Microalgae Derived Carbon for Energy Storage Devices

ENG-470 Engineering Honours Thesis 2017
Majoring in Renewable Energy Engineering and Instrumentation and Control Engineering


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Declaration

I hereby declare that this thesis is my own effort. All the information and knowledge from secondary sources have been cited in the bibliography section. If there are any mistakes regarding this report, it is not intentional in any way.

Signature :  

Date    :  28 April 2018
ABSTRACT

In this study, the electrochemical properties and sample characterization of activated carbon have been analysed to gain a clear understanding of its behaviour reflecting the energy storage performance. When tested in a three-electrode configuration for electrochemical characterization working with 2M NaOH electrolyte solution, the activated carbon exhibits excellent capacitance and energy density value which is 124.436 F g\(^{-1}\) and 62.218 Wh kg\(^{-1}\), respectively. The activated carbon showed large BET surface area and large pores area, which are 1133.8038 m\(^2\) g\(^{-1}\) and 891.909 m\(^2\) g\(^{-1}\), respectively, ascribed to micropores. Besides, 2h holding time at 200\(^\circ\)C by hydrothermal carbonisation of solid hydrochar from Chlorella algae species was used as precursor material. It is for the preparation of microalgae derived carbon by chemical activation method with KOH. An approach has been made to test the influences of the activation temperature on the pore structure and the energy storage performance. The macroalgal hydrochar is synthesized at two different temperatures, 800\(^\circ\)C and 900\(^\circ\)C, for 60 min under same impregnation ratio of KOH/hydrochar is being 4:1. Two samples thus synthesized present low capacitance and thus low energy density value which sample 1 (AC1-4:1-800) exhibited 10.679 F g\(^{-1}\) and 5.34 Wh kg\(^{-1}\), respectively, while sample 2 (AC2-4:1-900) exhibit 0.939 F g\(^{-1}\) and 0.47 Wh kg\(^{-1}\), respectively. From the BET and porosity analysis, it is concluded that both samples have low BET surface area, pores volume and low pores area. The conclusion from this experiment is that a high activation temperature, (i.e., 900\(^\circ\)C), may degrade the pore structure of electrode materials.
# LIST OF NOMENCLATURE AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>AP</td>
<td>Aqueous phase</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CD</td>
<td>Charge-discharge</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>dm³ h⁻¹</td>
<td>Cubic decimetre per hour</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electrochemical double-layer capacitors</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>Eqn</td>
<td>Equation</td>
</tr>
<tr>
<td>F g⁻¹</td>
<td>Farad per gram</td>
</tr>
<tr>
<td>GRC</td>
<td>Gold recovery granular activated carbon</td>
</tr>
<tr>
<td>HTC</td>
<td>Hydrothermal carbonisation</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water vapour</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>IST</td>
<td>In-situ transesterification</td>
</tr>
<tr>
<td>K</td>
<td>Potassium</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>K₂O</td>
<td>Potassium oxide</td>
</tr>
<tr>
<td><strong>Symbol</strong></td>
<td><strong>Chemical/Technical Term</strong></td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>Potassium carbonate</td>
</tr>
<tr>
<td>L ha$^{-1}$</td>
<td>Litre per hectare</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen gas</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Ni-Cr-Al</td>
<td>Nickel Chromium Alloy</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>pH</td>
<td>Power of hydrogen</td>
</tr>
<tr>
<td>PSD</td>
<td>Pore size distribution</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFE</td>
<td>Supercritical fluid extraction</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>Zinc chloride</td>
</tr>
<tr>
<td>Wh kg$^{-1}$</td>
<td>Watt hour per gram</td>
</tr>
<tr>
<td>wt. %</td>
<td>Percentage by weight</td>
</tr>
<tr>
<td>$^0$C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>%</td>
<td>Percentage</td>
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ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my thesis supervisors: Dr. Manickam Minakshi and Dr. Xiangpeng Gao for their continual support and feedback throughout the project. I would not have achieved the amount of work, nor the quality of work that I have achieved without their full supervision and guidance. In spite of having heavy workloads throughout the semester, both have offered me a considerable amount of time, kindness and encouragement for the duration of this project at Murdoch University.

Furthermore, I would also like to acknowledge with much appreciation the crucial role of the staff of laboratory technicians: Jacqui Briggs and Caitlin Sweeney who gave the permission to use all required laboratory equipment to complete the experimental aspects of the project and assisted me in SEM and BET analysis. I would not forget to remember Kenneth Seymour who is Technical Manager of School of Engineering and Information Technology for his encouragement by assisting me in XRD analysis. Without their help, this thesis would not be possible.

Special thanks go to Mrs. Rosie Price who is Academic Support Officer, who help me to organize things to be purchased from the Science Stores. A special gratitude I give to Ms. Yvettw Toyne who is Science Store Supervisor who always gives a constant suggestion regarding the equipment that needs to be purchased.

Last but not least, to my beloved family, friends, and employer, thank you for being understanding throughout this semester with constant motivation and support.
1 INTRODUCTION

1.1 BACKGROUND AND INDUSTRIAL CONTEXT

This project is concerned about using microalgae and also about energy storage devices. These two terms are much related in this project thesis.

Further research needs to be taken on the topic, because microalgae are believed to be a worthy source of renewable energy for liquid biofuels production such as biodiesel, bioethanol, and biogas. There are some advantages of using microalgae as a source of renewable energy. They can produce more oil per acre than other crops and plants (Jegathese and Farid 2014). Plus, they have rapid growth rate and are the fastest growing plant. Moreover, microalgae can be cultivated in a non-arable land with saline water which is not usable for cultivation of other crops. For example, algae can be cultivated in waste land or waste water.

