have a high reliability and a long life due to its simplicity [72]. This translates to an overall energy improvement **of 8%** in the electrolyser, as the recoverable energy of an electrolyser was shown to be approximately 20% in chapter 2.2.

As shown in figure 11, process 1–2 is an isothermal progression where the working fluid is compressed at a constant T_c. Excess heat leaves the cycle to the heat sink turning its temperature T_{L1} into T_{L2}. The working fluid passes the regenerator and is heated up to T_h throughout an isochoric progression 2–3. Throughout process 3–4, the working fluid expands at constant T_h course because it gains heat from the heat source, wherein its temperature is decreased from T_{H1} into T_{H2}, (as shown in figure 11b). 4–1 is an isochoric cooling process where the regenerator absorbs heat from the fluid.

The working fluid of the Stirling engine is used to take thermal energy and transform it to mechanical work (and vice versa). Hydrogen is optimal for that function but requires high quality materials to contain it like metals with coated nanoparticles such as CNTs to expand the binding capacity of hydrogen. [74]. A coat of CNT enables a fine containment of hydrogen thanks to its small scale. This would allow hydrogen to be used as a working fluid. Helium avoids the dissipation issue of Hydrogen, making it slightly less efficient but more economical. If the goal however is to reach carbon neutral systems, the working fluid should be air as no chemical processes are required to generate it.

The main reason why Stirling engines were analysed was due to their efficiency in low temperature gradients. It is reported that they can work on heat gradients of 1K which is ideal for an electrolyser which does not have an electrolyte at over 100ºC. As the temperatures of the electrolyte under study will not exceed 70ºC, the approximate temperature gradient would be of close to 50ºC, assuming ambient temperature is approximately 20ºC.

To analyse the efficiency of the Stirling Engine in the electrolysers' environment, the following variables must be considered [73, 75]:

$$\Delta Q_R = nC_v(1 - \varepsilon_r)(T_h - T_c) \quad (2.8)$$

where ΔQ_R is the regenerative loss, n is the number of moles, C_v is the heat capacity, and ε_r is the effectiveness of regeneration (=1 ideally). Regenerative loss is an energy value which shows the loss of energy in resistances. Subtracting the regenerative loss to the available energy form the heat source shows the energy efficiency of the engine.

To calculate the net work of the Stirling engine the following formula is used [76]:

$$W = mRln\left(\frac{V_2}{V_1}\right)(T_H - T_C) \quad (2.9)$$

Where m is the mass of gas enclosed in engine, R is the specific gas constant, V_1 is the volume at lowest position in its cylinder, V_2 is the volume when power piston is at its highest point in the cylinder.

2.3.3.1. Types of Stirling Engines

There are 3 main configurations of Stirling heat Engines. The simplest one is the **Alpha type.** Here, the pistons have a phase difference of 90º. This is the simplest configuration as the pistons separate easily maintaining different temperatures. Both pistons must have seals to contain working gas. However, the regenerator is a long pipe making it not efficient. Its drive mechanism can be a crank drive or Ross yoke [77].

The **Beta** type allows the piston and the displacer in the same cylinder. Both displacer and piston will have a phase difference of 90º as each will have its own linkage. Its drive mechanism can be a slider-crank drive or a rhombic drive [76]. Rhombic drive shows to be more efficient as thermodynamic processes in the engine fall closer to an ideal isochoric heating and isothermal compression [78]

Lastly, the **Gamma** type is the most efficient for low temperature gradients but the most complicated. This configuration can start operating by a minimum temperature difference of approximately 12K [79].

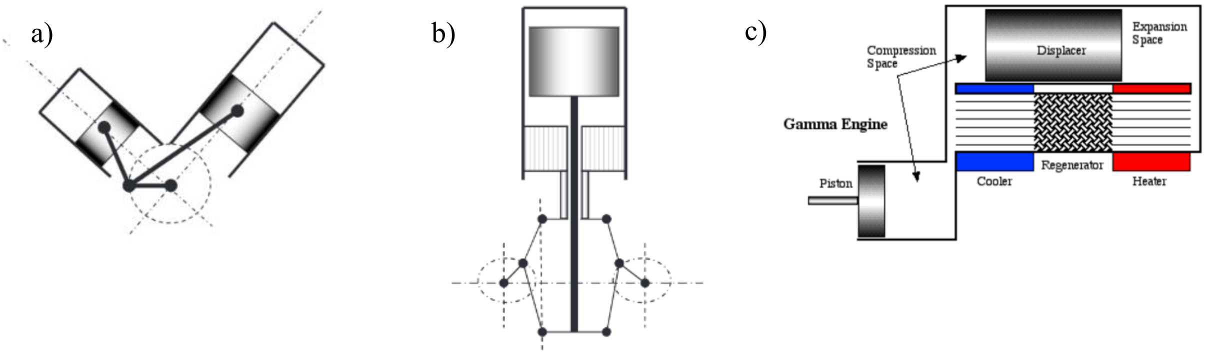


Figure 12 a) Alpha type Engine b) Beta type Engine (rhombic) c) Gamma type Engine [79]

It can have 2 different volume pistons to maximise efficiency by making the expansion piston as big as possible and phased piston much smaller. This is highly advantageous as an electrolyser tank has a large surface area where heat exchange occurs. In addition, the regenerator and displacer can be the same moving part for efficiency [77].

The compression space is split between two cylinders with an interconnecting transfer port. In between the passage from displacer cylinder and compression cylinder the cooler, heater and regenerator are connected serially. This arrangement provides advantage of simple crank mechanism [71].

2.3.3.2. Design of the Stirling Engine.

Configurations and drive mechanisms that allow higher compression ratios must be preferred for applications where high temperature difference is attainable, and those that allow low compression ratios must be used for low temperature difference applications [78].

$$CR_K(T_h\,,T_c) = 1 + \frac{T_h - T_c}{1100}, \text{[71]} \quad (2.10)$$

where 1100 is an empirically derived number obtained by Ivo Kolin and CR is compression ratio.

Engines with low temperature difference are especially sensitive to the compression ratio (CR). Therefore, an electrolyser must search a low compression ratio for its Stirling engine, which is achieved using a Gamma type engine. According to Ivo Kolin, a heat gradient with the hottest side being 300-400K, the CR must be between 1 to 1.5 [78]. This shows that ideally, the cold section of the engine must be at below 0ºC for its highest efficiency. However, studies like *An Analysis Model Combining Gamma-Type Stirling Engine and Power Converter* [77], show that at a minimum of ΔT=30K, a Gamma Stirling engine will start producing useful mechanical work. Combining a Stirling Engine with the previously mentioned heat pump would assist producing a higher ΔT if the Stirling engine reaches a minimum efficiency, as explained previously in the heat pump section.

To calculate the desired power output (P), the frequency of piston revolutions (f), the displacement of the piston in volume (V_p) and the P_m is the mean pressure. Those are the variables to modify to be able to reach the desired power output of the Stirling Engine [80]:

$$P = 10B_nV_pfP_m \quad (2.11)$$

Where the Beale number B_n , which oscillates from 0.05 to 0.15 at high temperature difference systems.

2.3.3.3. Heat exchanger in the Stirling engine

In a Stirling engine most of the time there are 4 heat exchangers. 2 of them are by the regenerator; one to add heat to the working fluid and one to cool it. The other 2 are placed by the heat source and by a cold source if needed. They benefit from a high surface area, high heat capacity, low conductivity, and low flow friction [78]. Therefore, a big tank with a large area for heat exchange is optimal to place the piston.

For low temperature difference (LTD) systems, the limiting heat transfer mechanism is the convection of the flow, transferring heat between the heat exchangers and the gas, rather than the heat conduction within the material of the heat exchangers [78]. For this reason, a key section of the Stirling engine to be developed is the convection flow through the regenerator. For example, a design that could be implemented is the research from *HRS Heat Exchangers*, where the convection of flow was improved with corrugated tubes, so that the heat exchange occurs faster than in smooth tubes as it makes the flow turbulent (or vortexual) therefore highly mixed. Similar technology is found in battery cooling systems where obstacles are designed to create turbulent flow on the cooling liquid for faster heat transfer.

Figure 13 HRS Heat map of flow of plain vs corrugated tube [81]

There is less heat conduction from the hot to the cold end so the distance here can be shorter in the piston.

The function of the regenerator is to store heat while the displacer pushes the heated air out. This increases the efficiency of the engine as the rate of heating increases per cycle. Close to the heat source, a heat exchanger with materials that have a good heat transfer by conductance is essential in an LTD system. Figure 14 shows where the regenerator would be placed in a heat engine system.

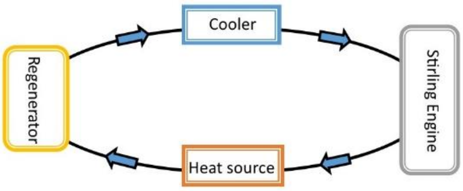


Figure 14 Regenerator Cycle in Stirling Engine

The heat transferred can be measured with the following variables [78]:

$$Q_h = h_h A_h \Delta T_h; \text{ where } A_h = \pi d_h n_h l_h \quad (2.12)$$

where d_h and n_h are diameter and number of heater tubes.

To analyse the cooler heat exchanger, the following variables are taken into account to measure the total heat transfer coefficient (h_t) [78].

$$h_t = \frac{h_w}{1+0.882h_w}; \; h_w = 0.35Re^{0.55}\mathrm{Pr}^{0.33}k_w d_o \quad (2.13)$$

where k_w is the water thermal conductivity, h_w is the heat transfer coefficient of the water film and d_o is the outer diameter of the tubes.

2.3.3.4. The Regenerator

Regenerators are components used in Stirling engines to increase the efficiency of the heat transfer. It stores the heat from one cycle to then provide heat faster to the next cycle.

A regenerator therefore must have a high heat capacity and a high heat transfer rate. This can be achieved with a large and finely divided separation between hot and cold environments. The flow must have minimum losses—a highly porous matrix is required. In addition, a minimum dead space (volume of air that doesn't become involved in heat transfer) and a dense environment in the pistons is required. Lastly, contamination must be avoided, therefore the environment requires no obstructions [77].

A material capable of conducting heat efficiently can increase greatly the efficiency of each cycle through the regenerator. Composite materials with nanomaterials like carbon nanotubes or nanofluids like aluminium oxide Al_2O_3 or SiO_2 are great examples [82].

2.3.4. *Turbine powered generator*

Turbines are commonly used for electricity production, where a force from a working fluid is used to turn the blades of a turbine, generating electricity. The working fluid can be naturally occurring, like wind, or by generating and heating a fluid (like a steam turbine) to create a force. Low temperature gradient systems cannot easily create a substantial force to create enough electricity, however a few ideas have been explored to overcome this issue.

2.3.4.1. Pump implementation

It is known that water and steam are the ideal and most preferred refrigerators due to the high specific heat of water, low viscosity, low price, and environmental footprint [83]. However, to use water, there must be a significantly high T_H higher than 100ºC. As the electrolysers in question have a low temperature gradient, modifications must be made to have a turbine powered recovery system.

A heat pump can be implemented, as long as the final electrical output of the recovery system achieves more electricity than the required by the heat pump. This condition is equivalent to the Stirling Engine case, where a heat pump of 400% efficiency must be used with a system at least 25% efficient.

2.3.4.2. Organic Rankine Cycle (ORC)

ORC systems offer an alternative to water/steam cycles. They essentially work with working fluids that require less energy to evaporate and generate a force. This cycle also powers a turbine with a working fluid. This option is more suitable for a low temperature gradient (LTD) heat recovery system. This is since a hot reservoir of only 65ºC (like the tank that holds the electrolyte for hydrogen electrolysis) could evaporate the working fluid and start the thermodynamic cycle. An ORC diagram is shown in Appendix 5.1. Figure 39, showing the components and its thermodynamic cycle in detail.

Here, a heat pump cannot work efficiently as refrigerants like R134a aren't as efficient for large temperature lift or vapor compression because refrigerants have a high working pressure with condensation temperature higher than 100ºC [84].

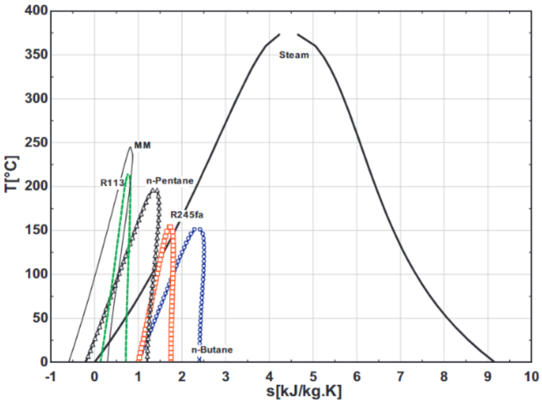


Figure 15 T-s graph Steam vs Organic fluids [83]

As Low temperature difference (LTD) systems have a low T_H, different substances instead of water must be used, which have a lower boiling point, achieving evaporation at <80ºC. There are many substances used for this purpose, generally used in refrigeration systems called organic fluids. Just like steam turbines, the refrigerant would absorb the heat until reaching its boiling point. In this case requiring less energy to evaporate than steam turbines and achieving a momentum big enough to turn the turbine. This makes refrigerants more practical for low temperature gradient electrolysers such as the one under study.

To achieve a higher velocity of the evaporated refrigerant, apparatus like nozzles can improve the efficiency of the turbine. The function of a nozzle is to change the cross-sectional area of the end of a system with a flow, with the purpose of increasing its final velocity, pressure, and temperature. This can result in a bigger change of momentum, in the same way aircraft engines propel themselves. A realistic way to achieve a substantial result, would be to use a turbo-expander as a nozzle. For small scale ORC systems, “positive displacement expanders” are used as they are characterized by lower rate, higher pressure ratio and a lower rotational speed. These components then expand the gas, decreasing the pressure after the fluid has gone through, which would allow the fluid to decrease its temperature and restart the cycle [84].

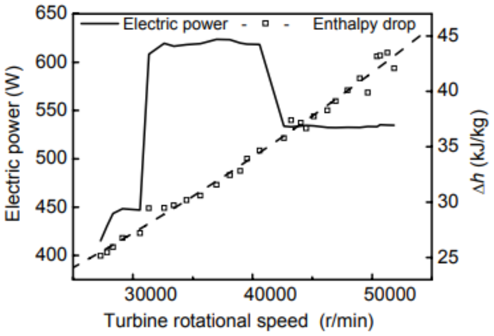


Figure 16 Electrical and enthalpy drop vs rotational speed on a common generator [85]

The efficiency of the turbine is proportional to the inlet pressure and its velocity. However, the efficiency of the generator has a peak performance at a given turbine velocity as at its specific point, energy losses start to increase. For this reason, it is important to analyse what generator is implemented in this system an adjust the parameters according to its needs [85]

An expansion valve or a condenser can in addition be used to lower the temperature of the fluid again to transform it back to a liquid fluid. Typical condensers/expanders for LTD parameters are plate heat exchangers (PHEs).

A pump is needed to move the working fluid, a typical pump for this type of cycle is a diaphragm pump. These are highly efficient and can work with most fluids and environments. However, most pumps require an electrical input lowering the efficiency of the process to approximately 4-8% on LTD systems below 75ºC [85], figures resembling TEGs.

This process can be efficient and useful if there is a safety protocol in place to handle flammable substances and a disposal protocol is set. [83]

2.3.4.3. Kalina Cycle and others

Another variant to the Rankine cycle is the Kalina cycle (see Figure 17). This process has proven to be 10-20% more efficient than the original cycle with steam. It essentially uses 2 substances, typically water and ammonia. The latter substance is added to provide thermodynamic reversibility achieving a higher thermodynamic efficiency [87].

Other cycles have also shown to be highly efficient in LTDs but fail to be a simple solution, such as the Organic Flash Cycle (OFC) or Power Flash Cycle (PFC), which are more complex than the Kalina cycle, adding components like flasher chambers and separating tanks. These components essentially filter mixture fluids into absolute gases or liquids as well as controlling its pressures.

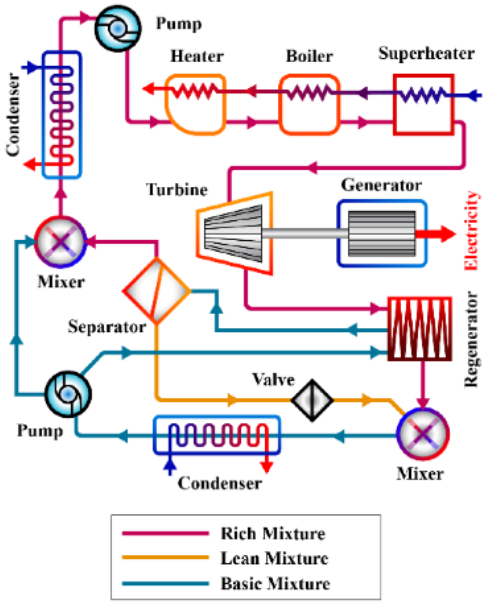


Figure 17 Kalina cycle [87]

These cycles have particularly been used in LTD systems. However, multiple loops and added steps in the system overcomplicate the heat recovery system which can only be useful in bigger scale projects.

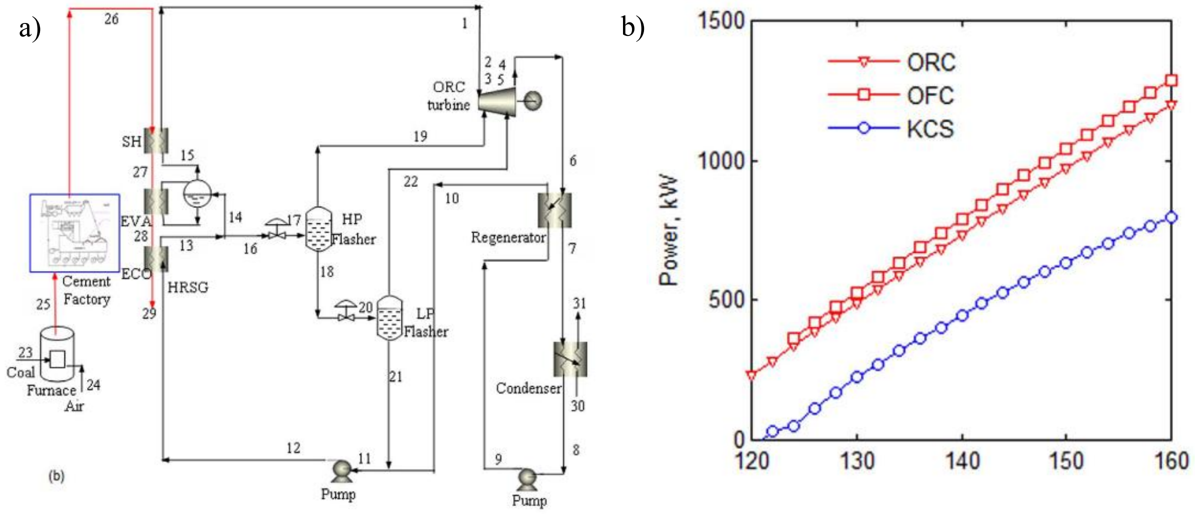


Figure 18 a) OFC in a cement factory for heat recovery b) Comparative study of ORC, OFC, and KCS plants [88]

These later cycles shown in Figure 18 prove to be optimal as heat recovery systems in industrial plants where electrolysers do not achieve a high temperature gradient en require temperature control. However, they require frequent maintenance and technical expertise to manage them. Plants which generate higher temperatures, reaching 300ºC, would benefit from steam turbines, as they are much simpler and produce energy more efficiently.