However, there are challenges to large scale biodiesel production from microalgae. Extracting the lipid components effectively and economically is the main problem for a large-scale biodiesel production from microalgae. High lipid productivity from dominant, fast-growing algae is a major prerequisite for the commercial production of microalgal oil-derived biodiesel (Sharma, Schuhmann, and Schenk 2012). From this overview, it can be seen that extracting the lipid components in microalgae is crucial to the commercial production of biodiesel. High attention has been focused on two main lipid extraction techniques, using liquid solvents such as hexane, or using supercritical fluid solvent (SCF) such as carbon dioxide. This is because both techniques provide lipid productivity in a large-scale biodiesel production where the algae are dried first. Nevertheless, drying process, which is high energy-intensive, will lead to negative net energy of biodiesel product.
Lipid extraction from microalgae receives high attention in this project plan. There is one successful method for high lipid extraction in microalgae, hydrothermal carbonization (HTC). This project focused on developing a novel method that generates high quality carbon using HTC of microalgae under several conditions. The product carbons undergo testing for suitability for supercapacitor applications.

The primary focus of this project is developing a novel method, based on hydrothermal carbonization (HTC) of microalgae, to produce high-quality carbon at a temperature below 250°C. Hydrochar is a by-product of HTC. Hydrochar will be provided as the starting material for the project. Hydrochar from microalgae will be synthesized to obtain the activated carbon. The synthesized microalgae derived activated carbon will then be analysed for supercapacitor applications in energy storage devices. Microalgae derived carbon with dopants could improve the storage capacity of supercapacitors because the ions could be transported into the carbon more efficiently. Besides, high productivity and large availability of microalgae could increase the activated carbon material for energy storage devices in supercapacitor applications. Microalgae are being chosen as a sustainable carbon source for supercapacitor production in this project, because they have a short harvesting cycle compared to other types of biomass.

A supercapacitor is also known as an electrochemical double-layer capacitor (EDLCs). A supercapacitor is more sustainable energy future compared to batteries, as supercapacitors can last for millions of charge-discharge cycles without losing energy storage capability. The synthesized microalgae derived activated carbon material will be used as electrodes in this project to be tested in the supercapacitor for energy storage devices. The activated carbon has a large surface area for electrodes, so high sorption of ions could occur to increase the performance in supercapacitor applications. The behaviour of these materials will be analysed for storage ability (Wei et al. 2011).

Recent advances in the synthesis of activated carbons have shown the possibility of fine-tuning their porosity and their chemical properties, thereby enhancing their
performance in supercapacitors. Potassium hydroxide (KOH) chemical activation has stood out among the activation procedure, as they allowing the synthesis of highly porous carbon materials with narrow pore size distributions. Besides, they also able to modulate the porosity via activation conditions. (Sevilla et al. 2014) Thus, KOH chemical activation will be carried out in this project.

1.2 STUDY AIMS AND OBJECTIVES

The sole project aim was to conduct proof-of-concept research on producing microalgae derived carbon materials for energy storage devices. This research was anticipated because it is believed that microalgae derived carbon could improve the energy storage devices. Several specific objectives had been proposed and were set to be achieved throughout this thesis work which are:

1. Conduct preliminary studies on behavior of activated carbon for supercapacitor applications.
2. Synthesize activated carbon derived from microalgal hydrochars for energy storage devices under prevailing conditions.
3. Test the energy storage performance of the synthesized activated carbon for supercapacitor applications.

1.3 THESIS OVERVIEW

The structure of this study is follows:

Chapter 2: Literature review, which includes:

I. Materials for activated carbon, the advantages of using microalgae as promising bioenergy feedstock, a novel algal biodiesel production of by-product hydrochar and the utilisation of microalgal hydrochar,

II. The pre-treatment technologies available in the industry,

III. A different method of the activation process.
Chapter 3: System implementation of quartz tube furnace that includes:
   I. Calibration and the physical laboratory setup of activation procedure.

Chapter 4: Preparation of microalgae derived carbon by adopting KOH activation, which includes:
   I. Preparation of KOH/hydrochar mixture by adopting impregnation technique,
   II. Preparation of the quartz tube furnace,
   III. The procedure of washing steps for the resulting microalgae derived carbon.

Chapter 5: Electrochemical properties of the materials, which includes:
   I. Electrochemical assembly in three-electrode configuration,
   II. The evaluation of the electrochemical analysis for the synthesized materials reflecting the energy storage performance.

Chapter 6: Covers the sample characterization of the materials, which includes:
   I. SEM images to study the surface morphology of the materials,
   II. BET and porosity analysis,
   III. The evaluation of the textural properties of the synthesized materials.

Chapter 7: Summarize the findings in this study.

Chapter 8: Covers the issues that were identified with potential strategies that could be implemented in future work.
2 LITERATURE REVIEW

2.1 MICROALGAE AS PROMISING BIOENERGY FEEDSTOCK

2.1.1 MATERIALS FOR ACTIVATED CARBON

Choice of materials is crucial for the production of activated carbons for supercapacitor electrodes regarding sustainable and economic stability (Sevilla et al. 2014). Production of highest yield of derived carbon would be the optimum condition for energy storage performance in supercapacitor applications. Biomass rises as a potential candidate for alternate sources of renewable energy for liquid biofuels production such as biodiesel, bioethanol, and biogas. There are many different sources of biomass feedstock which can be converted to liquid and gas for generation of energy fuels. Different kind of various biomass sources has been identified that can be generated for energy fuels as shown in Table 1. The listed various biomass is from different kind of sources like bio-wastes, edible and non-edible oilseeds, and aquatic plants. (Singh and Gu 2010)

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Crop</th>
<th>Oil yield (l/ha)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Corn</td>
<td>172</td>
</tr>
<tr>
<td>2</td>
<td>Soybean</td>
<td>446</td>
</tr>
<tr>
<td>3</td>
<td>Peanut</td>
<td>1,059</td>
</tr>
<tr>
<td>4</td>
<td>Canola</td>
<td>1,190</td>
</tr>
<tr>
<td>5</td>
<td>Rapeseed</td>
<td>1,190</td>
</tr>
<tr>
<td>6</td>
<td>Jatropha</td>
<td>1,892</td>
</tr>
<tr>
<td>7</td>
<td>Karanj (Pongamia pinnata)</td>
<td>2,590</td>
</tr>
<tr>
<td>8</td>
<td>Coconut</td>
<td>2,689</td>
</tr>
<tr>
<td>9</td>
<td>Oil palm</td>
<td>5,950</td>
</tr>
<tr>
<td>10</td>
<td>Microalgae (70% oil by wt.)</td>
<td>136,900</td>
</tr>
<tr>
<td>11</td>
<td>Microalgae (30% oil by wt.)</td>
<td>58,700</td>
</tr>
</tbody>
</table>

As shown in Table 1, microalgae show the highest production of oil yields from various sources of a crop in all year around which is useful for the production of activated carbons for supercapacitor electrodes. The quantity of oil production is much higher than
the yield of the best oilseed crops. For example, microalgae that even contains only 30% oil by wt. can produce 58700 litres per hectare (l ha⁻¹) in all year around are pretty much higher compared with the best oilseed crops which are 1190 l ha⁻¹ for Canola, 1892 l ha⁻¹ for Jatropha and 2590 l ha⁻¹ for Karanj. Microalgae have fast growth rate and many species with a broad range of oil content in between of 20-50% dry weight of biomass.

2.1.2 ADVANTAGES OF MICROALGAE OVER LAND CROPS

Microalgae are high productivity relative to terrestrial plants as the harvesting cycle is typically only 1-10 days in summer compared to canola, which takes once a year (Sevilla et al. 2014). Besides, microalgae are capable of assimilating carbon dioxide as they are high photosynthesis efficiency, and can cultivate in non-arable land with saline water such as wasteland or wastewater, and non-fresh water resources. (Levine et al. 2013) Microalgae do not need to compete with the land and other crops as they can be cultivated on marginal lands. The nutrients for its cultivation like nitrogen and phosphorus can quickly acquire from wastewater. Plus, their cultivation has a good impact on the environment because pesticides or herbicide application does not be applied. (Singh and Gu 2010) Moreover, Sevilla et al. found that enormous biodiversity of microalgae could obtain a broad range of textural and chemical characteristics of synthesized carbon materials. Their great availability could increase the production of activated carbon compared to other crops like canola or palm trees. (Sevilla et al. 2014)

By-product hydrochar from Hydrothermal Carbonisation (HTC) could be increased as microalgae have high productivity. Thus, activated carbon of microalgae could be increased as amount of hydrochar is increased. Hence, microalgae derived activated carbon could be potential for energy storage devices as the by-product hydrochar have spurred the interest of precursor of activated carbon materials with high performance as supercapacitor electrodes (Sevilla et al. 2014).
2.1.3 **PRODUCTION OF BIODIESEL FROM MICROALGAE**

In a production of biodiesel from microalgae on a large scale, there are two major techniques in the extraction of lipids. It is a challenge to extract the lipid components out efficiently and economically. Conventional lipid extraction techniques from microalgae are solvent extraction and supercritical fluid extraction (SFE), which works well for dried algae. Regarding solvent extraction, algae paste in water are extracted by adding liquid solvents, mostly hexane because it is the most efficient solvent based on its highest capability in the extraction of the lipids and low cost. In this approach, the algal cell wall is destroyed, and oil is extracted from the aqueous medium by solvent due to their higher solubility in organic solvents over water. Then, oil is separated from the solvent extract through a distillation process. Another technique in lipids extraction is SFE. In this technique, the advantage is time efficient. It operates at high temperature and pressure to break the algal cells that influence the extraction rate. (Singh and Gu 2010) However, drying is an energy-intensive process that leads to the biodiesel product being net energy negative. Wet extraction of algae is a low-efficiency due to the presence of a water layer between algae and solvent that avoid the access of solvents to lipids. Ensuring the sustainable production of microalgal biodiesel is crucial. One promising approach to overcome this problem is to adopt hydrothermal carbonization process.

2.1.4 **A NOVEL ALGAL DIESEL PRODUCTION PROCESS BASED ON HYDROTHERMAL CARBONISATION**

Hydrothermal Carbonisation is an economically viable process. Based on Levine et al. studies, they reported that hydrothermal carbonization (HTC) is a process to convert wet algal biomass into a lipid-rich hydrochar, then into biodiesel. Plus, it also can maximize the dissolution of non-lipid into an aqueous phase (AP) co-product that beneficial for algal biomass growth. As shown in Figure 1, hydrochar that are produced via HTC, which then undergoes in situ transesterification (IST) will produce biodiesel.
Initially, the algae are dewatered to produce a 10-25 wt. % total solids slurry, which undergoes HTC typically in a range of 190-250°C at autogenic pressures. During HTC process, algae cells will conglomerate into an easy filterable solid that retains almost all the lipid, which is carbonized solids or hydrochar. They reported that 50% of the algae biomass turns into a solid hydrochar by reacting the biomass at 200°C for 15min during HTC process. (Levine et al. 2013)