Simplifying these systems while decreasing as little as possible their efficiency allows them to be integrated in more industries.

2.4. Electrical circuit

In addition to the electrical generator, it being a TEG, a Stirling Engine or a turbine, a heat recovery system requires a complete loop to feed that generated power to the electrolyser.

For instance, turning components like turbines or engines are placed adjacent to generators to produce electricity. The desired output is DC because batteries require direct current for efficient charging and discharging, therefore generators like dynamos could be used [89].

A battery is needed to store the generated electricity. It can also supply the electrical output steadily to the electrolyser for an efficient process. In the case of using renewable energies for electrolysis, a small battery can store excess energy and supply the electrolyser when there isn't enough renewable power to generate hydrogen. Here, a heat recovery system would be able to supply the power to maintain a steady generation of Hydrogen.

In the event of generating AC current from the heat recovery system, components would be required to transform the current to DC. The simplest method is implementing rectifiers. They are typically constructed from diodes that force current to flow in one direction, therefore providing direct current. Once the current has been fixed it can then be stored in a battery.

The electrolyser's cells also require a DC power supply. This simplifies the system as common batteries require and supply DC current. In addition, most generators like dynamos give a DC output, therefore no current converter is required. However, voltage and current ratios must be analysed and fixed if necessary.

Supplying high voltage instead of high current saves losses in resistance generated by a high current supply. This is highly beneficial on any system, and more so in a process that doesn't produce much electricity like a low temperature gradient system.

The battery is used as a storage energy system in case of a surplus energy production, when the rate of electricity production becomes higher than the required by the electrolyser (likely in a system with HTD subsystem) allowing the energy created to not be lost.

On the other hand, in an LTD the electrical production only provides a percentage of the total electricity required to produce electrolysis. A battery can intake all electrical sources and then supply it to the electrolyser. Batteries like Redox Flow and Lithium-ion batteries show good properties for stationary applications [90].

2.5. Discussion

Having a low temperature gradient is a complicated environment for an efficient recovery of heat energy. Applying heat recovery systems in larger gradients would be more practical. For example, transforming the alkaline electrolyser into a pressurised alkaline electrolyser would generate temperatures between 363K to 403K [91]. Studying the possibility of implementing heat recovery systems could show to be more beneficial to control peak temperatures and to lower the electrical power input.

A practical system, that doesn't require much technical maintenance and has simple components can be a solution to save energy in many components apart from electrolysers. For example, thermal management systems for fuel cells are getting increasing interest in the aerospace sector. The heat released by the exothermic reactions in the fuel cell reach high temperatures. Being able to reuse this heat would mean an increase in efficiency in the electrical production system of the aircraft [92].

In addition, many common home and office devices radiate waste heat, such as fridges or computers among others. This constant waste of energy could potentially be reused for saving on electrical bills and create more eco-friendly buildings, where added weight is not a constraint in efficiency.

2.5.1. *Generating hydrogen from high temperature gradients.*

Increasing the temperature of the tank and the electrolyte decreases the voltage needed to produce a current density of 400mA/cm^2, for this same reason, less temperature in the tank means less current density (for the same Voltage input). In essence, decreasing the temperature decreases the performance of the electrolyser. For this reason, research has been made to utilise the heat to release hydrogen, instead of utilising it to generate electricity. Nevertheless, being able to have a temperature control shows to be a key factor in the efficiency of electrolysers as controlling temperature allows electrolysers to be smaller in size for the same power, decreasing the price of production and making hydrogen fuel more viable. Sudden changes in temperature can damage efficiency if the electrolyser is not built for certain temperatures, therefore having a heat recovery system can manage the temperature and avoid inefficiencies.

An electrolyser that cannot withstand high temperatures will require a system to control its internal temperature. The performance is limited by the materials used to store the electrolyte. Here, a heat recovery system would be beneficial.

2.6. Conclusion

A system that allows electrolysers to reuse its wasted energy must be versatile to different environments to assist LTD electrolysers in any scale project. In the case of green hydrogen generation, electrolysis relies on unreliable energy sources. Therefore, being able to create a steady supply of power for electrolysis is greatly beneficial and a heat recovery system is a potential method to do so.

In this chapter, many methods were analysed. The Stirling engine proved to be theoretically the most efficient under difficult environments and temperature scales. The Stirling Engine is believed to improve these systems, as well as most systems that emit heat as a by-product. As previously discussed, Stirling engines are also adaptable to specific temperature gradients by modifying the piston configuration. Unlike turbine generators, the maintenance is relatively low thanks to the simplicity of the engine. It is however important to note that like any real solution, the desired product depends on the variables on the project.

TEGs also proved to be highly valuable in any project that cannot provide constant maintenance and does not have the parameters for a more complex solution. TEGs are becoming increasingly popular thanks to new advancements in material science, particularly with methods to improve the efficiency of semiconductors. These advancements allow TEGs to increase their relatively low efficiency compared to other heat recovery systems.

Lastly, thermodynamic cycles proved to be complex and inefficient, but highly useful and used in large scale H_2 projects with high temperature gradients. Thanks to the variety of cycles and fluids, these turbine engines can be adapted to specific projects for maximum efficiency.

Theoretically, it was shown that the most efficient recovery system can provide a 40% return of energy from waste to useful, which translates to an overall potential **increase of 8%.** This improvement pushes the efficiency of an electrolyser from 75% to as much as 83%.

A practical heat recovery system can go beyond sustainable hydrogen production. Waste heat in big scale batteries and computers or households could have a big impact on energy demands.

This project hopes to promote heat recovery systems to projects anywhere in the world, as it only requires heat waste, a highly common byproduct. Sustainable projects and projects with scarce resources benefit from projects that maximise the efficiency of tools. In a world increasingly demanding a higher energy supply, this type of projects must be incentivised.

The first chapter identified hydrogen generation as an important aspect of a sustainable energy sector and the use of waste generated as essential to this process. This chapter has explored how to increase the efficiency of LTD hydrogen electrolysers and has identified materials capable of heat transfer as essential for success.

3. GROWING CARBON NANOTUBES FROM POLYESTER CLOTHING

3.1. Introduction

As identified in the previous two chapters, new materials, specifically Carbon Nanotubes, produced sustainably from waste could potentially revolutionise sustainable energy systems. This chapter details the experimental attempts to create and characterise these materials in a sustainable manner.
For this chapter, experiments were carried out to analyse the production of CNTs using polyester waste as a source of hydrocarbons. To do so, CNT growths were compared with and without polyester added to solution injected inside a Liquid Injector Reactor (LIR). Analysis of the samples was performed with Raman microspectrometry, SEM microscopy and Thermogravimetric analysis (TGA).

The aim of these experiments was to find sustainable carbon sources to generate carbon nanotubes. Finding cheap and sustainable sources enable new technologies in the energy sector. Special interest in CNTs was given due to its thermal and electrical conductivity, which can aid heat recovery systems in electrolysers.

Thermoelectric generators (TEG), reviewed in the last chapter, require special semiconductors to generate electrical current from a temperature difference. CNTs have an average heat transfer coefficient of approximately 49.11 $Wm^{-2} \cdot K^{-1}$ [93]. Therefore, they provide high thermal conductivity. For this reason, CNTs can be used to dope n-type semiconductors, allowing TEGs to release electrons more frequently. Research suggests that the power output of CNT doped n-types is the highest among organic TEG materials and close to that of the most promising inorganic materials, such as Bi_2Te_3 [94].

Carbon nanotubes also offer improved performances in hydrogen and electrical storage technology, because CNTs increase the surface area of active areas of electrochemical systems [95]. Metal hydrides for example, benefit from an increase in surface area to improve its desorption kinetics to release hydrogen more efficiently [96].

CNTs also provide a carbon-based method to transport electricity, thanks to its high electrical conductivity. Therefore, generating CNTs from carbon waste, provides a sustainable material that can substitute precious and rare materials. This makes these experiments relevant to innovate in the energy industry as well as in waste management methods.

3.1.1. *Background literature review*

Since the discovery of spherical structures composed of unsaturated carbon atoms called fullerenes, new carbon structures have been researched to find new materials with desirable chemical and mechanical properties.

Eventually, cylindrical structures were synthesised with a similar carbon structure to graphene. These carbon-based cylinders are carbon nanotubes (CNTs) and have proven to produce fascinating mechanical and electronic properties, such as light weight, high tensile strength, and thermal conductivity. These properties opened doors to useful applications such as hydrogen and lithium storage, electron-field emitters, nanoprobe devices, new composites, and substitutes of heavy metals, harmful to the environment [97]. These new materials can then aid new systems in sustainable projects, like hydrogen or electric transportation, where weight is a great disadvantage for efficiency [98].

Currently, at Swansea University, research is being conducted to optimise this promising material with the hopes of mass production and availability. To do so, various plastics used as a source of hydrocarbon chains are being trialled to increase the yield in carbon nanotube production. If successful, production of CNT could be another method of recycling and reusing polyester plastic, vastly used in the clothing industry, among others.

3.1.2. *Polyester as a hydrocarbon source*

Polyester is a common plastic used worldwide due to its durability and low price. For these reasons, polyester fibres are used in clothing, fabrics, furnishings, and insulation; products from massive industries which produce tonnes of product every year [99]. Combining the massive production to the high rate of consumerism worldwide, the rate of waste is high and increasing. These products therefore must be disposed in a manner that doesn't accumulate waste, for the wellbeing of humanity and nature. Typical ways to achieve this are methods like recycling the materials to produce the same or similar products. This study researches the ability to chemically recycle waste material to restructure it into new high-performance materials.

Currently, the most used method is burning the disposed waste. This process generates toxic gases like polycyclic aromatic hydrocarbons, carbon monoxide, as well as microplastics, harmful for breathing organisms [100]. The proposed chemical recycling process is an innovative way to eliminate polyester waste faster as it creates a new demand for the disposed plastic. In addition to this solution, this process could find a cheaper method to create new materials which are highly useful for new technologies but lack availability [101].

Carbon based materials like carbon nanotubes, carbon fibre and graphene have astonishing properties thanks to their atomic structure. Carbon is also found in plastic, as plastic is made of polymer chains, which are hydrocarbons (mostly carbon and hydrogen atoms).

The reason why polyester is an interesting plastic to investigate is its chemical composition. Polyester is a plastic made of carbon chains with the presence of a highly polar sp^2-hydridised carbonyl bond (C=O), which is susceptible to nucleophilic attack [101]. Carbonyl bonds in polyester have oxygen atoms which are, in theory, a pollutant element in chemical vapour deposition (CVD); a method to restructure carbon chains. However, new studies have shown that presence of oxygen and carbon dioxide in the process can increase the yield of carbon nanotubes. For instance, the University of Tokyo has proven that adding CO_2 slows the growth rate due to carbon removal from catalysts [102]. This extends the lifetime of the growth, which lengthens the nanotube arrays. It was also found that the density of the carbon nanotubes increased, by analysing the time at which the CO_2 was supplied compared to the start of the nanotube growths. Their paper mentioned that the effects of the added oxidants can be explained by the alteration of the supersaturation level of carbon on the catalyst, suggesting the importance of choosing the appropriate balance of carbon sources and oxidants for the simultaneous control of density and length of carbon nanotube arrays.

Pyrolysis on polyester will create small carbon and oxygen molecules, many of which can be CO_2, therefore these particles being present in the growth process, could potentially improve CNT samples.

Thermal pyrolysis allows complex polymers in plastics and composite plastics to be reused to create new non-plastic materials by applying heat to decompose the long carbon chains [98]. Mixing plastics in a solvent has been shown to increase carbon density in the process, which can lead to increased production capacity of CNTs via chemical recycling of mixed plastics and solvents [104].

Other plastics like polystyrene have been analysed in the past showing increase in CNT yield, and a similar quality in electrical resistance, showing that CNTs from plastic can also be used in electrical materials [105].

3.1.2.1. Dissolving Polyester

To choose a dissolving method, it must be considered that the solvents must be deoxygenated. Strong reducing agents can be applied to do so, such as chromium sulphate, vanadous sulphate, hydrazine, and sodium sulphite. Oxygen solubility generally decreases as solvent polarity increases; therefore, polar solvents can help avoid oxygen in the solution. Other factors to consider are the pressure and temperature at which the experiment is conducted, and the solvent composition of mixed solvent systems. refluxing was the most effective technique followed by helium purging, vacuum degassing, and ultra-sonification [106].

These processes do not eliminate completely the oxygen in the solution. This proved to be advantageous as there is evidence to suggest that carbon oxides were produced improving the quality of the growths performed in this experiment decreasing the CNT diameters [106].

The principle “like dissolves like” is commonly used to know what compound dissolves what. The comparison relies on dispersion cohesive energy (ED), polar cohesive energy (EP), and hydrogen bonding (EH). Esters are known for not being good solvents compared to only “carbon and hydrogen”-based molecules. Therefore, presence of electronegative elements like oxygen or nitrogen in an organic compound produce a compound that is non-solvent to materials which have a low level of electronegativity.

Looking at these properties in polyester, mainly in its polarity, it can be concluded that a slightly polar solvent is needed for ketone bonds [107]. Even though it has non-polar aromatic compounds, it still has oxygen, making the compound slightly polar. From this information, it can be concluded that polyester should dissolve, but a rapid dissolution is not guaranteed using only toluene and m-cresol [104]. Toluene was used because polyester was considered non-polar enough to be dissolved by it and because toluene has a low viscosity. In addition, in the gas phase, toluene can form C2 units, which leads to CNT nucleation [108]. M-cresol can also be used with Toluene because it is slightly polar, with oxygen in its composition, making it similar in polarity to polyester.

3.1.2.2. Chemical vapour Deposition (CVD)

CVD is achieved by creating gaseous carbon molecules, which are decomposed on a substrate in the presence of catalyst metal particles under a high temperature environment. CVD was chosen because it is a method known for not generating high levels of impurity, as well as being a method that allows scaling the process for mass production [109]

CNTs can be synthesised using injection chemical vapor deposition method (CVD) inside a Liquid Injector Reactor (LIR). This method consists of injecting a carbon-based mixture in a high temperature environment. The environment is generated by the LIR. The LIR consists of 2 furnaces revolved around a detachable quartz tube, where the CNTs deposit. This environment breaks down the carbon chains, generating single carbon molecules, which are the building blocks of CNTs.

The dissolved plastic and the solvents require a catalyst for carbon molecules to form CNTs. Ferrocene is a proven high-quality catalyst for CNT growth [110]. Ferrocene allows carbon to deposit on the surface of the quartz tube under CVD and allows carbons to bond with each other, creating carbon nanotubes [111].

3.1.3. *Raman Spectroscopy for CNT analysis*

Raman spectroscopes determine the bonds by exciting an electron. That electron has a characteristic change in energy which is noted by the spectroscope. That value determines the type of atom bonds in the sample [109].

Putting carbon samples under a Raman microscope allowed to determine the carbon characteristics of the synthesised carbon. Thanks to the specific characteristics of CNTs, it is possible to estimate if the sample contains CNTs and similar structures.

3.1.2.3. G:D peaks

The G peak is located around $1590cm^{-1}$. This peak tends to break into 2, called the G^+ and the G^-. G^- is indirectly proportional to the cross-sectional area of the nanotubes, so the smaller the peak the larger their diameter. The D peak is adjacent to the left of the G peak. It is placed at around $1350cm^{-1}$. The intensity ratio between the G and D peak (G:D ratio) shows the quantity of defects in the CNTs. The higher the G:D ratio the less defects will be found in the CNTs [111].

The nature of the D peak gives information on the type of nanotube in the sample. As shown in the graphs, a small D peak show semiconducting properties and highly oriented pyrolytic graphite (HOPG) or SWCNT with semiconductive properties. A broad and high D peak tells us that the nanotubes have metallic properties. The difference between metallic and semiconducting is caused by the diameter and the chiral angles of the carbon bonds. Metallic SWCNTs (m-SWCNTs) can resist ultrahigh current densities due to ballistic electron transport (negligible resistance), while semiconducting SWCNTs have high current on/off ratios and high carrier mobilities [113].

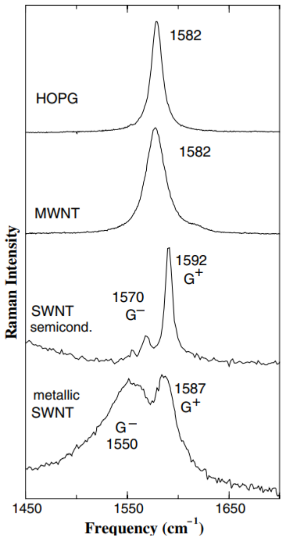


Figure 19 Types of G peaks [114]

The reason why CNTs can adopt either property is because a change in the chiral angle between the carbons give the electrons different energy levels for their valence and conduction bands. The chiral angle of the carbon bonds changes the overall carbon structure. To differentiate between the two main carbon configurations, the two types have been called “Armchair” and “Zigzag” due to the shape each configuration portrays. The “Armchair” shape in the carbon structure can produce metallic or semiconducting properties as the valence band and the conduction band can overlap or not overlap. A “Zigzag” shape will always give a metallic property as there’s a presence of a localised edge states at the Fermi level, therefore the valence and conduction bands always overlap [115].

Normally, the D peak and G$*$ peak dispersion would be 53 and 106 $cm^{-1}eV^{-1}$, respectively for the D peak and the G$*$ peak for SWNTs [115]. If the length of dispersion of the peak is larger, it is a good indication of CNTs with metallic behaviour.

3.1.2.4. RBM (Radial Breathing Mode)

The RBM peaks are unique to CNTs as they are not present in other graphene related structure [116]. These peaks are approximately between 100 to $300cm^{-1}$ in the frequency axis (Raman shift). RBM allows us to predict the diameter of the nanotubes. If the peak appears with a higher Raman shift, the diameter of the tubes within the sample is smaller [117, 118]. Analysis on the SEM gives a more accurate measurement of the diameter size on each nanotube.

To know the number of layers in each tube, the initial section of the Raman shift is analysed, with a high sharp peak early if there are single wall nanotubes and a later peak around 250 cm^{-1} to $350cm^{-1}$ if there's a presence of double walled nanotubes [117].

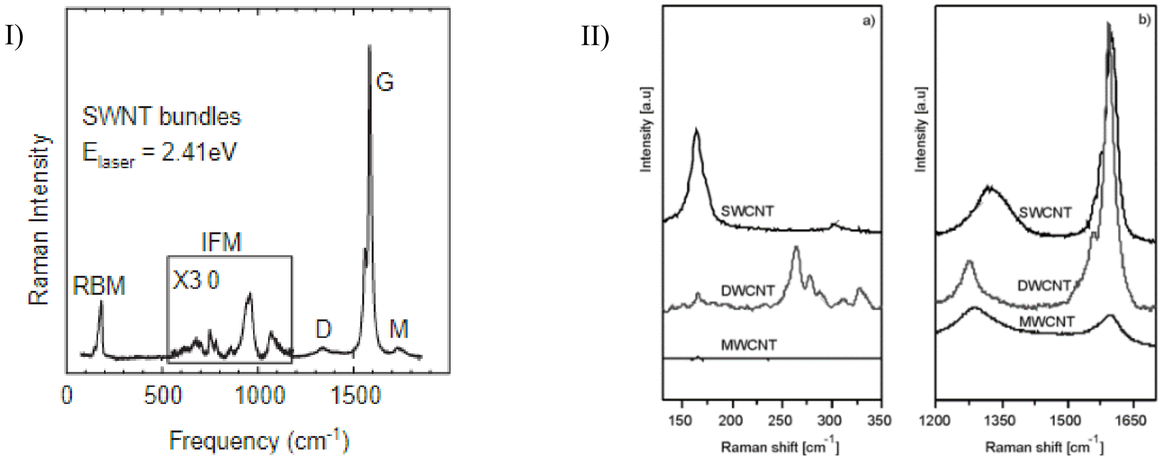


Figure 20 I) Raman graph showing IFM II) a) RBM band b) D and G peaks (laser 785nm) [117]

The D and G bands also show the number of walls as shown in figure 20 I) and II). Two small and broad D and G peaks, reveal the presence of multi-walled CNTs. The D and G peaks are illustrated in the right-hand rectangle of figure 20 II). There, it can be seen how the larger the G peak, the likelihood of single wall nanotubes (SWCNT) increases.

Next to the RBM there can be disturbance as shown in figure 20 I), called IFM peaks. These small peaks are a characteristic of SWNT bundles, that is imperfect nanotubes with stuck extra structures on its side but single walls, nonetheless. [119]

3.1.4. *Understanding carbon structures under SEM images*

The Scanning Electron Microscope (SEM) is a highly precise instrument, useful to analyse a material structure to its nanoscale [120]. As CNTs' diameters range from as little as 1nm to over 100nm, it is necessary to use a microscope with the high precision of a SEM.

The SEM works by emitting a beam of electrons under vacuum to the surface of a sample. This beam scans the topography of the surface sample. The microscope can detect the scattered electrons after being in contact with the surface. The level of energy of the electrons deflected by the sample is measured and mapped. With that information the SEM can produce a high-quality image on a nanoscale.

3.1.2.5. Potential structures to be captured under SEM.

Tubular structures under the SEM can be difficult to interpret as there are more than one structure resembling CNT's.

Polyester chains are fibres much thicker than nanotubes. However, as they were broken down, they can still be present in smaller form. The average length is approximately 10 μm and a method to check their presence is through thermogravimetric analysis (TGA). Literature shows degradation at T_m=250°C [119] for polyester fibres, therefore after CVD, where the solution is at over 800ºC, it is unlikely to find them.

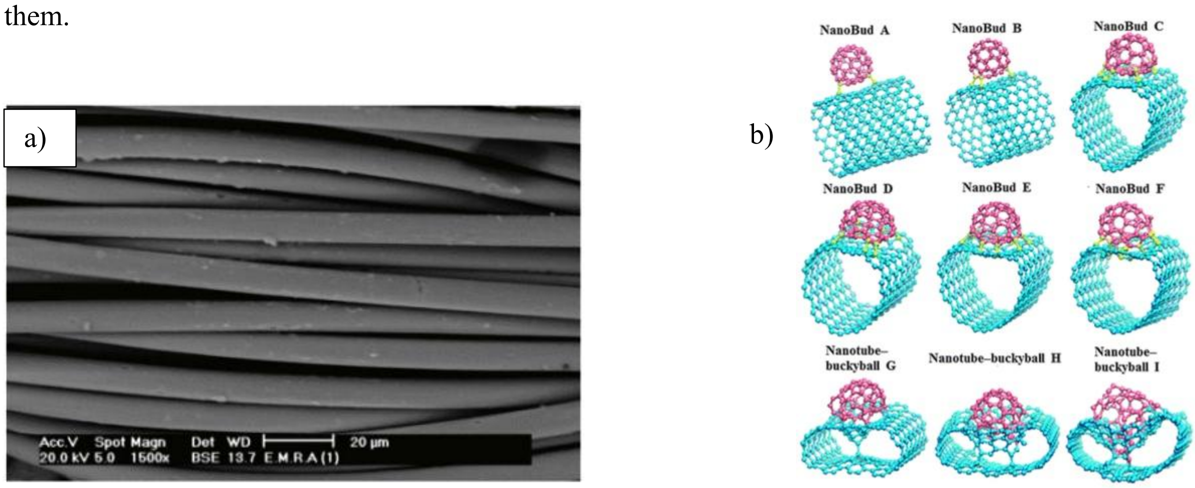


Figure 21 a) SEM Image of Polyester fabric [121] b) Diagram of CNBs [123]

As shown in figure 21 b), Carbon nanobuds (CNB) are structures that can also appear in most samples. These carbon chains are carbon nanotubes with spheroidal fullerenes attached to the tubes [123].

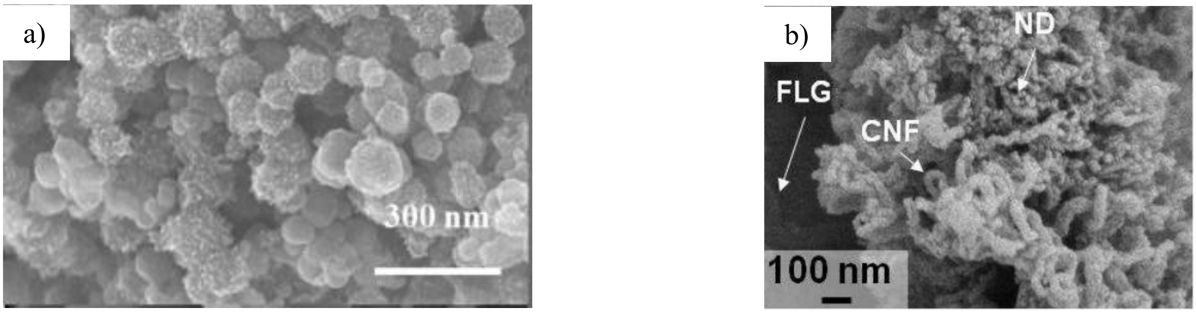


Figure 22 a) SEM Image of CNHs [125] b) Carbon nanofiber (CNF) and nanodiamond (ND) [127]

Other variations are carbon nanohorns (CNH), containing a cone (or horn) shape with a graphene structure, as shown in Figure 22 a). CNHs are highly porous, making it useful in fuel cells and gas storage [124].

Lastly, some carbon nanofibers (CNF), also known as vapour grown nanofiber, can be formed in the CVD process and can show characteristics of CNTs. These particles resemble nanotubes entangled into themselves as shown in figure 22 b). These structures can be expected to be found in CNT growths, as they are also layers of graphene. These structures aren't perfectly cylindrical, but they are still highly valuable as additives in composite materials [125].

3.1.5. *Using Thermogravimetric Analysis (TGA)*

TGA is a technique used to analyse the components of a sample, by increasing the temperature and mapping the loss of mass of the sample. The weight change on specific temperatures reveal what elements are present in the sample. The thermal stability and the purity of synthesised CNTs can be studied by thermogravimetric analysis be observing how much the sample withstands heat before decomposing.

To understand what structures are shown by the TGA, analysis must be done on the ignition temperatures of expected structures. The ignition temperature of SWNT is around 425ºC, although in practical experiments this value has reached 600ºC. Multiwalled carbon nanotubes have a higher ignition temperature at approximately 700ºC. Other materials like highly graphitized carbon fibres reach up to 800ºC [121].

In summary, A study on Raman, SEM and TGA was completed to be able to analyse the results of the synthesised CNTs. To develop on the studied methods, polyester waste was dissolved in 50:50 toluene:m-cresol solvent system and injected into a LIR at 500ºC and 900ºC for CVD. This was the base example for creation of CNTs. The produced carbon nanotubes were then to be examined using Raman, SEM and TGA to investigate the properties of the resultant CNTs and their suitability to the use cases raised in chapters 1 and 2.

3.2. Experimental Method

3.2.1. *Dissolution and Chemical Vapour Deposition experiments*

Growths were completed by dissolving polyester clothing in m-cresol and toluene solvents in a 50:50 ratio. Polyester was shredded to increase the rate of dissolution, and it is submerged in the solvents.

During the dissolution process, the solvents conveniently clean the plastic. In addition, the non-soluble materials crash out of solution [128].

Figure 23 a) Dissolution of polyester plastic utensils. b) Reflux system for dissolution

The mass of Polyester inserted in the solvent mixture was 10wt% (10% of the total solution weight, 90% being the M-cresol and Toluene solvents). To achieve a faster dissolution, the mixture was heated under a reflux condenser, as shown in Figure 23, to allow a higher temperature without evaporating the solvents. The mixture was heated to 100ºC and left until the mix was homogeneous. The reflux was kept under a nitrogen atmosphere to avoid oxygen ingress, an issue for the CVD process [106].

A sample was collected and centrifuged to eliminate non-dissolved particles. Ferrocene was the chosen catalyst for the chemical process. Ferrocene was added at 5wt% of the mixture.

Ultrasound and other vibration methods were used afterwards to spread the catalyst evenly through the mixture. In addition, ultrasound released the dissolved oxygen from the solution by providing energy for oxygen molecules to form bubbles in the mixture [106].

10ml were extracted to be injected in the Liquid Injector Reactor (LIR) at a rate of 0.8ml/min. The solution containing carbon molecules is injected steadily from a syringe into the quartz tube with the aid of an injector control rate device.

Hydrogen and nitrogen gases are pumped in the LIR at hot conditions. To achieve chemical vapor deposition, the LIR furnaces were heated to 500ºC and 900ºC separately. Such a high temperature was chosen as it’s been proven to increase the purity of the carbon nanotube growth [116]. Gases are then extracted at the opposite end of the LIR. The LIR was layed out as shown in Figure 24.

The mixture is injected for a period of approximately 12.5 mins once the LIR is heated on a stable environment. Following this, the LIR is left to cool down and Hydrogen and Nitrogen are turned off at 600ºC and 400ºC respectively. Once the LIR is close to room temperature the carbon was extracted and measured to then be weighted.

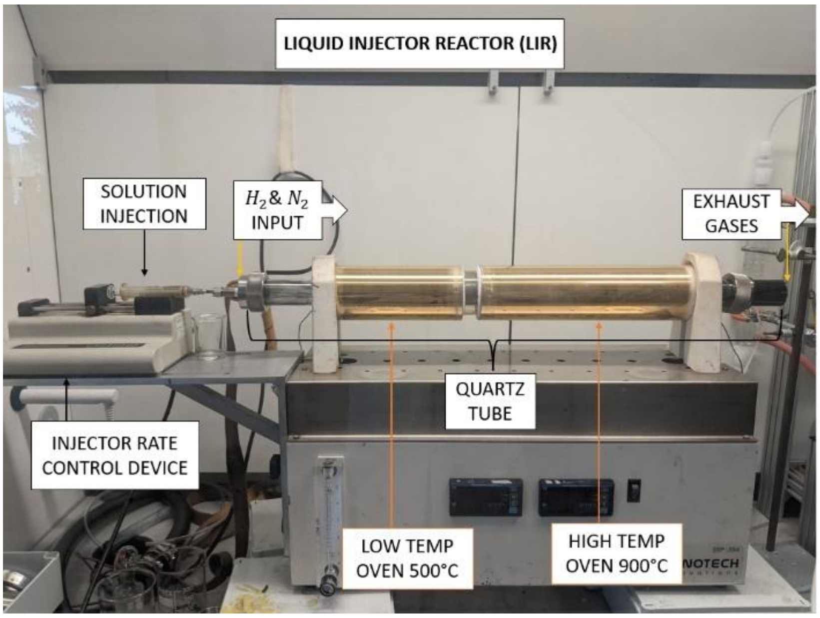


Figure 24 Experimental LIR for CVD of CNTs

3.2.2. *Raman microspectroscopy for CNT analysis*

Analysis was done using a Renishaw inVia Raman Microscope, at 633 nm and 785nm wavelength, (or 1.96eV and 1.58 eV excitation), using a 50× LWD lens. The data was acquired with 2 accumulations between $100\ cm^{-1}$ and $3300\ cm^{-1}$ with cosmic-ray background removal applied. The objective was to observe if the samples with polyester produced a different G/D peak ratio compared to the control samples and estimate if multi-wall or single wall nanotubes have been produced. The reason why different frequencies were used was to expand the number of CNTs detected by the Raman [97, 109].

The CNT samples were placed on microscope slides and placed inside the microscope section of the Raman. The microscope inside the Raman offered visual aid to search for potentially CNT rich locations. Then, spectroscopy was performed in the desired locations of the sample, first using 1.96eV and subsequently 1.58eV frequencies on the same coordinates. 3 measurements in different locations were completed per sample, with evidence of CNT presence, judging by the spectroscopy graph output. All samples were studied.

3.2.3. *Scanning Electron Microscope (SEM)*

Zeiss Evo LS25 SEM was used to take images of the surface morphology. With these images, the diameter of the CNTs was be measured.

To prepare CNT samples for SEM, silicon plates were used to deposit the sample. A base to fit the sample into the microscope was added and carbon-based tape was stuck to improve the conductivity of the plate to avoid disturbances in the image quality [129]. Then, the SEM is vented to generate a vacuum atmosphere. Multiple checks were completed to ensure maximum vacuum was reached, to avoid any distortion in the imagery generated by the SEM microscope. Once the SEM is properly set up, the proximity of the sample to the lens is modified. For the CNT samples, the distance chosen ranged from 6.5mm to 7.5mm. Then, the eV of the beam was set up to 5KV. The samples were scanned until a group of CNTs was found. A picture was then captured, and a second augmented picture was taken to later measure the diameter of the CNTs.

ImageJ was utilised to measure the diameter of the CNTs within the SEM pictures obtained. To compare results, histogram graphs were made per sample with their respective average and median. To achieve a high precision, the scale indicated in each picture was added in the "Set Measurements" tool. Then, the equivalent length (in pixels) was indicated. With that similarity, lines were drawn perpendicular to the CNTs zooming in until the limits of the CNT were clear. This was then repeated until there was an appropriate sample size (higher than 80 measurements). Once the sample was taken, the values were put in Origin where they were analysed with the histogram tool. The histograms and the calculated average and median allow a comparison of the samples, as shown in Table 5.

3.2.4. *Thermogravimetric Analysis (TGA)*

A sample with polyester and a sample without were put under TGA. To do so 50mg were placed on the precision balance. Once placed, the furnace generates an increasingly high temperature under a controlled atmosphere. The temperature increased from ambient temperature to 1000ºC. The loss of mass was recorded, and a graph was generated to analyse the content of the sample.

The percentage of iron present in the samples stays similar (6.5%-7%) in all samples. That value was measured and controlled in the creation of each solution before it was injected in the LIR. Therefore, it doesn't interfere with the comparison of CNTs with and without polyester.

3.3. Experimental results

3.3.1. *CVD mass results*

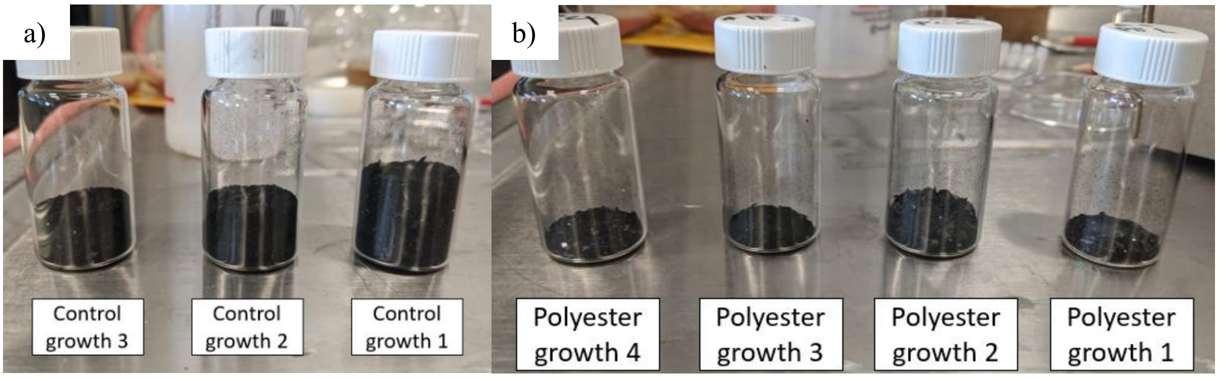


Figure 25 a) CNT growths without polyester AC3 AC2 and AC1 b) CNT growths with polyester P4, P3, P2 and P1

Table 4 Mass of all CNT growths

	CONTROL GROWTHS	PE GROWTHS
MASS (g)	1.254	0.410
	1.335	1.014
	1.195	0.361 (Outlier)
		0.662 (Retry)
AVERAGE (g)	**1.261**	**0.695**

Figures 25 a) & b) show the growths made according to the explained method. A smaller yield of carbon was synthesised adding polyester using the same liquid injection process and CVD for all growths. A 45% decrease in total mass was found, as shown in Table 4. However, a key factor to consider is that the current method used has been previously tailored to obtain the maximum yield in growths out of toluene and m-cresol solvents only.

3.3.2. *Raman spectroscopy results*

5 Raman samples were taken of each growth on different locations. Figure 26 and 27 are graphs drawn from the real values obtained in this thesis' experimental data. They are some of the many graphs made with Raman, picked because they showed the clearest relevant peaks. A full library of Raman spectra taken is shown in the appendix.

3.3.2.1. Description of growths without polyester (control samples)

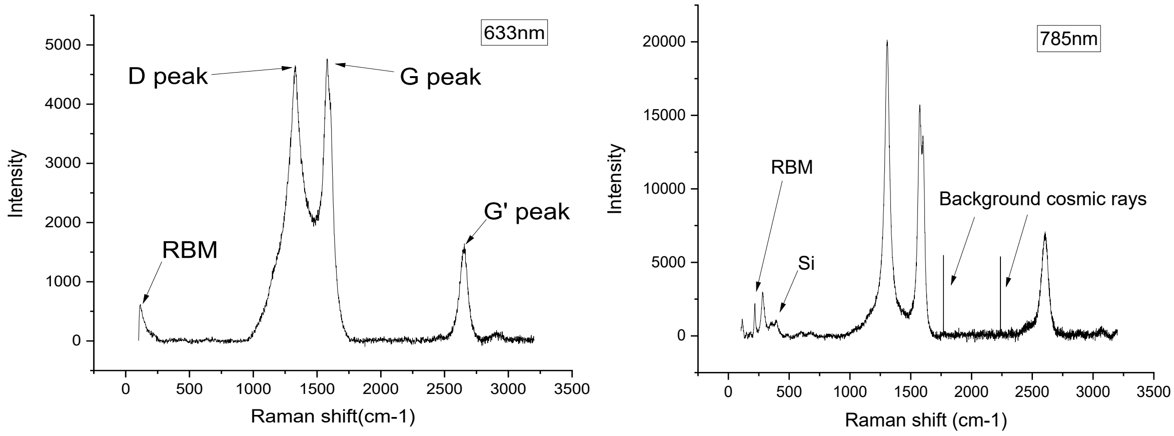


Figure 26 Raman spectroscopy of experimental samples without polyester at 633nm and 785nm

The control samples are samples solely made from solvents (m-cresol and toluene). The Raman spectroscopies of these samples show clear signs of carbon nanotubes with RBMs at 150 cm^{-1} as shown in Figure 26. These RBM peaks and the presence of a G peak are characteristics of SWNT [130]. The G:D ratio > 1 also implies well defined CNTs. All samples showed a peak at around 2800 cm^{-1}, called the G' peak. This band gives an indication of the doping of the structure, given by the reaction with all sp^2carbon electrons. This was expected and is irrelevant as using CVD method is known for producing some impurities [131]. Other (more expensive) methods will yield samples with a higher purity. Peaks next to RBM in the 785nm graph of figure 26 shows other elements present like Silicon (Si) which can come from the plate of the sample [115]. The RBM peaks close to 0 indicate the diameters of the nanotubes to be on the larger side of the spectrum.