In their studies, lower temperature and shorter times are being applied respectively at 180-215°C for about 15-45min to reduce the energy and pressure required for HTC process and to ensure a production of lipid-rich hydrochar. They concluded that lipid retention could increase with reaction severity up to 200°C maximum for about 15-30min due to the limited hydrolysis of polar and neutral lipids plus the formation of hydrophobic char particles, which firmly retained all the lipids. HTC process will result in densification of algal biomass into a hydrochar with increased heating value, which energy yield and energy densification ratio play a role for the conditions. Levine at al found that 53% and 63% of the energy content of biomass contained by hydrochars whereas 37% and 47% of the biomass energy is released as dissolved components in the AP. Hence, HTC also is likely an important source of energy and nutrition for algae growth instead of biodiesel production. (Levine et al. 2013)
2.1.5 Utilisation of Byproduct Hydrochar

The production of hydrochar from hydrothermal carbonization has spurred interest in its use as a precursor of activated carbon materials for high performance supercapacitor electrodes (Sevilla et al. 2014). Electrode materials could be improved under prevailing conditions for energy storage device in supercapacitor applications. Microalgae derived activated carbon is the electrode materials that will be tested experimentally to observe the behaviour in supercapacitor applications for energy storage devices. Moreover, this could be an efficient way to enhance the economic performance of algal biodiesel production, as the by-product microalgal hydrochar is fully utilized for energy storage in supercapacitor applications via activation process under prevailing conditions.
2.2 PRE-TREATMENT TECHNOLOGIES

Pre-treatment technologies is a required phase of heating procedure for biomass feedstock before they are synthesized to produce activated carbon material as a promising energy storage. There are four type of pre-treatment technologies such as slow pyrolysis, gasification, dry torrefaction and hydrothermal carbonisation. These pre-treatment technologies are categorized on their operating conditions like temperature, holding time and heating rate. Slow pyrolysis, gasification and dry torrefaction process somehow produce carbon-rich solid product known as biochar, while hydrothermal carbonisation process produce a slurry mixture known as hydrochar. As this project focussed on hydrochar-based material, so pyrolysis and hydrothermal carbonisation process are mainly discussed.

2.2.1 PYROLYSIS

A thermochemical decomposition process is called pyrolysis at which the biomass is heated to an elevated temperature in the absence of oxygen. The typical temperature of pyrolysis process is in the range of 300-650°C. There are three main products of pyrolysis which are a carbon-rich solid product called biochar, a volatile matter called bio-oil and non-condensable gases, which change with different kind of microalgae species. The pyrolysis process is characterized into four categories which are slow, fast, flash and intermediate pyrolysis. Slow-pyrolysis is the primary pyrolysis process because the production of biochar has a higher solid yield which is typically around 25-35% compared to other pyrolysis process. A typical value of operating conditions of slow-pyrolysis is shown in Table 2. Hence, biochar is simply a solid by-product material obtained in a dry carbonization process like slow-pyrolysis process resulting in a stable carbon-rich solid by-product. Based on Kambo and Dutta’s (2015) studies, biochar that were produced by slow-pyrolysis at high temperature in the range of 600-700°C, have high surface area and
porosity with oxygen functional groups which are good for activated carbon adsorbents. Regarding sorption capacity, biochar somehow is activated to improve its performance and are thus known as ‘activated carbon’ materials. Regarding main parameters of pyrolysis process, the residence time, operating temperature, pressure, heating rates and initial moisture content of biomass are considered. In their studies, carbon percentage and BET-surface area of biochar are influenced by high operation temperature and fast heating rate whereas high solid product yield is affected by low operating temperature and slow heating rate. (Kambo and Dutta 2015)

Table 2: Classification of different thermochemical pre-treatments in terms of operating conditions and product(s) yields (Kambo and Dutta 2015)

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Operating temperature (°C)</th>
<th>Residence time</th>
<th>Heating rate</th>
<th>Typical product yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification</td>
<td>690-900</td>
<td>10-20s</td>
<td>50-100 °C/s</td>
<td>Solid: &lt; 10 Liquid: &lt; 5 Gases: &gt; 85</td>
</tr>
<tr>
<td>Dry-torrefaction a</td>
<td>200-300</td>
<td>30min-4h</td>
<td>10-15 °C/min</td>
<td>Solid: 60-80 Liquid: - Gases: 20-40</td>
</tr>
<tr>
<td>HTC</td>
<td>180-260</td>
<td>5min-12h</td>
<td>5-10 °C/min</td>
<td>Solid: 45-70 Liquid: 5-25 Gases: 2-5</td>
</tr>
</tbody>
</table>

a Generally solid product from these technologies is not regarded as Biochar, because either solid yield is very low does not have same properties as those of biochar.

Slow-pyrolysis in a fixed-bed reactor was investigated for the biochar production from algae (Spirulina Sp.) (Chaiwong et al. 2013). In their study, 125g of dried spirulina Sp. algae was fed into stainless steel fixed-bed reactor under 30mlmin⁻¹ Nitrogen gas (N₂) until the temperature reached a set of temperature in a range of 450-600°C. Then, the reactor was maintained at constant temperature for 60mins. The reactor has a dimension of 21cm height and 6cm diameter. The reactor was cleaned for air using N₂ for 30mins before testing. A schematic overview of the experimental pyrolysis setup is shown in Figure 2. The pyrolysis process was yielding a gas from the reactor, then was condensed in two-cooled condensers and was retrieved in liquid form in two collected flask resulting
condensed liquid called bio-oil whereas the solid residue called bio-char was collected inside the reactor. (Chaiwong et al. 2013)

**Figure 2**: A schematic overview of the pyrolysis experimental setup (Chaiwong et al. 2013)

### 2.2.2 HYDROTHERMAL CARBONISATION

Hydrothermal carbonization (HTC) is a thermochemical process which converts the biomass feedstock into a high carbon-rich solid product (Kambo and Dutta 2015). HTC can conglomerate and carbonize the biomass feedstock into a solid form called hydrochar. The primary product of HTC ishydrochar yielding a mass around 40-70%, which can further be improved by activation for energy storage performance in supercapacitor applications and are thus referred to as ‘activated carbon’ materials. In their study, the typical temperature of HTC process is in range of 180-260°C, and it operates at which the biomass is submerged in water and then is heated in a confined pressure which controlled at the 2-6MPa pressure level. It is a great advantage to the high moisture content of biomass like microalgae because they will not influence the process as the process itself is carried out in the presence of water. The basic parameters of HTC process are shown in Table 2. Notice that the reaction pressure is not controlled because it is autogenic with the saturation vapour pressure of water corresponding to the reaction temperature. The physicochemical properties of the product are influenced by residence time and
temperature. On top of that, the operating temperature remains the governing process parameter. HTC process is less energy intensive as it can get rid of the pre-drying requirement of wet biomass compared to other conventional pre-treatments like slow-pyrolysis. As shown in Table 2, the operating temperature of HTC process is low compared to other conventional pre-treatments which are beneficial for hydrochar production, mainly from wet biomass feedstock like microalgae (Kambo and Dutta 2015).

Sevilla et al. found that HTC is a necessary procedure for successful conversion of microalgae into a carbon material. They successfully obtained N-doped hydrochar materials from S. Platensis microalgae and glucose mixtures by HTC at a mass ratio microalgae/glucose of 1.5 when the temperature is about 180°C for 24hrs. Hydrochar is collected by filtration once the autoclave has cooled down to room temperature, then washed with distilled water, and lastly dried at 110°C for few hours. (Sevilla et al. 2014)

In this project, 200°C at 2h of microalgal hydrochar is provided for starting material. It was done by previous student. Thus, the microalgal hydrochar will be synthesized under prevailing conditions to obtain microalgae derived activated carbon for energy storage devices.
2.3 ACTIVATION PROCESS

Two techniques are usually performed for activation of hydrochars, physical activation and chemical activation. Activation steps are often required to synthesize highly porous carbon materials and increase their surface area and pore size distribution (Sevilla et al. 2014). Several factors determine the success of activation of hydrochars.

2.3.1 PHYSICAL ACTIVATION

Physical activation is the development of porosity via gasification where an oxidizing agent is injected into a furnace containing the sample at relatively high temperature. Carbon dioxide (CO₂) and steam are commonly used as oxidizing agents (Azargohar and Dalai 2008).

Based on Wang and Kaskel’s (2012) studies, physical activation needs an extra pre-step called carbonization. Carbonization of carbon precursors in an inert atmosphere is adopted before physical activation to eliminate non-carbon elements. Then followed by physical activation where oxidizing gasifying agents like Oxygen (O₂), CO₂ or steam is injected to develop the porosity of carbon materials. Commonly, it operates at high-temperature ranges from 600-1200°C. The expected reaction for physical activation is shown in (eqn (1) and (2)), where a development of porosity through the gasification of carbon occurs. The process eliminates less ordered carbon atoms to develop pores. The reaction’s products, carbon monoxide (CO) and hydrogen gas (H₂) are removed by the flowing gas. (Wang and Kaskel 2012)

\[
C + H_2O \rightarrow CO + H_2 \tag{1}
\]

*Equation 1: The expected reaction of physical activation*

\[
CO_2 + C \rightarrow 2CO \tag{2}
\]

*Equation 2: The expected reaction of physical activation*

In Kwiatkowski and Broniek’s (2017) studies, they found that porous structure of carbonization products is poorly developed. Therefore, the carbonisate should undergo
physical or chemical activation to enhance the development of the porous structure. They suggest physical activation is carried out at a temperature range of 800-1000°C in the presence of water vapor (H₂O) or CO₂. Still, physical activation yields activated carbons with specific surface area less than 2000 m²/g. In their studies, they conducted physical activation on hazelnut shells in the presence of H₂O and CO₂ as the activating agent using a self-constructed thermogravimetric apparatus. The carbonization of raw material degassed to 500°C under 30 dm³ h⁻¹ of argon atmosphere at the heating rate of 10°C min⁻¹ until the final temperature of carbonization, which depends on the activating agent, was reached, where it was 800°C if H₂O whereas 900°C if CO₂. Then, the sample is stabilized for 0.5h, followed by replacing of argon with H₂O or CO₂. Activation in isothermal conditions could be performed until 50% of mass decrement of samples is reached. Furthermore, the activating agent could again be replaced with argon, and the sample cooled to room temperature. (Kwiatkowski and Broniek 2017)

2.3.2 CHEMICAL ACTIVATION

In Wang and Kaskel’s (2012) study on KOH activation of carbon-based materials for energy storage, chemical activation is described as mixing carbonaceous materials with activating agents like potassium hydroxide (KOH), phosphoric acid (H₃PO₄) and zinc chloride (ZnCl₂). The specific surface area over 2000 m² g⁻¹ and large pore volume made up of micropores can be created after activation. They found that KOH is widely used as activating agent compared to others because it can result in activated carbon with define micropore size distribution, increased micropore volume and profoundly high specific surface area of up to 3000 m² g⁻¹. (Wang and Kaskel 2012)

Studies by Lozano-Castello et al. conclude the prominent global reaction stoichiometrically occurring during KOH activation at 400°C, which proposed in eqn (3). Hydrogen gas (H₂) is eliminated, potassium (K) and potassium carbonate (K₂CO₃) are expected to be found in the solid form. (Lozano-Castelló et al. 2007)
\[ 6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \]  