The discrete bands at the G peak are characterised as G^- and G^+ bands. These bands do not show in HOPG (pyrolytic graphite) and barely appear from MWNTs [117], while they do exist distinctively in SWNT as described in Figure 19. Therefore, the Raman graphs extracted from the samples are encouraging, showing samples with not too protuberant peaks, suggesting nanotubes are present.

3.3.2.2. Description of growths with polyester

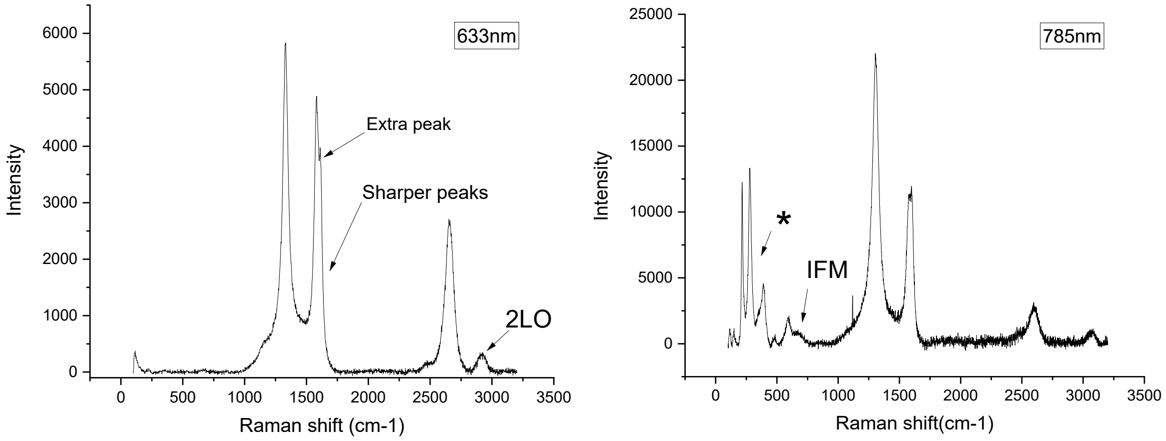


Figure 27 Raman spectroscopy of experimental samples with Polyester at 633nm and 785 nm

Most Polyester samples showed a similar quantity of single walls and double wall nanotubes, due to differences in their RBMs. Data from the experimental growths vary, but polyester samples show to have less SWNT predomination compared to the control samples (growths made of solvents solely) [132].

The high and discrete G peak shows that the samples have higher semiconducting properties, as explained in the literature review, when polyester is applied. This means that the structure of the nanotubes tends to be an *armchair structure*. The data also suggests *zigzag structures* are present as the peaks of all the samples vary without showing a clear trend.

Polyester samples also showed a tendency to have multiple peaks higher up in the Raman shift. This can indicate smaller diameters, as explained in previous chapters. The RBMs of polyester in a higher Raman shift also predicts smaller diameters.

The asterisk “ * ” inserted in the 785nm graph of Figure 27, indicates the peaks that represent potential impurities from different elements present. Not all Raman graphs showed peaks as high as the peaks shown in Figure 27. In essence, the level of impurities varied on each sample.

The IFM section in the 785nm of Figure 27 shows that there are bundles present in the nanotubes, but it also shows presence of SWNT. These peaks indicate a presence of some non-smooth tubes which can potentially be CNB (carbon nanobuds).

The Low G:D ratio peaks on all samples show the presence of amorphous carbon [133]. Carbon nanofibers (CNF) have a high D and G peak as the ones produced by this experiment’s sample, making CNF the most likely particle produced.

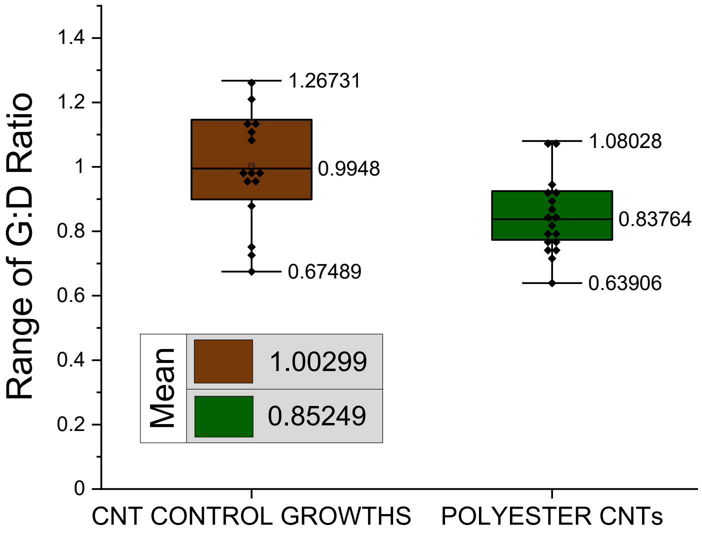


Figure 28 G:D ratio comparison of CNTS without vs with polyester. Each black dot represents a discrete sample.

The used Raman graphs showing G and D peaks are given in the appendix.

The height ratio of the G and D peaks was taken and plotted in Figure 28 to compare the product quality of CNTs with polyester and CNT growths with no polyester.

3.3.3. *SEM results*

3.3.3.1.Control samples

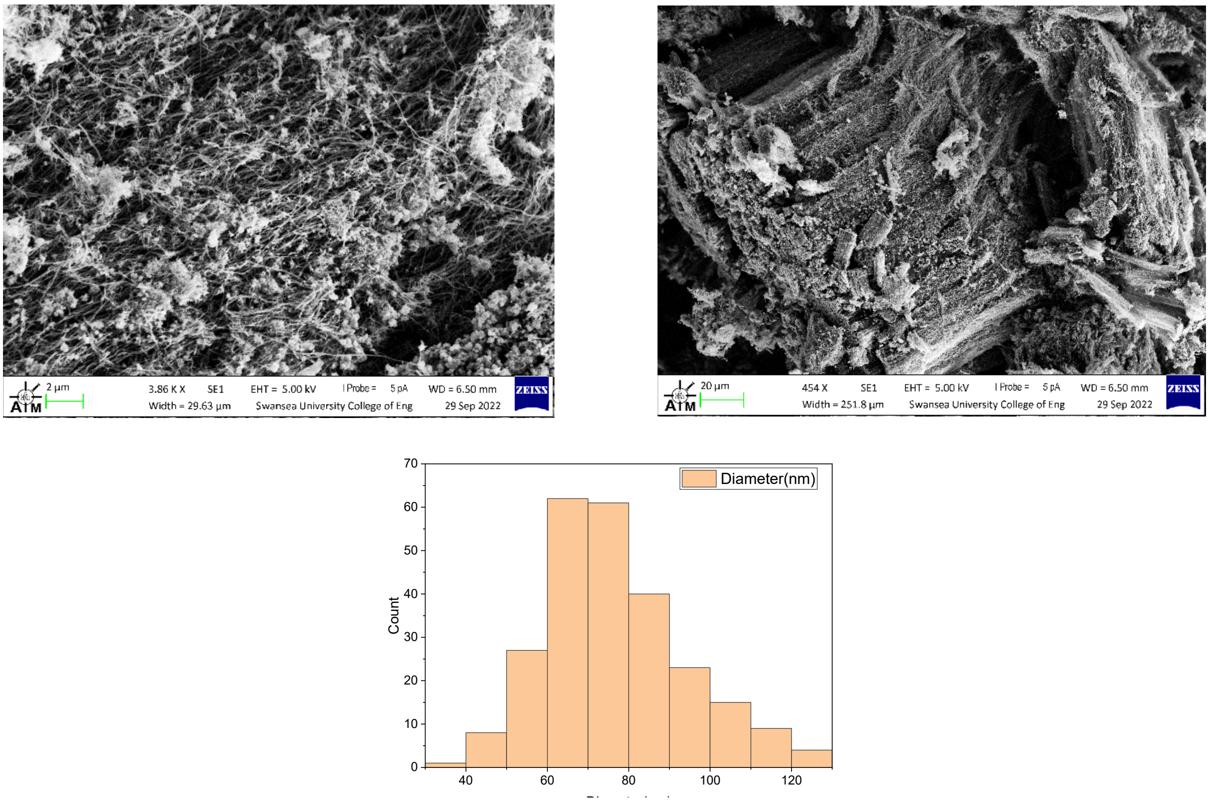


Figure 29 SEM Images at 2µm and 20µm scales and histogram of CNT diameters of First Control sample AC1

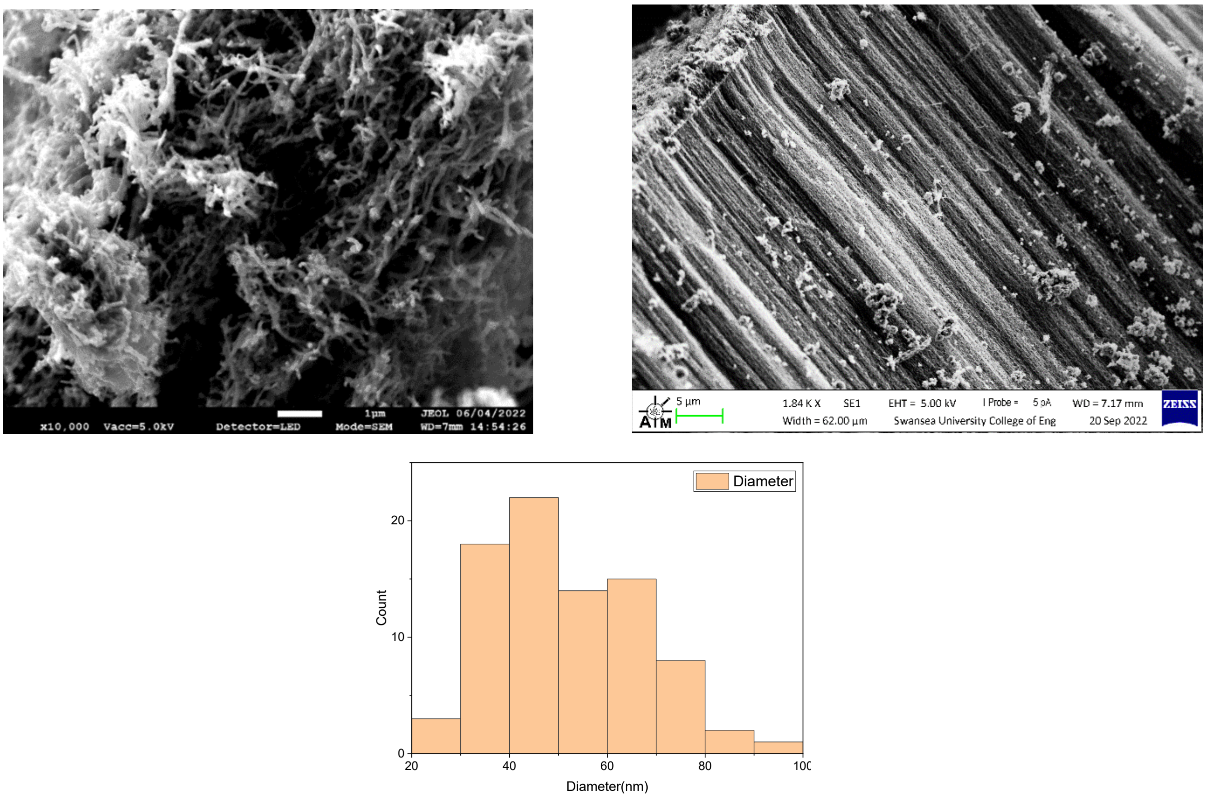


Figure 30 SEM Images with 1µm and 5 µm scales and histogram of CNT diameters of Second Control sample AC2

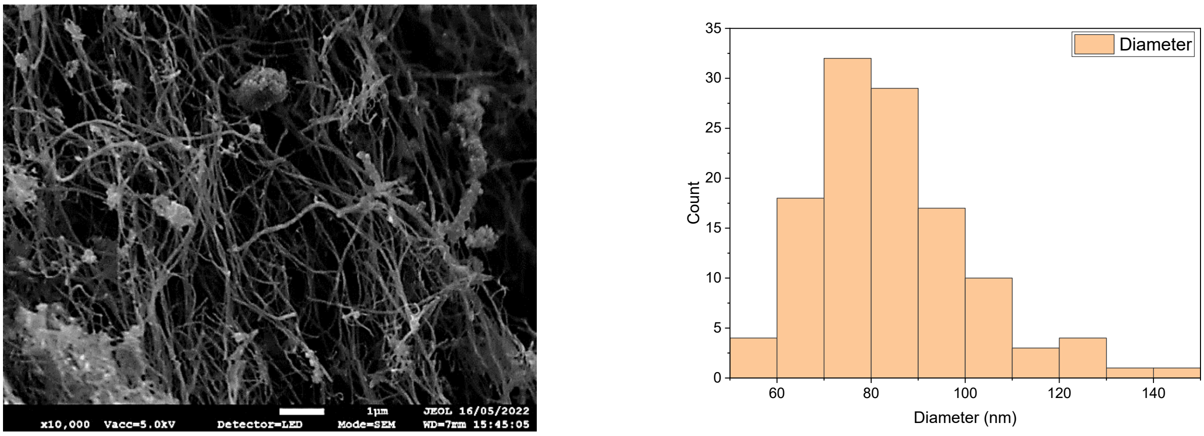


Figure 31 SEM Image with 1µm scale and histogram of CNT diameters of Third Control sample AC3

3.3.3.2. Polyester samples

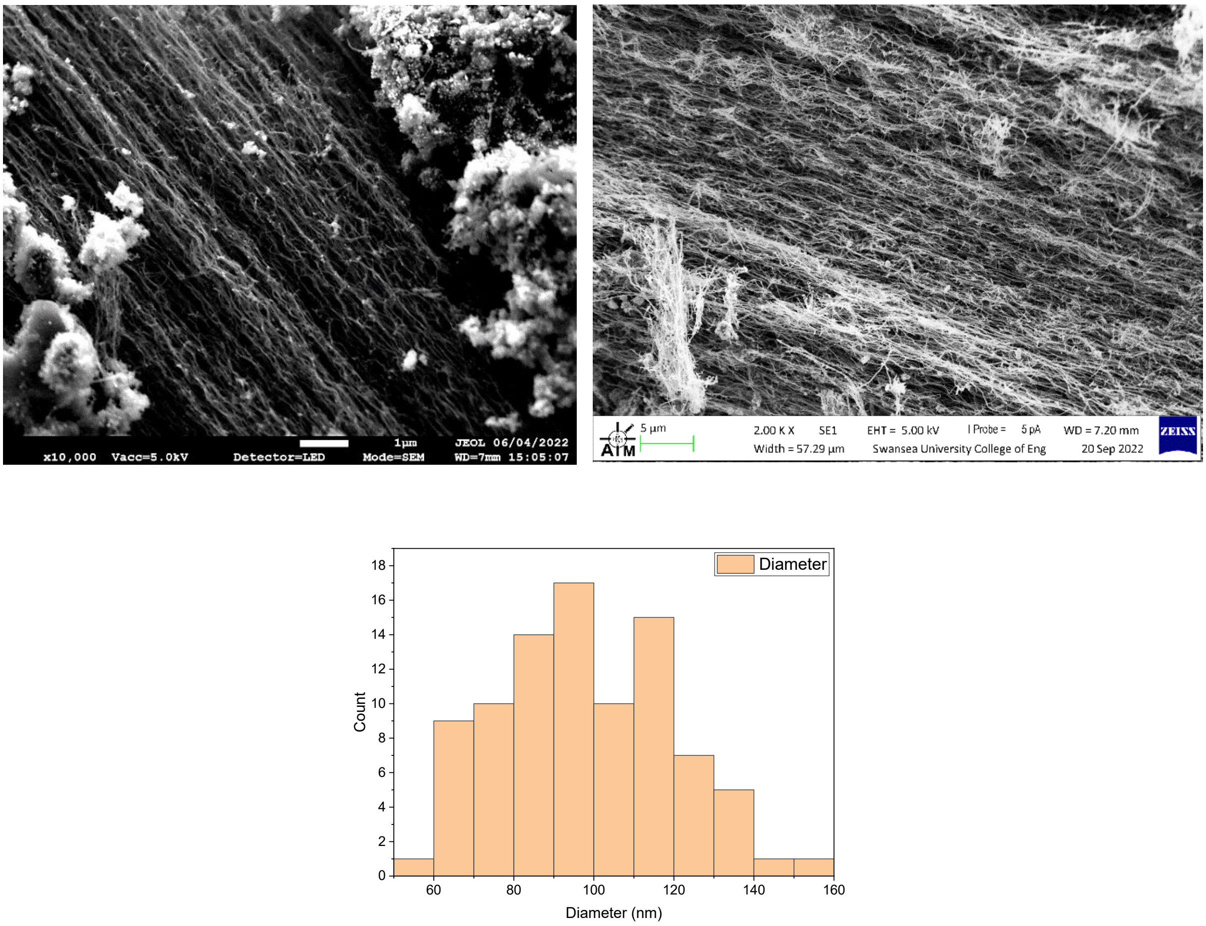


Figure 32 SEM Images at 1µm and 5µm scales and histogram of CNT diameters of polyester sample 1 (P1)