Equation 3: The expected reaction of KOH activation at 400°C

KOH is consumed when activation occurs at 600°C. \( \text{K}_2\text{CO}_3 \) in eqn (3) will be decomposed into \( \text{CO}_2 \) and \( \text{K}_2\text{O} \) when temperature greater than 700°C (eqn (4)), totally disappear at 800°C. Moreover, metallic K can be produced at a temperature over 700°C by reducing the K compounds (\( \text{K}_2\text{O} \) and \( \text{K}_2\text{CO}_3 \)) via carbon (eqn (5) and (6)). (Wang and Kaskel 2012)

\[ \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2 \]  

Equation 4: The expected reaction of KOH activation over 700°C

\[ \text{K}_2\text{CO}_3 + 2\text{C} \rightarrow 2\text{K} + 3\text{CO} \]  

Equation 5: The expected reaction of reducing K compounds via carbon over 700°C

\[ \text{C} + \text{K}_2\text{O} \rightarrow 2\text{K} + \text{CO} \]  

Equation 6: The expected reaction of reducing K compounds via carbon over 700°C

Successful activation depends on activation parameters like peak temperature, activation time, gas flow rate, heating rate, activating agent, the mass ratio between raw material and an activating agent, and choice of carbon sources. They influence the pore microstructure and surface area of materials that affect the performance of KOH-activated carbons for supercapacitor electrodes. In Wang and Kaskel’s (2012) study, the production of KOH-activated carbon in laboratory scale goes through several steps, which are mixing of powder, activation process and washing steps. Mixing of KOH and chars is either by impregnation or by physically using an agate mortar. The mass ratio KOH/carbon is in ranges from 2 to 5. Drying process is required if impregnation method is applied to help evaporate the water. It is usually dried at low temperature by using laboratory oven. Then, the samples can be synthesized inside the tube furnace at activation temperature ranges from 650-950°C. After activation, washing steps remove the remaining KOH, salts, and K, so then the products are recovered and dried. (Wang and Kaskel 2012)
In Sevilla et al. (2014) studies, they physically prepared the mixture and conducted KOH activation at temperatures ranges from 650°C-750°C and the mass ratio KOH/hydrochar being 2 in a vertical furnace, which resulting surface area up to 2200 m²g⁻¹ (Sevilla et al. 2014). While in Muniandy et al. studies, they performed KOH and sodium hydroxide (NaOH) activation on rice husk under normal atmospheric flow with the heating rate of 10°C min⁻¹ and impregnation is applied. They found that KOH is promisingly activating agent compared to NaOH. Among those various conditions tested, the impregnation ratio of rice husk/KOH being 1:5 at 850°C for 1h shows the best result of surface area for activated carbon, which is 2696 m²g⁻¹. However, the subsequent increase of activation time to 120min and at a very high temperature over 950°C could become detrimental to micropores and surface area of activated carbon. (Muniandy et al. 2014)

2.3.3 DISCUSSION

Physical activation and chemical activation have their advantages and disadvantages. Primary advantages of chemical activation over physical activation is that the process normally occurs at a lower temperature and for a shorter time compared to those used in physical activation. Moreover, yields of carbon produced by chemical activation is usually have high surface area activated carbon than those in physical activation. The activation temperature, residence time, gas flow rate, choice of raw material plays a role for the success of physical activation. The activating agent, washing step, and ratio between raw material and activating agent plays an additional role for the success of chemical activation. Sevilla et al studies found that highly microporous carbons have been successfully fabricated from microalgae by the combination of HTC and industry-adopted KOH activation processes (Sevilla et al. 2014). Thus, chemical activation using KOH as an activating agent will be chosen for this project.
2.4 SUMMARY AND RESEARCH GAPS

In summary, microalgae are prominent biomass for the production of activated carbon for supercapacitor electrodes compared to other biomass since they offer numerous advantages. Highest yield production of derived carbon can be the optimum condition for energy storage performance in supercapacitor applications (Singh and Gu 2010). According to Kambo and Dutta’s (2015) studies, they found that HTC is a promising thermochemical pre-treatments process of biomass, especially wet feedstock like microalgae, which an alternative to slow-pyrolysis because it does not require any pre-drying of feedstock for char production (Kambo and Dutta 2015). HTC can conglomerate and carbonizes the materials to produce hydrochar. Hydrochar is a solid by-product of HTC while biochar is a solid by-product of slow-pyrolysis. By-product microalgal hydrochar from HTC will be synthesized to activated carbon, as combination of HTC and industry-adopted KOH activation process yields highly microporous carbons, which influences the performance for supercapacitor applications. Slow-pyrolysis is not suitable for biochar’s production from wet feedstock like microalgae due to the pre-drying requirement of the feedstock (Kambo and Dutta 2015). Sevilla et al. also found that low cost and low temperature of HTC is an effective procedure for homogenizing biomass includes removing the mineral matter and increasing structure aromaticity as well as increasing the carbon yield (Sevilla et al. 2014). Porous activated carbon materials are the foremost selection for the construction of supercapacitor electrodes. Sevilla et al. suggest that activation is possible for fine-tuning the porosity and surface area of carbon materials, which enhances their performance in the supercapacitor. They conclude that chemical activation where KOH acts as an activating agent is the promising method to synthesize the highly porous carbon materials with narrow pore size distributions under prevailing conditions (Sevilla et al. 2014).
Much of the research relating to energy storage has focused on derived carbon of KOH activation from hydrothermally carbonized microalgae (Sevilla et al. 2012, Sevilla, Fuertes, and Mokaya 2011, Sevilla et al. 2014) and more research on chemical activation with KOH on carbon-based materials for energy storage by adopting impregnation method (Wang and Kaskel 2012, Muniandy et al. 2014). However, very little is known about synthesizing microalgae-derived carbon for energy storage devices via KOH activation by adopting impregnation method instead of physically mixing by using an agate mortar. What is the optimum process conditions for the production of microalgae-derived carbon with the highest yield and the best energy storage performance?
3 SYSTEM IMPLEMENTATION

Before the preparation of activated carbon, there are experimental process need to follow. Firstly, the quartz tube furnace need to be calibrated. Then, there are few procedure to quench the sample inside the furnace. Precaution steps can be performed during gas flow regime check-up, so that gas leaking can be avoided.