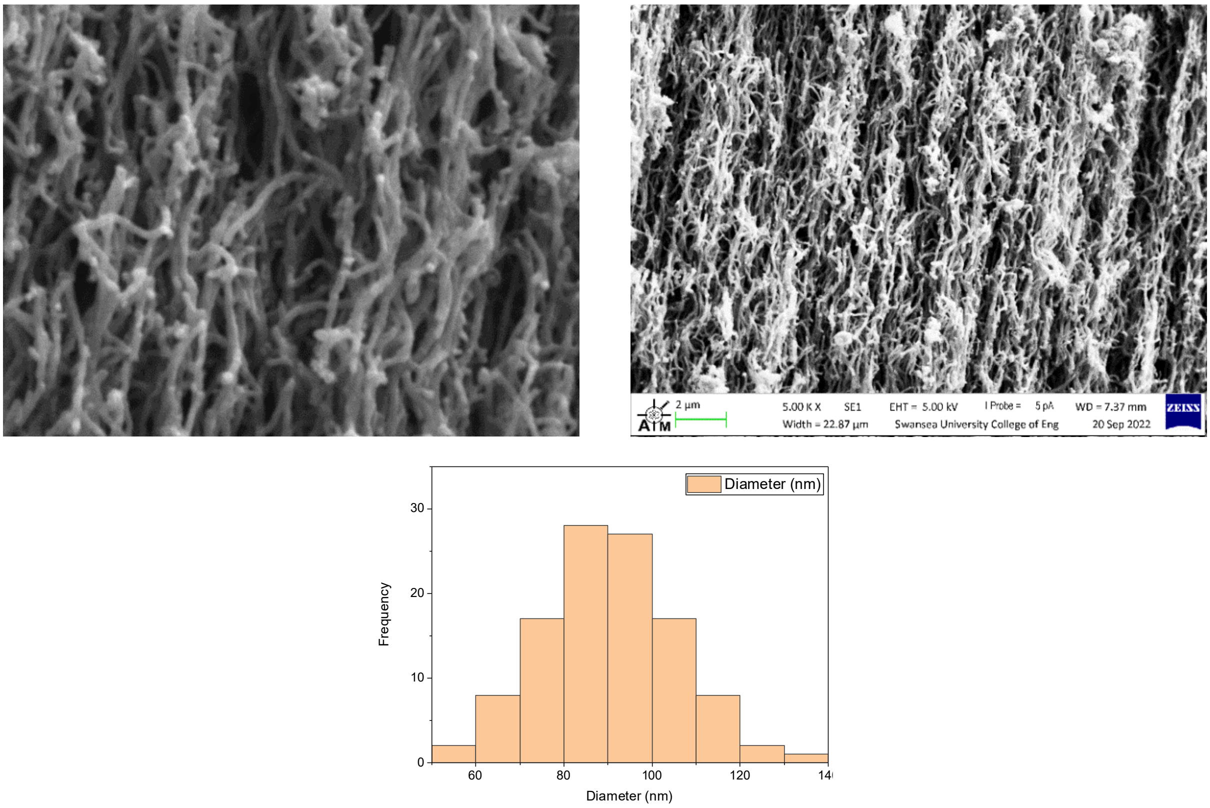


Figure 33 SEM Images at 10µm and 2µm scales and histogram of CNT diameters of Polyester sample 2 (P2)

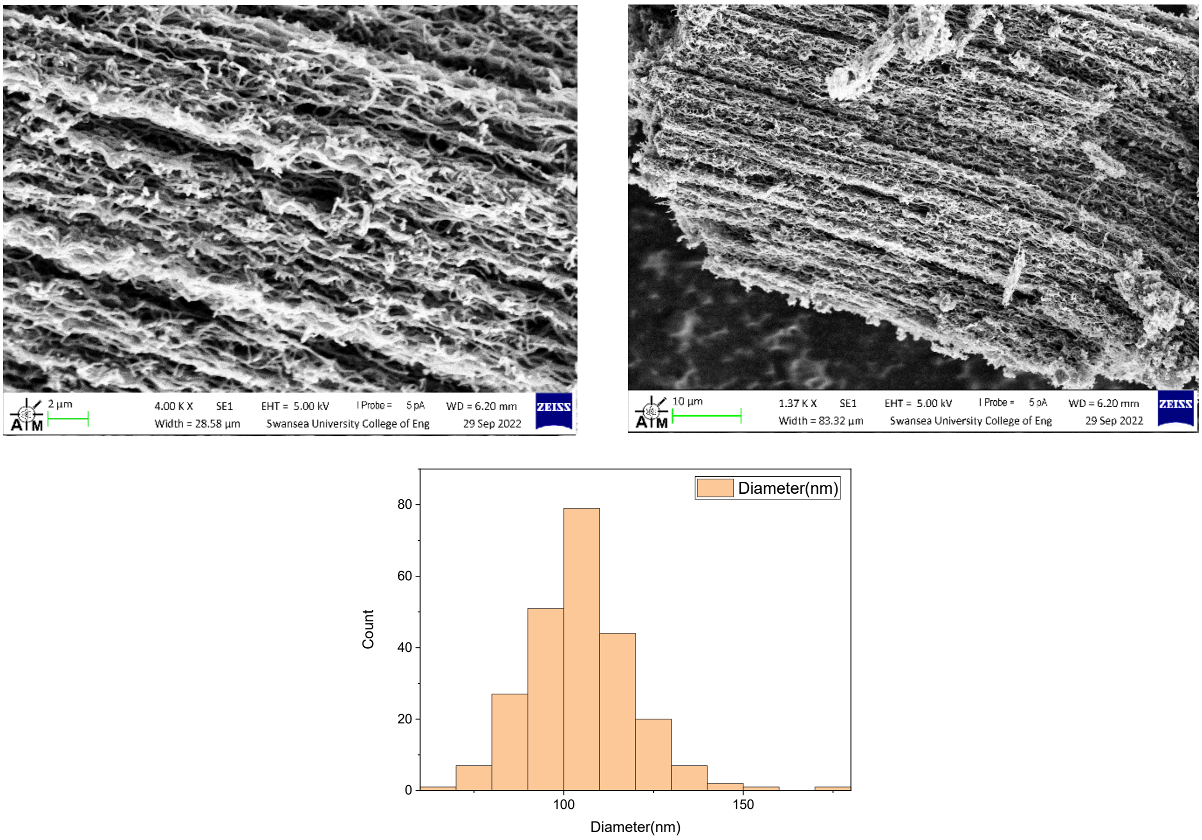


Figure 34 SEM Images at 2µm and 10µm scales and histogram of CNT diameters of Polyester sample4 (P4)

Figures 29 to 33 show SEM images of CNTs in the samples with and without polyester. Each Figure represents a sample. For each Figure an image is taken in a location with abundant CNTs, as well as a close-up SEM image of the same location. The zoomed in image enables an accurate measurement of the diameter of the synthesised CNTs. The histograms on each Figure indicate the median CNT diameter of each sample, as well as the overall distribution of the measured diameters, for a better understanding of the quality of CNTs produced in each sample.

3.3.3.3.Scanning electron microscope (SEM) Results

Table 5 Average and median values of CNT diameters with polyester and without polyester

PE samples	Diameter Averages (nm)	Diameter Medians (nm)	Control Samples	diameter Average (nm)	Diameter Medians (nm)
Sample 1 (P1)	51.28	48.00	Sample 1 (AC1)	146.12	145.00
Sample 2 (P2)	77.5	79.50		76.04	74.00
	89.67	89.50	Sample 2 (AC2)	96.80	96.00
Sample 4 (P4)	104.42	105.00	Sample 3 (AC3)	83.30	81.00
Average	**80.72**	**80.50**	**Average**	**100.57**	**99.00**

The control samples, containing only M-cresol and Toluene as hydrocarbon sources produced and average of **100.57nm**, while the samples with polyester showed a diameter of **80.72nm.** This is a **19.7%** decrease in the diameter of the nanotubes. Tensile strength and elastic modulus of the CNT sheets are increased with decreasing CNT diameter [133]. Therefore, if the polyester samples are purified, their properties could be higher than a carbon source without polyester.

3.3.4. *TGA results*

The Antioxidant properties of CNTs can be compared by observing the starting oxidation and end oxidation levels (Start of the red peak to the end of the red peak in the TGA graphs, Figure 35). Logically, the higher the temperature required to oxidise, the better the antioxidant properties.

The samples that showed the cleanest Raman spectroscopy graphs, with polyester and without polyester, were compared. It was shown that for polyester-CNTs, the starting oxidation level occurs at lower temperatures averaging 370ºC compared to 410ºC. As the polyester sample showed to have higher impurities, this value is of no surprise. However, the end-oxidation level occurs later at 710ºC compared to 680ºC showing a portion of the sample with polyester has better antioxidant properties [134].

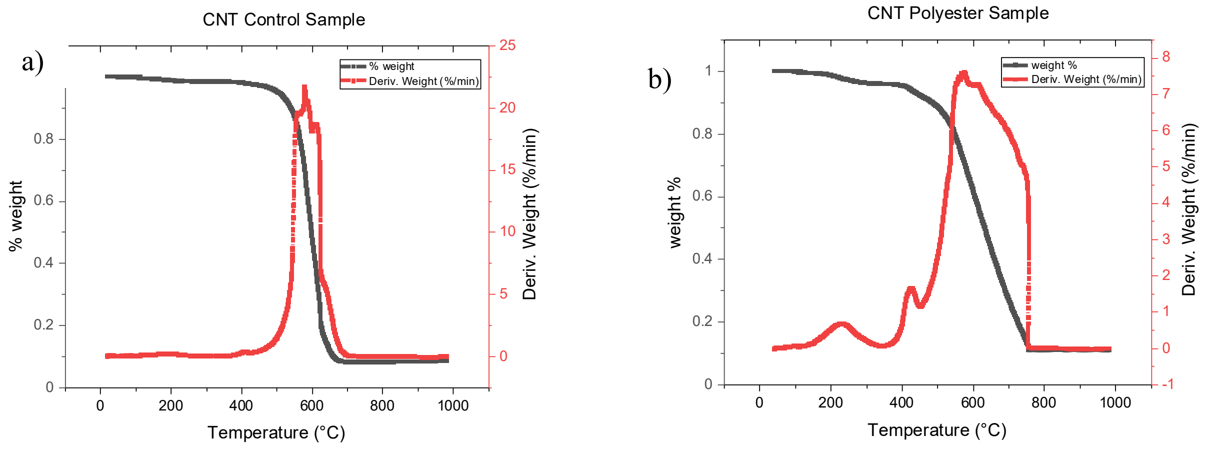


Figure 33 TGA of CNT samples a) Without polyester b) With polyester.

Smaller peaks in the polyester sample in earlier temperatures indicate carbon impurities at approximately 420ºC, showing C_{60} content [136]. Pure polyester under TGA also has a peak under 400ºC [137]. Therefore, the TGA could indicate some traces of polyester structures in the sample. The main *derivative of weight percentage* peak widens due to a higher variance of structures. The fact that the highest peak occurs much later than 400ºC indicates that most polyester was broken down successfully and the broken carbon chains generated new structures.

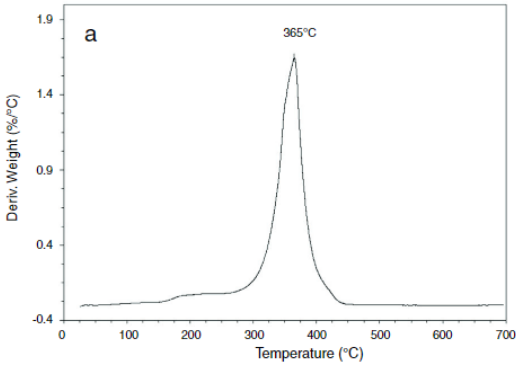


Figure 34 TGA of polyester [137]

Peaks nearing 700ºC are an indication of graphene structures. CNTs' carbon structures are equal to graphene; therefore, the experiment shows promising indications of non-graphite structures in polyester samples. In addition, no mass was decomposed at over 800ºC, the temperature expected to decompose graphite.

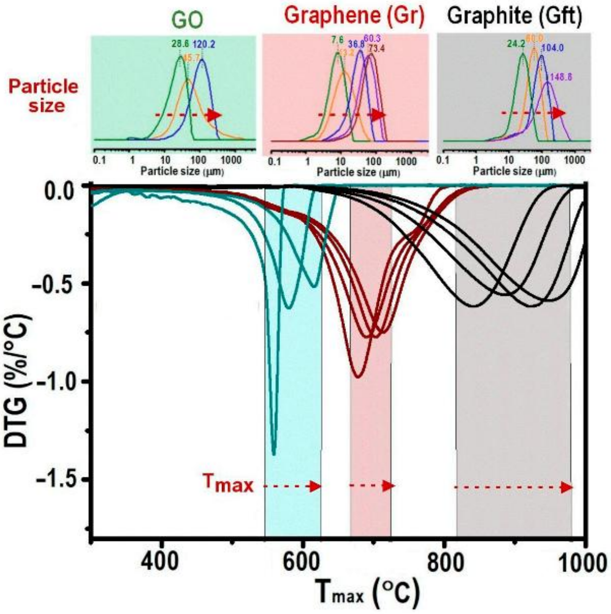


Figure 35 Analysis of Carbon structures under TGA [138]

Graphene oxides (GO) are graphene structures with oxide functional groups attached. As shown in Figure 37, the peak of GOs appears at an earlier temperature (570-620ºC) compared to graphene. The TGA of CNTs with and without polyester show a starting oxidation at a similar temperature, which indicates no real difference in potential oxide functional groups in the CNTs with or without polyester. The graphs start at 550ºC therefore there are potential GOs in the sample.

The *annealing* process is a heat treatment which can be applied to CNTs to increase the graphitization degree of the sample and to improve its thermal stability of the material [134]. This process elongates the range the peak of the TGA graph (the Deriv. weight %mass peak). As the sample improves its thermal stability, the peak drop occurs at a later temperature. The Polyester-CNT sample shows the same behaviour as annealed CNTs.

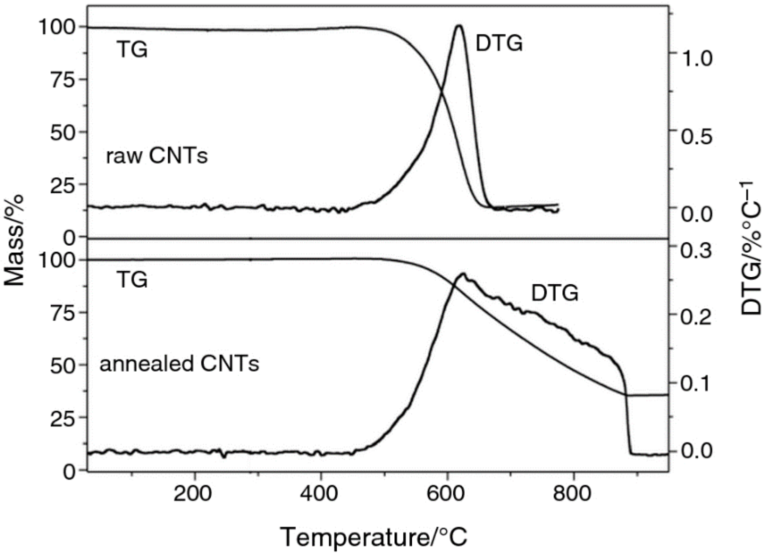


Figure 36 TGA of raw CNTs and annealed CNTs [139]

All CNT samples with polyester had a wider peak with end values at higher temperatures reaching over 750ºC, indicating CNT structures due to their oxidation resistance property.

3.4. Discussion of results

Polyester's chemical composition doesn't allow it to dissolve easily. This is because polyester fibres are generally resistant to organic solvents [140], therefore m-cresol had to be heated to cause an effect on the fibres. The viscosity of m-cresol also contributed to the slow dissolution of polyester, which lasted approximately 3 weeks.

As polyester polymers have Oxygen-Carbon bonds, there is a strong reason to believe that there are carbon oxides present in the formation of CNTs. In the experiment, the CNT count decreased mildly, and the diameters also decreased. This conclusion supports the previously mentioned article [103].

In this article, scientists intentionally added CO_2 gas in the formation of CNTs. Their results showed that the quality of the carbon nanotube growths improved. Their results also showed a decreased count of nanotubes with smaller diameters. This translates to a smaller yield but with a higher quality of CNTs.

CO_2 is expected to produce carbon nanotubes with longer lifetime, as shown in the graph from the article *Carbon Dioxide Triggers Carbon Nanotube Nucleation: Isotope Labelling Study on the Growth Process of Individual Nanotubes* [103].

The explanation for a longer lifetime is the fact that additive oxidants prolong the growth lifetime through the inhibition of carbon coating on the catalyst. This explanation is also concluded in other studies on nanotube aggregates [140]. Therefore, if CO_2 is indeed present thanks to the polyester chains, the produced CNTs potentially have a longer lifetime.

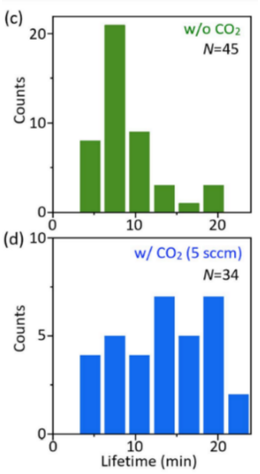


Figure 37 Lifetime of CNTs with vs without CO_2 [141]

Oxygen is believed to be an impurity in the CVD method, which is the reason why gases like hydrogen are applied, so undesired gases don't interact with the product. However, the optimum amount of oxygen must be an exact controlled value to achieve improvements in the yield of carbon-based structures. For example, in different studies about the production of graphene, it was found that an oxygen:propylene ratio of 1:9 produces single-layer graphene [142]. Other studies show that in some cases oxygen is only beneficial when it is implemented while CNTs are growing [143]. Therefore, it is key to analyse when and how much oxygen is applied, depending on the method used and the desired product.

3.5. Conclusion

Experiments using SEM, Raman and TGA have proven that polyester is an interesting candidate to assist in the production of carbon nanotubes. The composition of polyester allowed the synthesised CNTs to have thinner diameters, which can be attributed to carbon oxides being involved in the process. The number of nanotubes did not increase, and the total mass of the CNT production was slightly lowered. This means that further studies must be done to explain why that is the case and how to increase the yield.

This study has proved that polyester from plastic waste can produce CNTs with potentially better properties, as well as producing highly valued materials such as carbon fibres, and graphene. This means that there is a new real solution for reducing plastic waste and reach a circular economy, as well as a new way to synthesize ground-breaking materials, making them more available for future technologies.

3.6.Suggestions for further development

This study would benefit greatly with the addition of a method to quantify the final amount of oxygen in the solution for further analysis. There was evidence of oxides present but no detailed prove of what type of carbon oxide was present to aid in the production of thinner CNTs.

Previous experiments performed at Swansea University showed that the greatest yield was produced at 900ºC. However, most previous parameters have been optimised to produce CNTs for solely solvents. For future studies, a gradient of temperatures should be considered to optimise the yield of CNTs when polyester is used, as well as the rate of injection, gas flow of N_2 and H_2 or the mass of the catalyst.

In the case of the temperature parameter, studies on the temperature of pyrolysis under the LIR, by the Military Technical College in Cairo, must be over 650ºC to produce CNTs, but temperatures over 850ºC synthesise more fullerenes than CNTs. Therefore, the optimum temperature was shown to be between 700ºC and 800ºC [144], which could have been the cause of the amount of amorphous carbon and CNTs with defects.

This proves that varying these key parameters can change greatly the type of carbon structure formed and its yield.

3.6.1. *Purification of CNTs*

As explained in previous sections, CNTs from plastic showed a high number of impurities according to Raman spectroscopy. To purify samples extra steps can be implemented. These steps are: “deletion” of large graphite particles with filtration, and dissolution to eliminate catalyst particles and fullerenes. To remove amorphous carbon clusters, microfiltration and chromatography can be used [145].

A method to separate semiconducting and metallic SWNTs is “size exclusion chromatography”. This is highly useful to be able to achieve specific properties that only a type of CNT can provide fully [145].

3.6.2. *Recovery of by-products*

The LIR used for CNT production emits a flow of by-products, some of which are useful. A great further development in this process would be to filter these useful gases (including hydrocarbons like benzene) from other by-product gases and harvest them. This can promote CNT production and make it more economically viable.