3.1 CALIBRATING QUARTZ TUBE FURNACE

3.1.1 SCOPE

The purpose of the calibration is to record the discrepancy of temperature, T and measure the temperature profile at a target temperature. The temperature profile is important to recognize the isothermal zones which means where the constant heating zone occurs inside the furnace. Plus, temperature discrepancy is required to notice the offset between the temperature inside the furnace, T2, and temperature display on the controller panel of the furnace, T1. Quartz tube furnace was calibrated before use to obtain accurate temperature inside tube furnace during heating. Model OTF-1200X-S-VT Compact Vertical Split 2" Quartz Tube Furnace was used to perform the activation. Two desired activation temperatures were performed which is at 800°C and 900°C. Essential features and technical specifications of OTF-1200X-S-VT is shown in Appendix A. External K type thermocouple shown in Figure 3 with 40" length manufactured by Marlin Manufacturing Corporation and model Shinko BCS2 TCA Control Box shown in Figure 4 were used to perform the calibration.

Figure 3: TCA Control Box
3.1.2 PROCEDURE

At first apply, the furnace is heated at 120°C for 1h and elevated up to 300°C for 2h holding time. This has been done to avoid the furnace module from splitting. In calibration, there is two temperature reading. The first one is called T1, which the temperature display on the controller panel of the furnace. The other one is called T2, which temperature inside the furnace. T2 might be different because external thermocouple is connected to external temperature controller called TCA Control Box. Then, the procedure of calibration as follows:

1. Porous ceramic blocks were placed in two ends of the tube furnace before heating. The installation of the vacuum sealing flanges including the ceramic blocks are shown in Figure 5.

2. K type thermocouple with enough length, which 25” from the centre of the furnace to one end of the tube is placed through ¼” feedthrough port of the furnace. The schematic layout of the furnace while doing this step is shown in Figure 6.
3. Then, a thermocouple is connected to the external temperature controller called TCA Control Box as shown in Figure 7.

4. Follow the general heating process described in Operation Manual to heat the furnace to desired temperature.

5. The desired temperature, 800°C is set up on the furnace controller, then the furnace is heated to the desired temperature and hold for 3h. After that, temperature reading displaying on the controller panel, T1 is recorded as shown in Figure 8.
Figure 8: Temperature displaying on the controller panel, T1

6. Temperature reading on the TCA Control Box, T2 is recorded.

7. Temperature discrepancy, T is recorded as T = T2 - T1.

8. After that, temperature profile is measured by adjusting the external thermocouple with increment and decrement of 1 cm from the centre, which resulting a total of ±16 cm as it fully occupied the size of heating chamber of the furnace.

9. The procedure of step 5 until 8 is repeated for the desired temperature at 820°C, 900°C, and 920°C as there was an offset between T2 and T1.

3.1.3 RESULTS

The typical temperature profile under different desired temperature as shown in Figure 9. It is concluded that the constant heating zone which is in isothermal zone for 2” quartz tube furnace of an OTF-1200X-S-VT model is about 10 cm at tube center area within +/− 4.0°C. Hence, the samples should be placed inside the tube furnace at within that center area, which is in constant temperature zone.
Based on Figure 9, a temperature of discrepancy between T1 and T2 is -20°C. It means, there is an offset between temperature display on the controller panel of the furnace, T1 and temperature inside the furnace, T2. During activation, temperature controller of the furnace, T1 should be programmed at 820°C and 920°C to achieve desired activation temperature, which is at 800°C and 900°C.

### 3.2 QUENCHING SAMPLE INSIDE FURNACE

OTF-1200X-S-VT is a compact vertical-split vertical tube furnace with a vacuum sealed 5cm diameter quartz tube. It provides continuous temperature 1000°C and fast heating rate up to 20°C/min. It also provides quenching that can prevent undesired low-temperature process and can heat up the samples either under vacuum or flowing gas atmospheres like argon, nitrogen, carbon dioxide or oxygen. Setup and use tips for tubes and vacuum flanges is fully described in Appendix B. Figure 10 below shows the physical

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**Figure 9: Temperature profile under various temperature (T1: temperature display on the controller panel of the furnace, T2: temperature inside the furnace)**

Based on Figure 9, a temperature of discrepancy between T1 and T2 is -20°C. It means, there is an offset between temperature display on the controller panel of the furnace, T1 and temperature inside the furnace, T2. During activation, temperature controller of the furnace, T1 should be programmed at 820°C and 920°C to achieve desired activation temperature, which is at 800°C and 900°C.

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setup on how to quench the sample inside the furnace. The sample should be hung up at about 10cm of tube centre area inside the furnace to ensure the isothermal zone.

Figure 10: Quenching sample in furnace

Figure 11 shows a top flange with hook ring that was welded inside. It is for hanging the samples by wire. High-temperature alloy wire is required to hang the quartz basket. Ni-Cr-Al wire with 1100°C working temperature is used during activation.