One of these useful gasses is hydrogen, a gas that is becoming increasingly popular due to its property to store energy There are already various methods to filter hydrogen which could be implemented in the CNT production. Electrochemical purifiers are an interesting method to filter hydrogen molecules. They do this by electrolysing H_2, oxidising it to H^+. Through a PEM membrane, H^+ protons migrate and are reduced back to H_2 in a container that can be pressurised. There is currently research being done at ESRI in Swansea University to collect this valuable gas.

Most of the by-product is unused carbon form the benzene group because more energy is required to break carbon bonds in benzene rings [146]. Plastics have benzene rings with small carbon chains attached to one carbon. In the process of pyrolysis, carbon structures degrade and, as the attached carbon chain requires less energy to break than the carbon bonds of a benzene ring, most of the carbon particles to build CNTs come from the attached chains.

Therefore, plastics with larger and simple chains attached with the benzene ring are encouraged like polystyrene or plastics without a benzene ring at all like polyethylene. Further research could focus on analysing the possibility to decompose the benzene rings, perhaps with increasing CVD cycles and increasing the temperature. This would improve the yield of CNTs and avoid carbon waste.

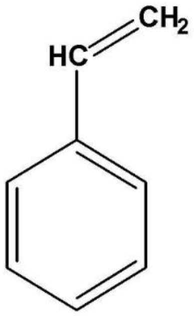


Figure 38 Polystyrene monomer showing a benzene ring and its hydrocarbon chain attached [147].

The idea to harness by-products can also help with the environmental footprint of the process. It becomes more important if plastics like polyester are implemented, as they contain oxygen creating traces of carbon oxides like CO_2 which are greenhouse gases.

3.6.3. *Characterising CNTs*

A practical additional analysis would be to characterise the type of CNT configuration that is being produced with polyester plastic. This analysis would shed light on the physical characteristics of the produced CNTs. Being able to produce a specific type of CNT configuration allows the generated product to be optimal for a specific purpose. For example, a "Zigzag" configuration for technology that require an increment in electrical conductivity.

4. THESIS CONCLUSION

Throughout this thesis, various topics related to energy and waste management have been studied. The study focused on finding solutions to move towards a sustainable economy. To achieve this, the two main bottlenecks addressed were the increasing human energy consumption and human waste.

From this thesis' point of view, it was shown how hydrogen production has a key role to support future energy consumption. To achieve this, green hydrogen production must continue to improve its efficiency. New methods to improve efficiency must rely on sustainable solutions, and this was attempted with the generation of CNTs from plastic waste, to improve heat recovery systems in electrolysers, with the additional capacity to assist in a wide variety of projects, such as efficient batteries and metal hydrides for optimal hydrogen storage.

Initially, state-of-the-art energy storage systems were analysed. This analysis identified hydrogen as a potential solution to assist in sustainable energy transport and storage. Therefore, to support green hydrogen production, various systems were considered to enhance hydrogen electrolysers to increase their productivity. Hydrogen production has the potential to slow down the previously shown global usage of non-renewable energy production, a major contributor to global pollution. In addition, it was shown that the effort to electrify technology has limitations. These limitations can be solved with hydrogen as an energy vector.

The study of heat recovery systems found various methods to harvest waste heat energy. The main issue with alkaline electrolysers was its low temperature gradient (LTD). Therefore, heat engines compatible with such low temperature difference were analysed.

Stirling engines offered a theoretically higher efficiency. This engine was studied to be practical due to its variety of configurations, to adapt to different temperature gradients, even under minimal differences. Thermoelectric generators (TEGs) offered different advantages. TEGs offer simpler systems that require no maintenance. Lastly turbine generators were studied for LTDs, by modifying the working fluid to change its physical state under low temperatures. It was shown that they can theoretically work but for an efficient system, they require higher temperature gradients and working fluids with higher heat capacities.

All the systems reviewed require materials able to conduct heat as good as possible, to transform heat into electricity. The thesis showed therefore, how adding materials with exceptional physical properties greatly benefit most systems. The primary challenge for sustainable and effective technology, including hydrogen, is finding materials capable of resisting, conducting, facilitating chemical reactions, as well as substituting rare metals. For all these reasons, carbon nanotubes were studied.

The goal of this research was to facilitate the production of carbon nanotubes sustainably. Various methods of waste management were reviewed, including modular designs, where production considers how the product will be dismantled at the end of its lifecycle. Sustainable waste management also consider what materials will be used in each component. This is considered to predict the time it will take to dismantle the parts and to know what can and cannot be recycled. This was another reason to consider carbon-based materials to substitute rare metals.

In addition, to achieve a sustainable production of nanomaterials, chemical recycling was studied. It was reviewed how pyrolysis allows waste to break down and provide building blocks to generate new chemical structures. This process allows carbon nanotubes to be formed from the carbon chains of plastic waste.

The plastic studied was polyester from clothing waste. Polyester was used as carbon feedstock. To be able to synthesise CNTs, laboratory experiments were carried out, using CVD for pyrolysis. The results were analysed using Raman spectroscopy, SEM microscopy and TGA.

This research concluded that plastic can be used as a source of CNTs. This allows the nanomaterial to be more affordable while creating a new method for waste reduction. Other promising plastics were also suggested, such as polystyrene, to generate CNTs efficiently.

The thesis aimed to promote nanotechnology to improve the energy sector as well as sustainable technology for the energy industry. It also intended to shed light on key issues of human consumption and hopes to have a positive influence on emerging technology to address energy demands sustainably.

5. APPENDIX

5.1. Organic Rankine Cycle diagram

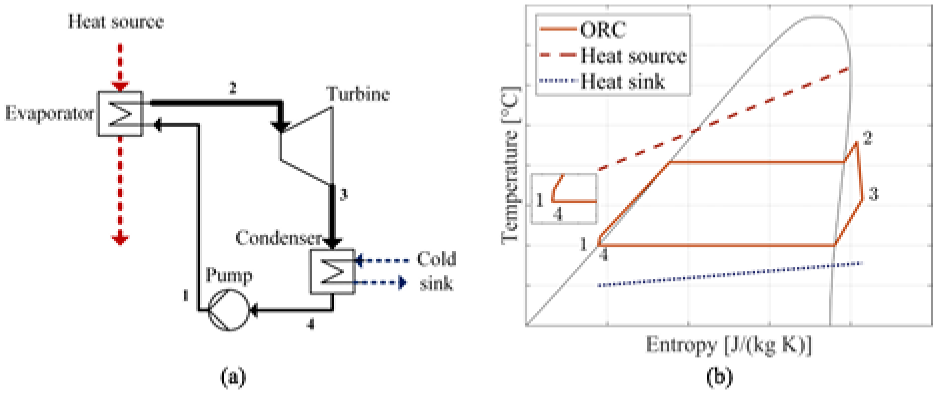


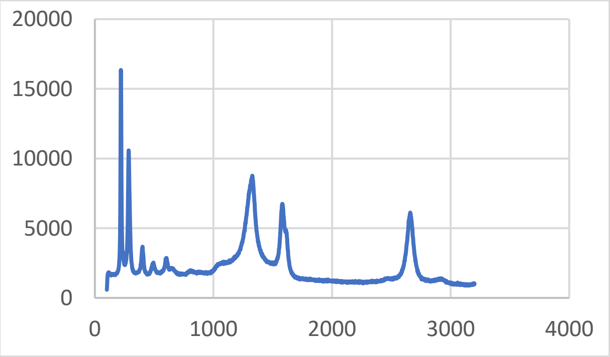
Figure 39 (a) Flow sheet of a simple subcritical one-staged ORC, and (b) corresponding T-s diagram.

5.2. Raman shift Results

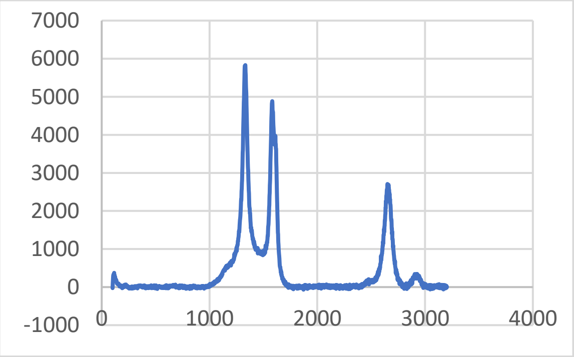
The wavelength 633nm and 785nm indicate the laser frequency used in the samples, 30s indicate the time of exposure and the 5% and 1% is the laser power percentage. The value 2_X numbers the repeated tests, as various spots in the same sample were taken. First column shows all control results and column two (right) shows all polyester results.

CONTROL 1 Samples Column **POLYESTER 1 Samples column**

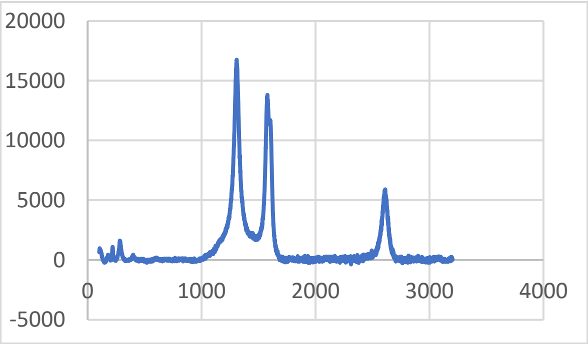
633nm 30s 5% 2_1



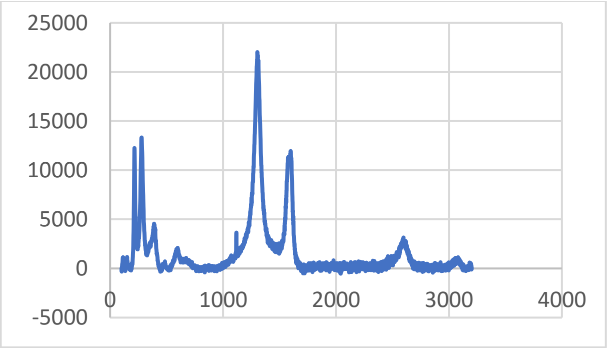
633nm 30s 5% 2_1



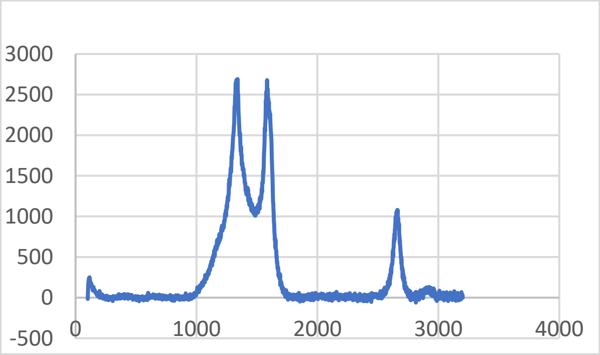
785nm 30s 1% 2_1



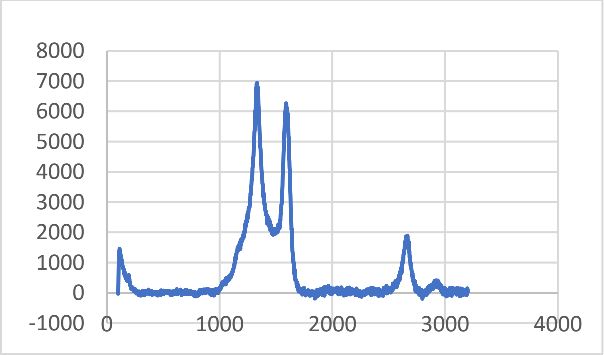
785nm 30s 1% 2_1



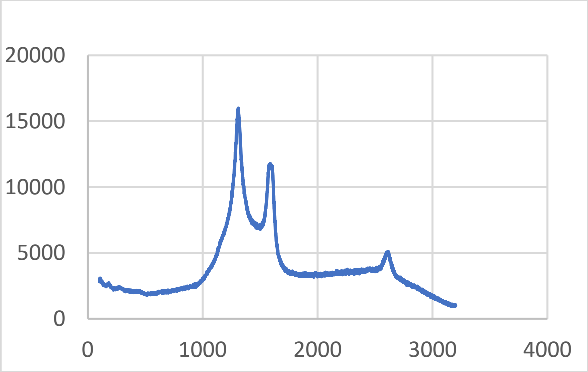
633nm 30s 5% 2_2



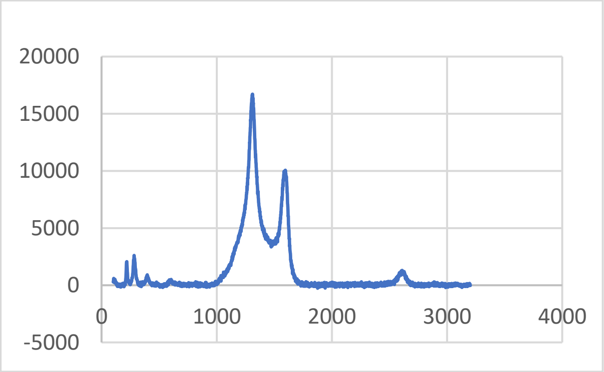
633nm 30s 5% 2_2



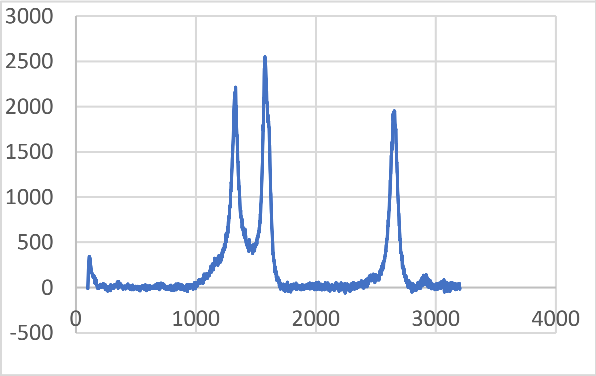
785nm 30s 1% 2_2



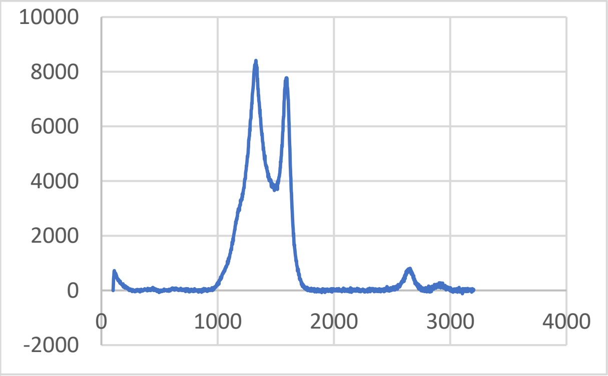
785nm 30s 1% 2_2



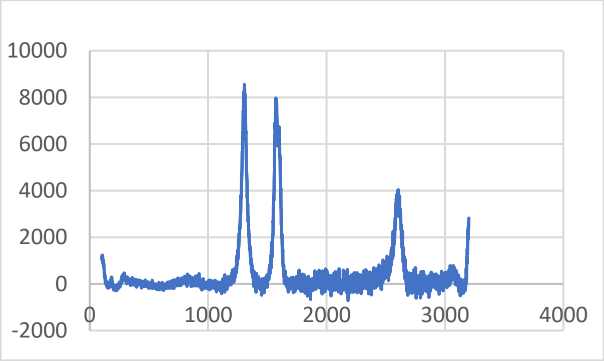
633nm 30s 5% 2_3



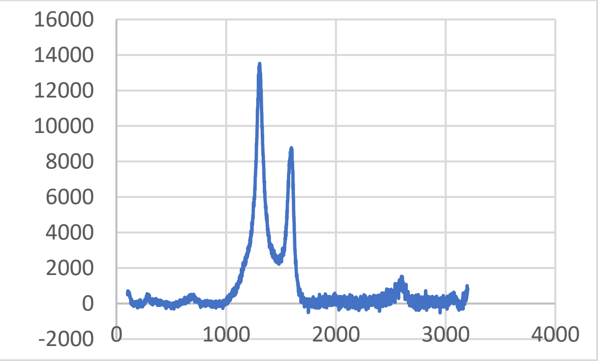
633nm 30s 5% 2_3



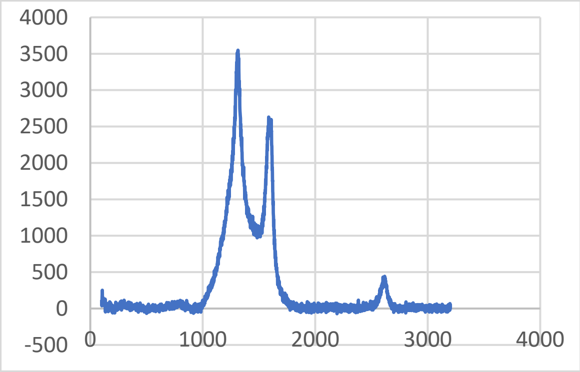
785nm 30s 1% 2_3



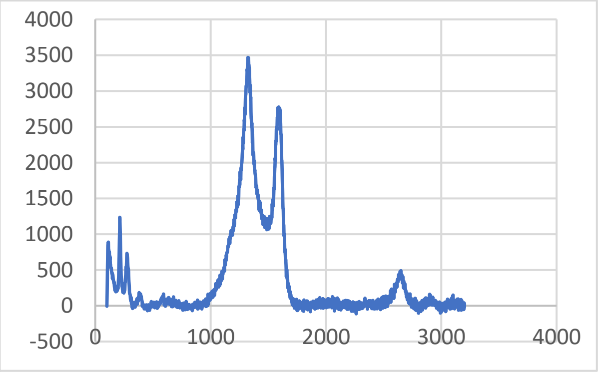
785nm 30s 1% 2_3



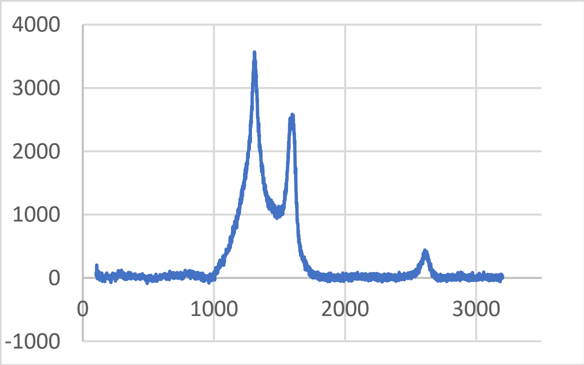
633nm 30s 5% 2_4



633nm 30s 5% 2_4



785nm 30s 1% 2_4



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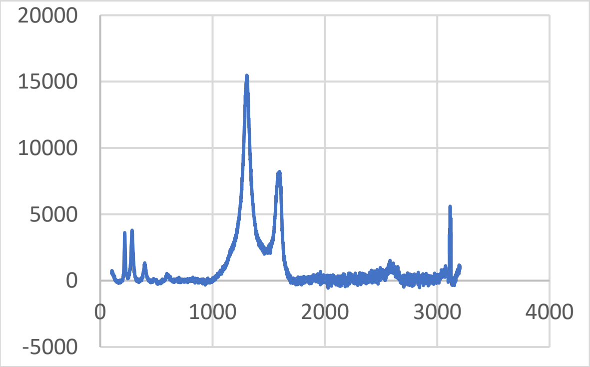
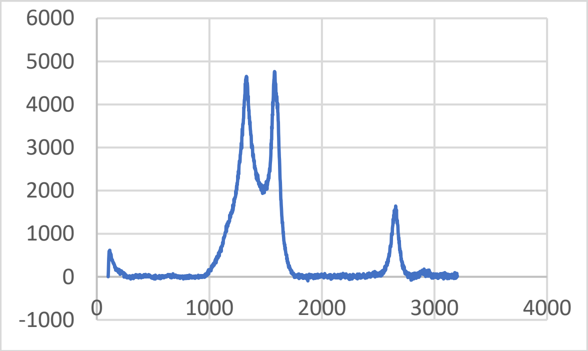
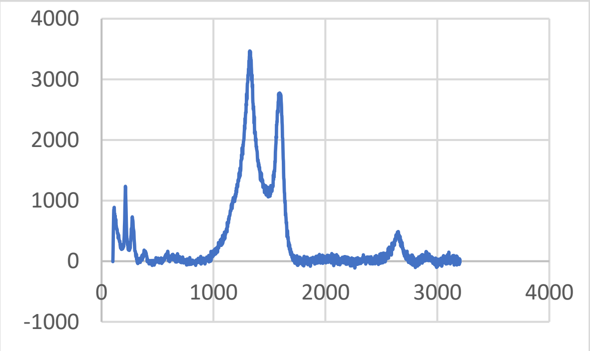


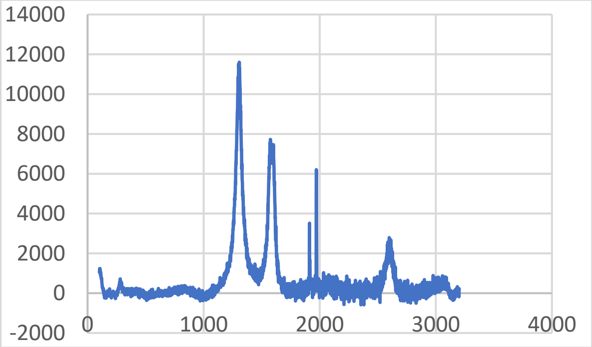
633nm 30s 5% 2_5



633nm 30s 5% 2_5



785nm 30s 1% 2_5



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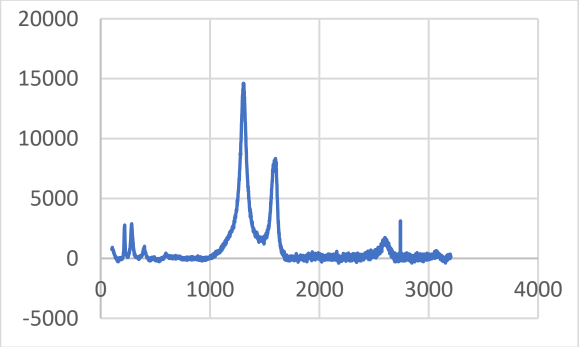
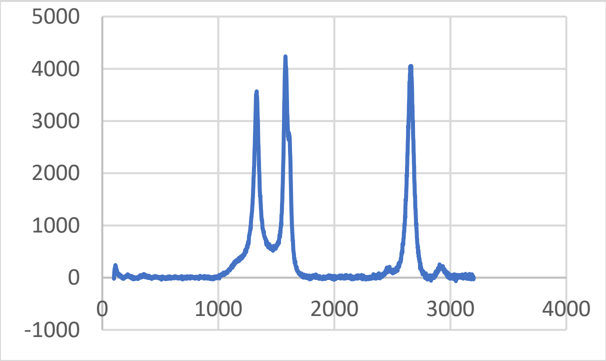


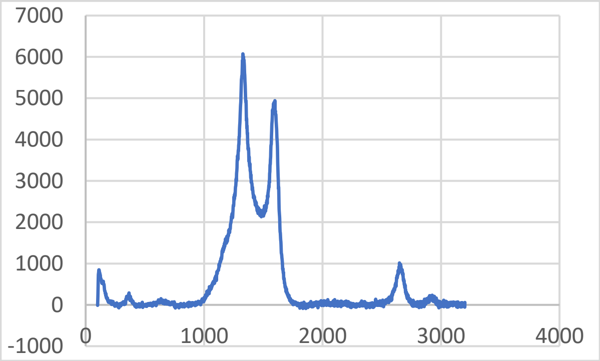
CONTROL 2 Samples Column

633nm 30s 5% 2_1

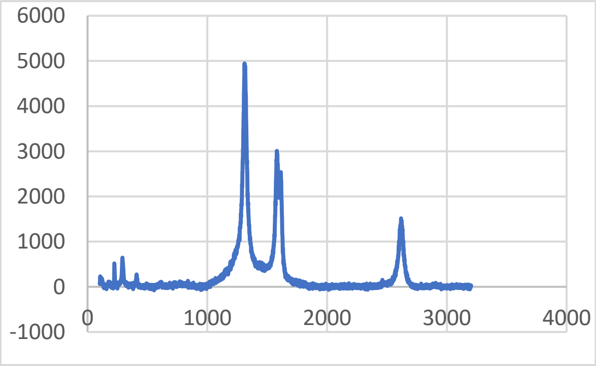


POLYESTER 2 Samples Column

633nm 30s 5% 2_1



785nm 30s 1% 2_1



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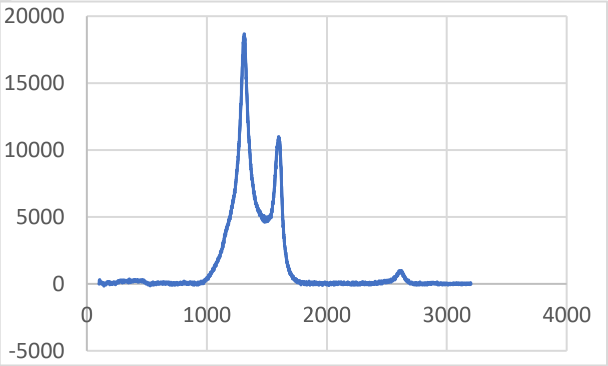
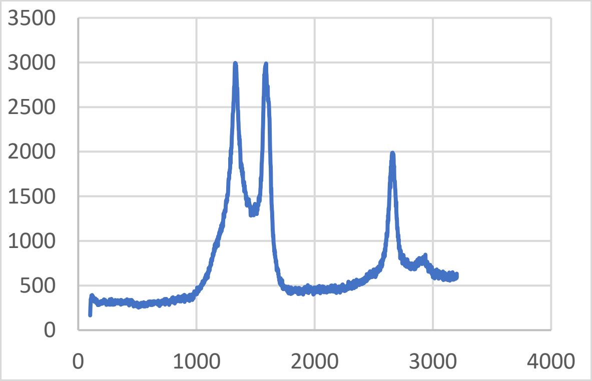
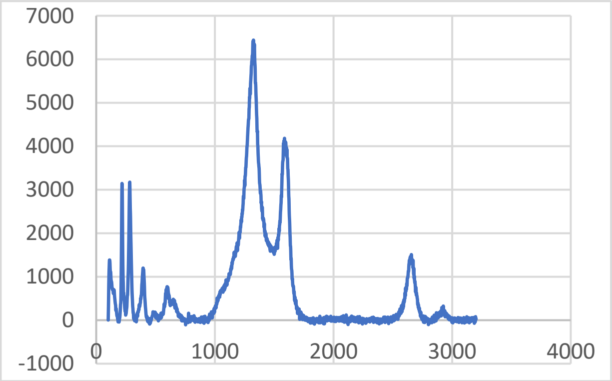


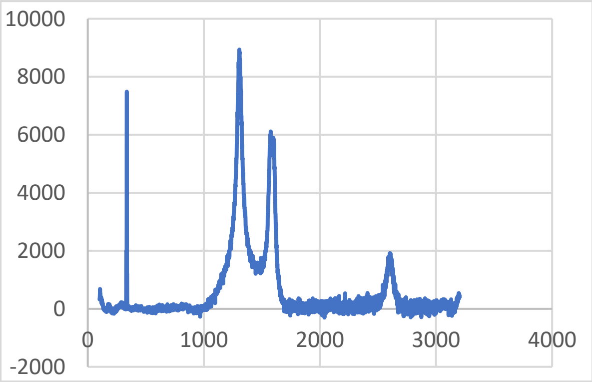
633nm 30s 5% 2_2



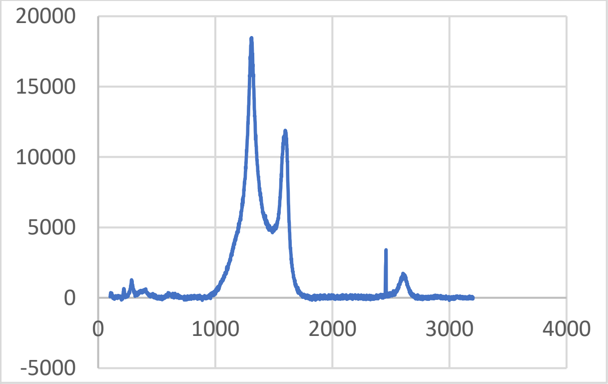
633nm 30s 5% 2_2



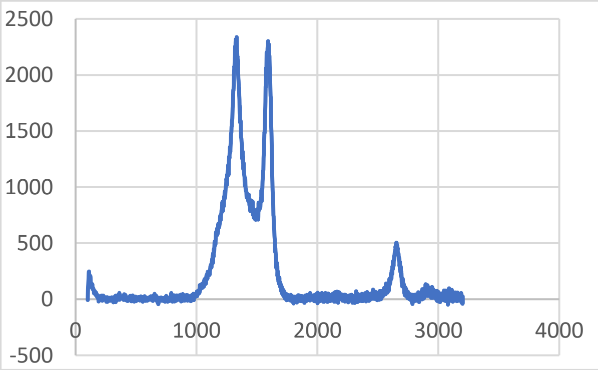
785nm 30s 1% 2_2



785nm 30s 1% 2_2



633nm 30s 5% 2_3



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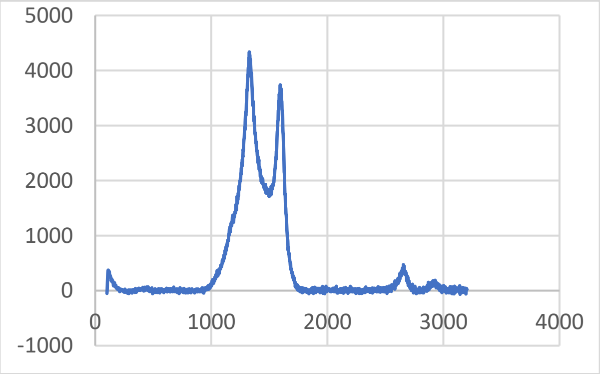

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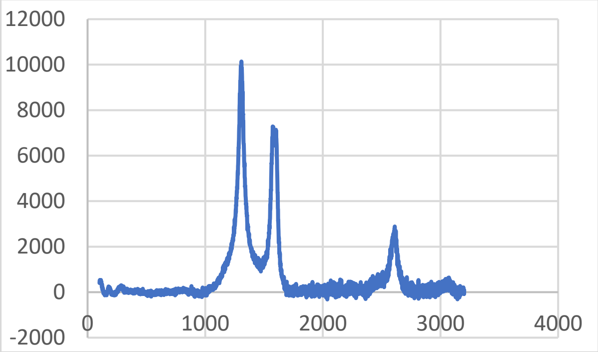

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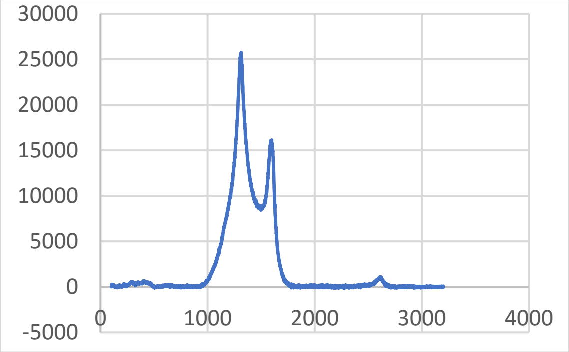

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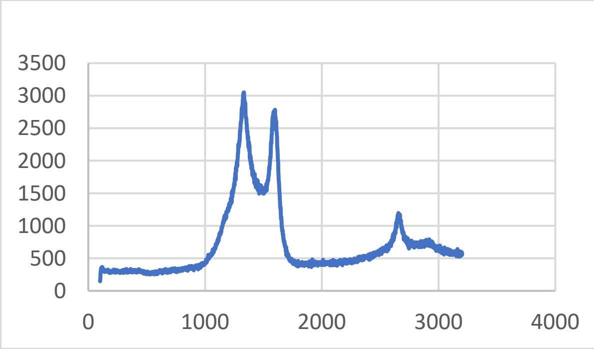
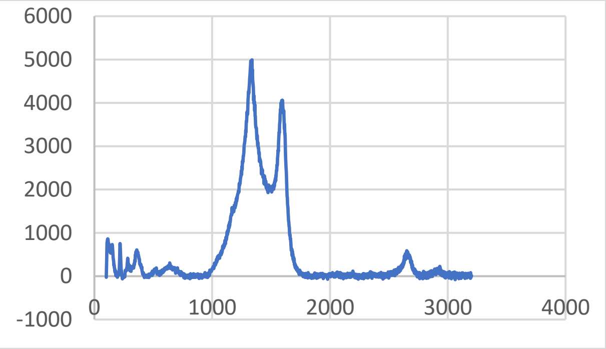
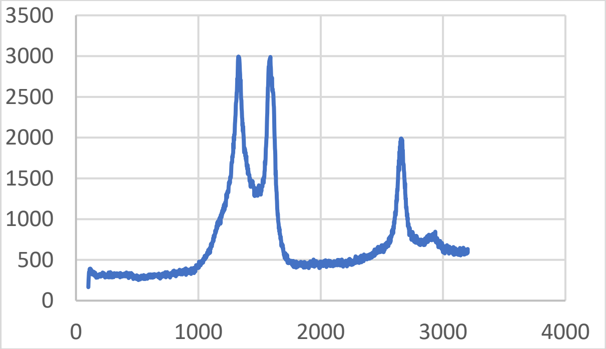


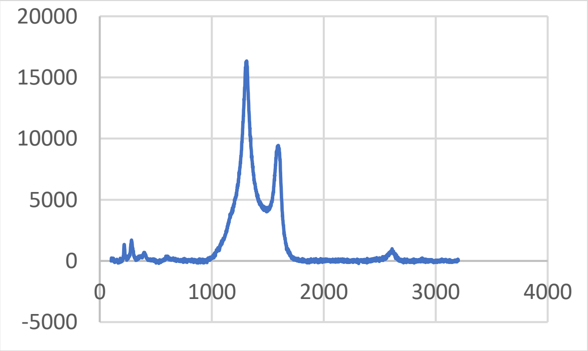
633nm 30s 5% 2_4



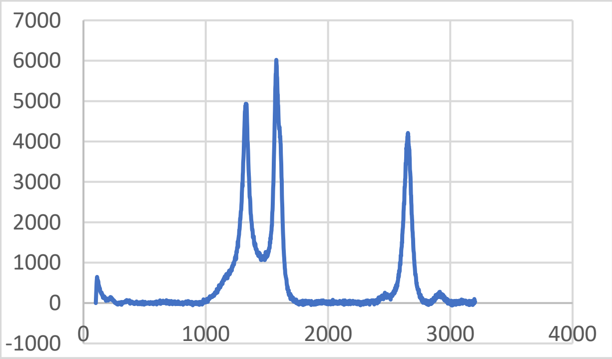
785nm 30s 1% 2_4



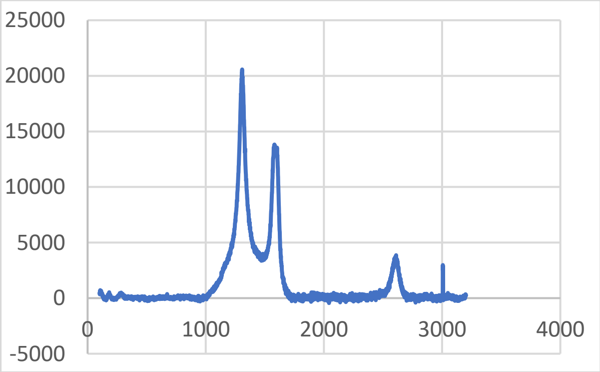
785nm 30s 1% 2_4



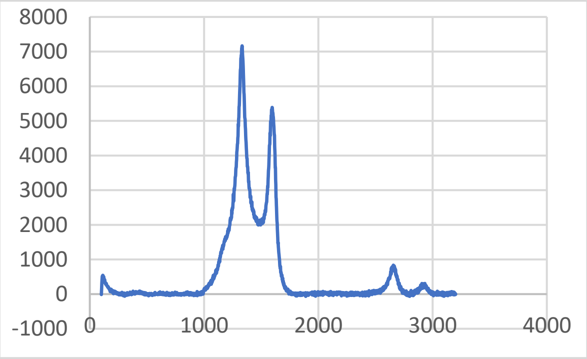
633nm 30s 5% 2_5



785nm 30s 1% 2_5



633nm 30s 5% 2_5



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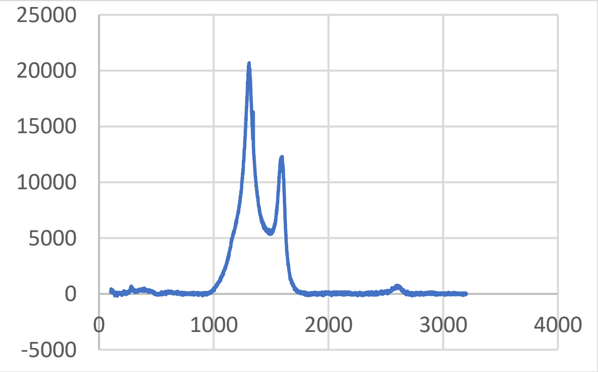

CONTROL 3 Samples column

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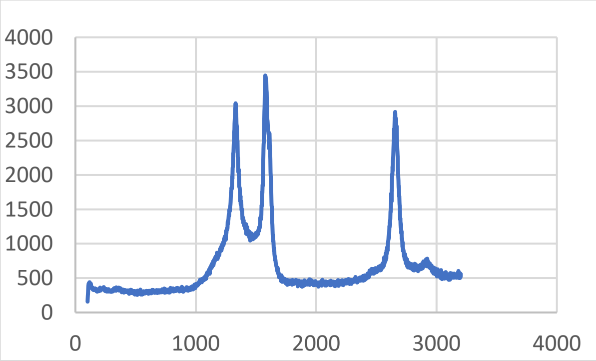
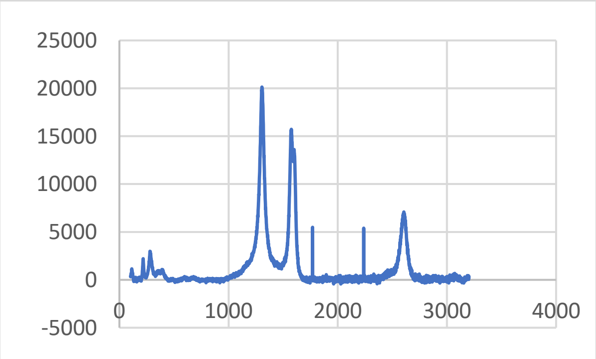


785nm 30s 1% 2_1



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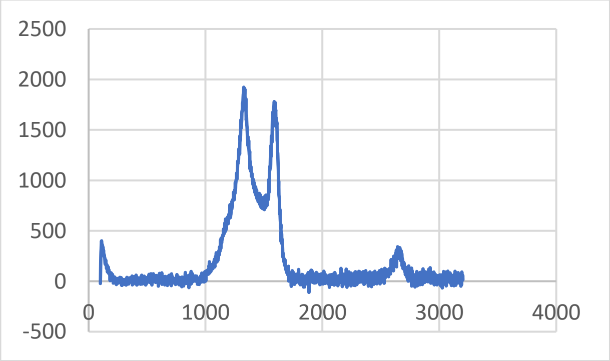
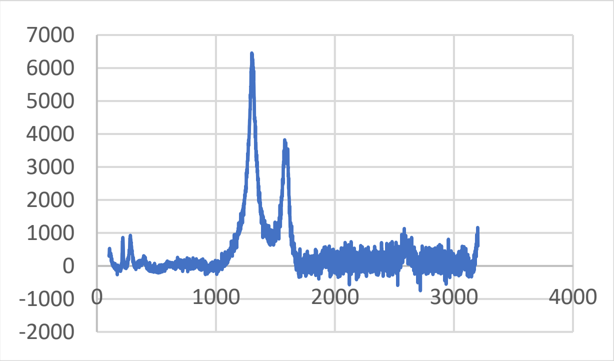


785nm 30s 1% 2_1



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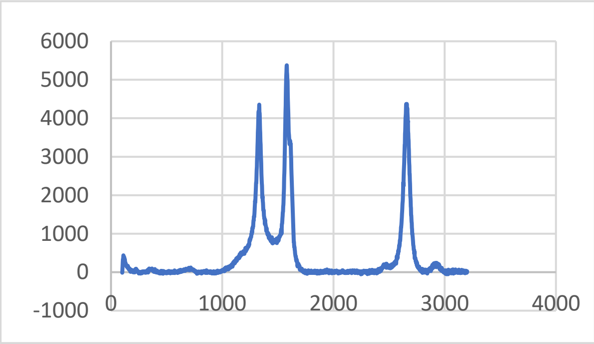
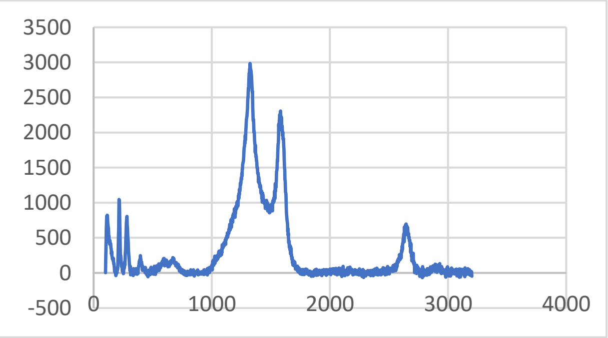
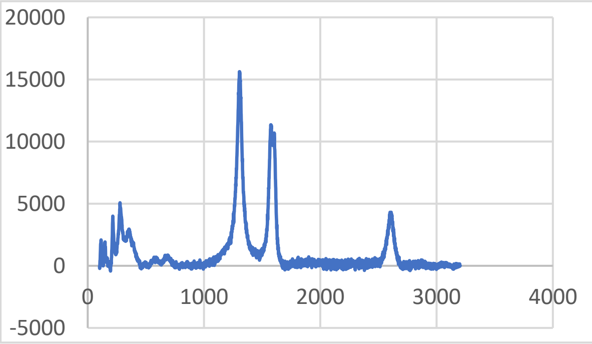


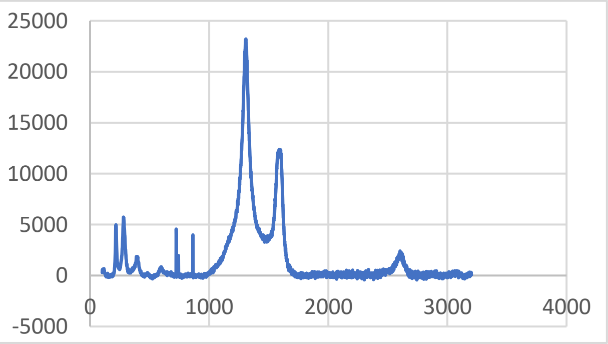
633nm 30s 5% 2_2



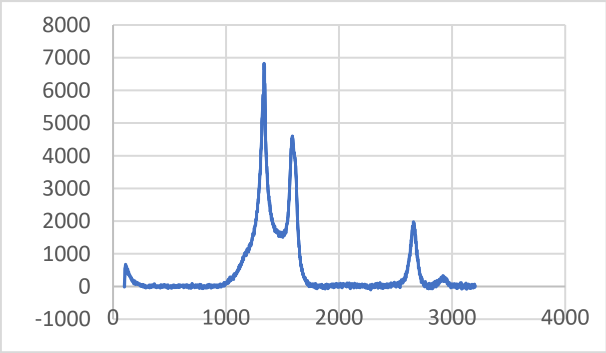
785nm 30s 1% 2_2



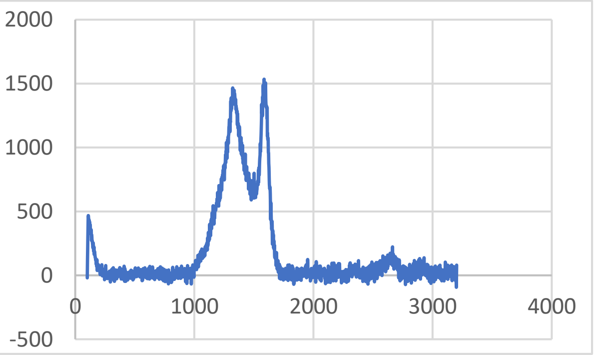
785nm 30s 1% 2_2



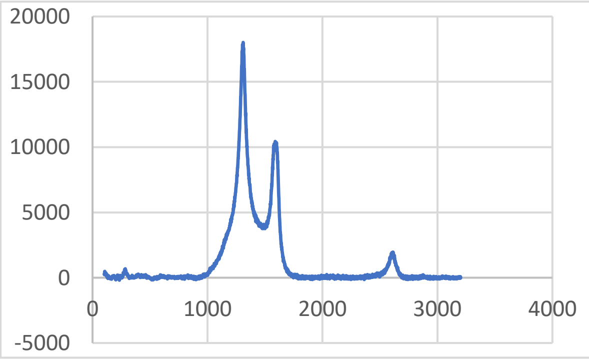
633nm 30s 5% 2_3



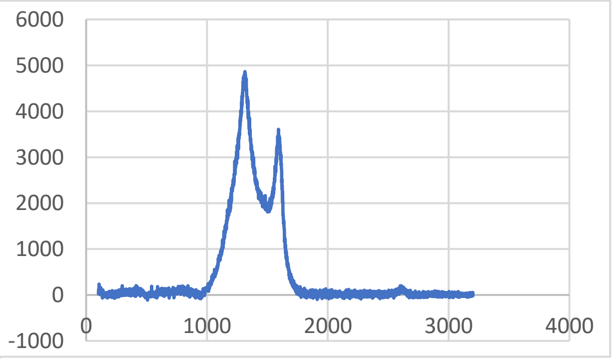
633nm 30s 5% 2_3



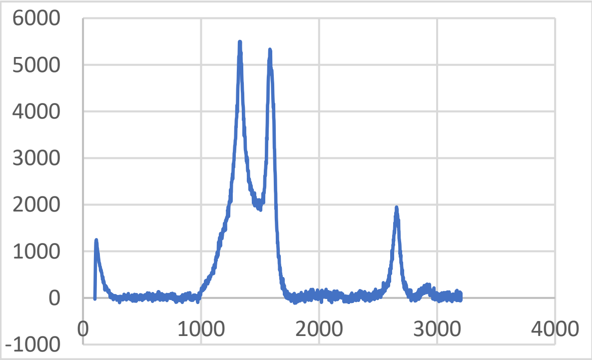
785nm 30s 1% 2_3



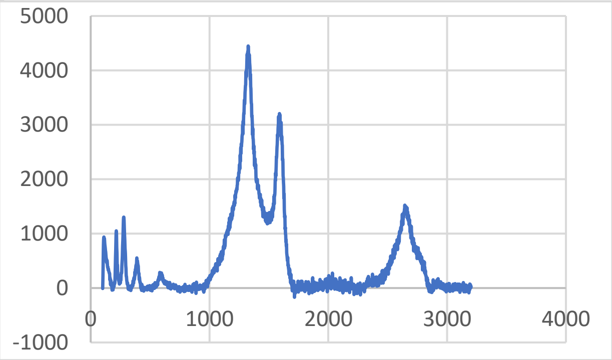
785nm 30s 1% 2_3



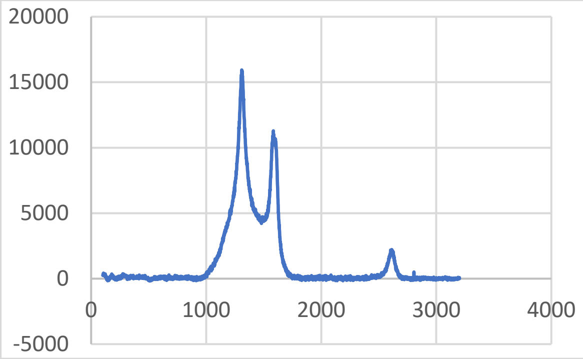
633nm 30s 5% 2_4



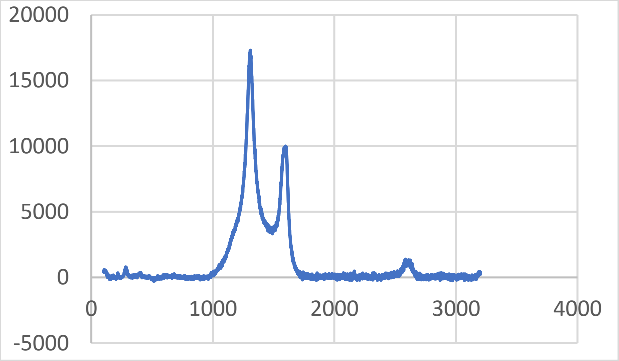
633nm 30s 5% 2_4



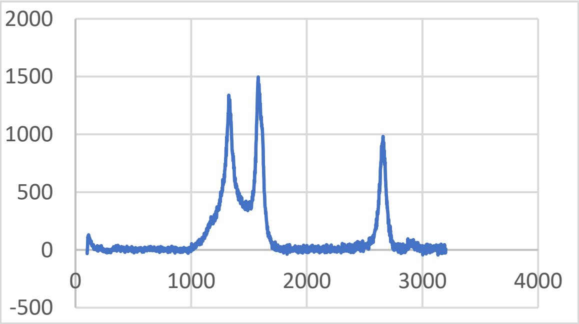
785nm 30s 1% 2_4



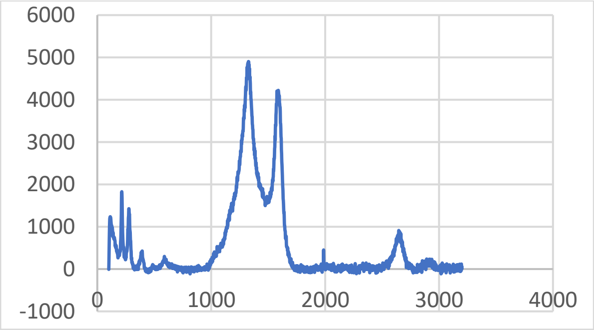
785nm 30s 1% 2_4



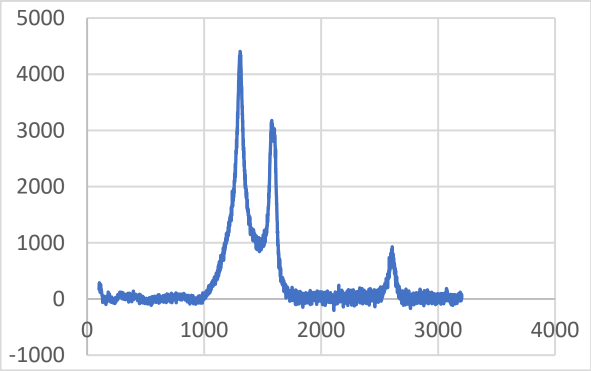
633nm 30s 5% 2_5



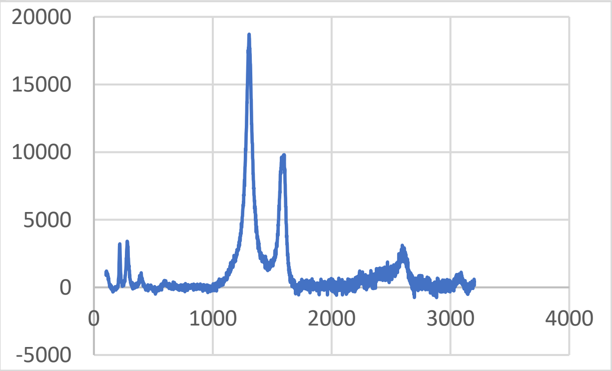
633nm 30s 5% 2_5



785nm 30s 1% 2_5



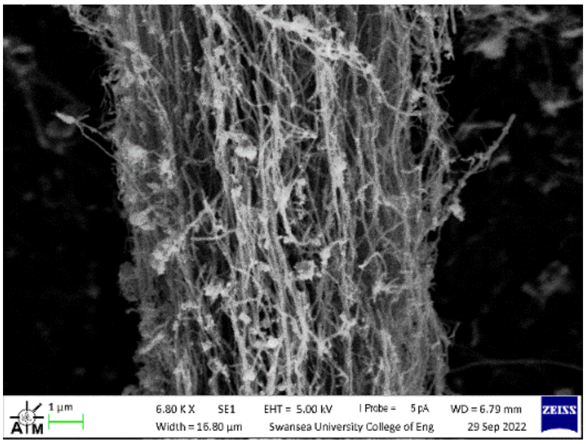
785nm 30s 1% 2_5

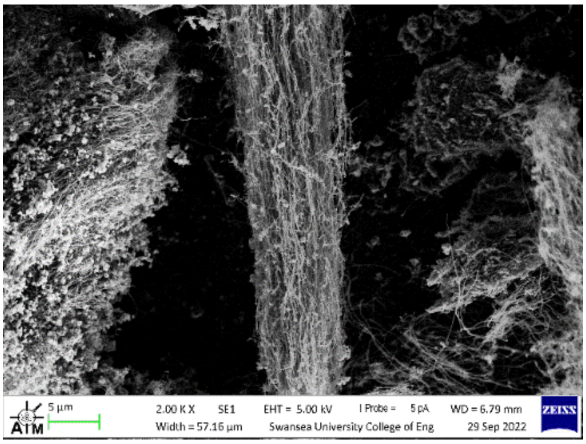


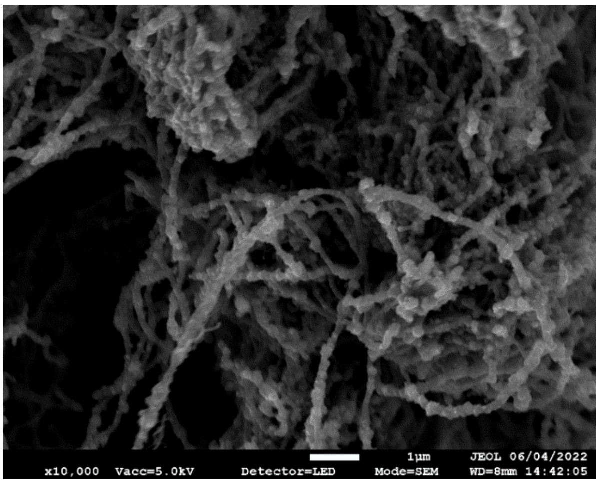
5.3. SEM PICTURES

5.3.1. *Further images from SEM microscoy*

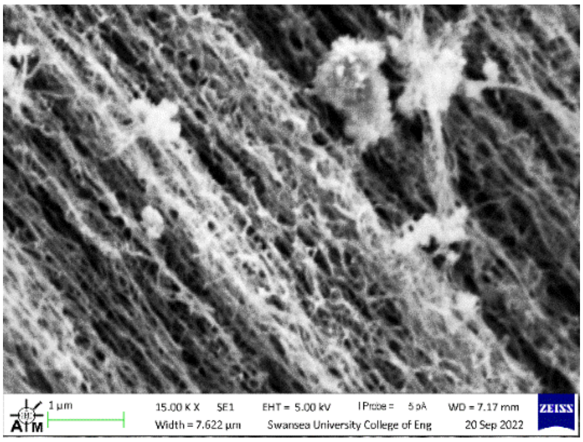
AC1

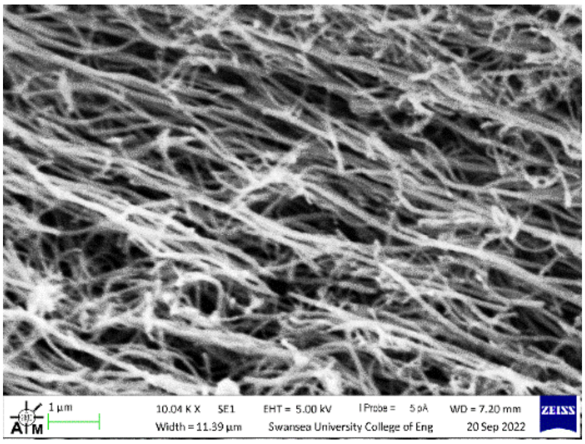




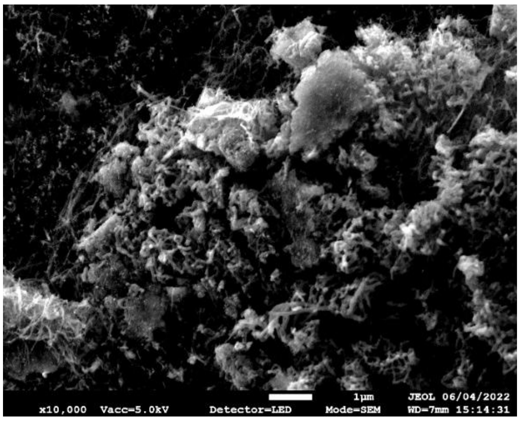


AC2

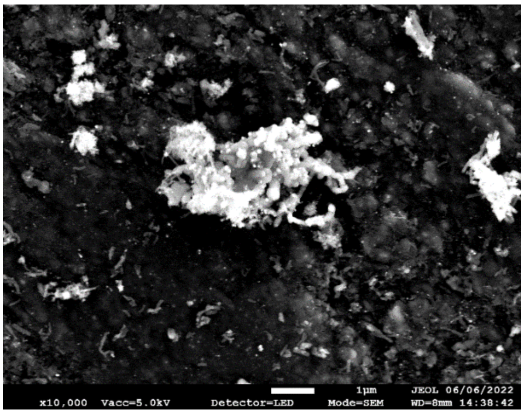




PE3


x10,000 Vacc=5.0kV
Detector=LED
1µm
Mode=SEM
JEOL 06/04/2022
WD=7mm 15:14:31

PE4


x10,000 Vacc=5.0kV
Detector=LED
1µm
Mode=SEM
JEOL 06/06/2022
WD=8mm 14:38:42

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