Figure 11: A flange with hook ring to hang the sample

The sample is stored inside the 10ml of porcelain crucible, then placed into the quartz basket as shown in Figure 12. It is because the bottom surface of quartz basket is porous such that liquid or air may pass, which have to be avoided. After that, the quartz basket is hanged properly on Ni-Cr-Al wire.
3.3 GAS FLOW REGIME CHECK-UP

KOH activation is performed under $N_2$ gas flow at the desired temperature. In Jakobsen's studies, they performed KOH activation for Microalgae Scenedesmus under $100\text{cm}^3\text{min}^{-1}$ and $200\text{cm}^3\text{min}^{-1}$ flows at various activation temperatures from $600^\circ\text{C}$ to $900^\circ\text{C}$ (Jakobsen 2016). Cole Parmer flow meter, which in range a from $2\sim20$ LPM Air, is installed vertically and source of $N_2$ gas is connected to the inlet of the flowmeter by vinyl tubing as shown in Figure 13. It is suggested to use a lower range indicator of the flowmeter to ensure the accuracy of reading as $N_2$ gas flow rate is kept around 0.2 LPM Air. Somehow, no small range of flow meter available in the laboratory.
Before activation is running, quartz tube furnace should be purged with flowing N\textsubscript{2} gas for about 20mins to ensure the furnace is cleaned. The activation is performed with continuous N\textsubscript{2} gas. Hence, the gas flow meter indicator is required to monitor the measurement.

Then, the outlet end of the flowmeter is connected to the gas inlet of the furnace as shown in Figure 14. Bear in mind that, the vacuum gauge should not have any pressure as both needle valve at the inlet and outlet end are fully opened as shown in Figure 14. Otherwise, exceeding the pressure limit can result in the vacuum flange apart from the tube and cause damage.

Then, a gas outlet of the furnace goes to fume hood as shown in Figure 15-16. Afterwards, the system is now ready for a run.
A schematic overview of gas flow regime experimental setup is shown in Figure 17. The figure shows that N₂ source, flowmeter, a valve, and furnace are required to perform the activation procedure.
4 PREPARATION OF ACTIVATED CARBON

4.1 ACTIVATION OF HYDROCHAR USING CHEMICAL ACTIVATION

In this chapter, the procedure for the activation will be presented. The purpose of activation is to generate new pores and enlarge the specific surface area of activated carbons (Li, Han, et al. 2017). Hydrochar materials are provided as the starting material for this project as shown in Figure 18. Initially, it was prepared at 200°C for about 2h holding time during hydrothermal carbonisation (HTC). The purpose of carbonization is to develop pore structure for activation and carbon concentrate with suitable mechanical strength (Li, Han, et al. 2017). Chemical activation has several factors that play a role for the success of activation process such as activation temperature, activation time, gas flow rate, choice of raw material, activating agent, washing step, and a ratio between raw material and activating agent either by impregnation method or physically mixed. Since there have many factors and a short period of a thesis project, only a few level approaches are developed in this preliminary study regarding activated carbon. The activation temperature is the only variable that will be tested. Potassium hydroxide (KOH) was chosen as an activating agent for chemical activation since it has already proven its good abilities in energy storage for carbon-based materials in other studies (Wang and Kaskel 2012, Muniandy et al. 2014, Sevilla et al. 2014). Plus, chemical activation is better for creating a porous material with pore structure (Ahmadpour and Do 1996).

Initially, the process conditions for the production of activated carbon for the purpose of energy storage are varies. Microalgae have wide range of species and its enormous biodiversity would obtain wide range of textural properties. Thus, there is no ideal characteristics of activated carbon because the process conditions are varying as the
biomass material varies. However, there are studies on the carbon-based materials for energy storage, which can be useful for this project.

From literature, it was suggested that KOH activation of carbon-based materials should be performed in the furnace at temperature ranges from 650-950°C. Therefore, few approached has been made, which two different activation temperature is performed to test this theory (Wang and Kaskel 2012). Table 3 below shows the variable of this process that been applied in this project. These activation temperatures were selected because M. Sevilla et al. studies reported that highest BET surface area is obtained when the samples is synthesized at 750°C. In addition, BET surface area is increased when the activation temperature is increased. (Sevilla et al. 2014) Thus, increasing the activation temperature over 800°C in this project is possible to generate higher BET surface area and shows good performance in energy storage.

Table 3: Variable of the activation procedure

<table>
<thead>
<tr>
<th>Activation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
</tr>
<tr>
<td>900</td>
</tr>
</tbody>
</table>

Hence, two samples of different activation temperature were prepared with the following fixed parameters as shown in Table 4:

Table 4: Fixed parameters of the activation procedure

<table>
<thead>
<tr>
<th>Impregnation ratio (KOH/Hydrochar)</th>
<th>4:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate</td>
<td>10 °C min⁻¹</td>
</tr>
<tr>
<td>Nitrogen flow rate</td>
<td>&lt; 2 LPM</td>
</tr>
<tr>
<td>Holding time</td>
<td>1h</td>
</tr>
</tbody>
</table>

By preparing the samples this way, it was possible to test the influence of different activation temperatures on the outcome. The activated carbons thus synthesized were denoted as ACn-X-T, where AC is the activated carbon, n is the number of samples, X is the impregnation ratio (KOH: Hydrochar), and T is the activation temperature. Therefore, two
samples were prepared as follows for preliminary studies regarding activating carbon for energy storage in supercapacitor applications based on provided hydrochar materials from hydrothermal carbonization (HTC) of microalgae which performed at 200°C for 2h:

1. Sample 1: AC1-4:1-800
2. Sample 2: AC2-4:1-900

### 4.1.1 Preparation of Powder Mixture

There are two ways in preparation of powder mixture which is either impregnation method or just physically. Regarding the physical preparation of powder mixture, both the solid KOH and solid hydrochar were ground together in an agate mortar. In this thesis, impregnation with KOH aqueous solution is chosen as a procedure to prepare the mixture. In this way, KOH is mixed with hydrochar homogenously.

As KOH pellets were used which is in solid form for the activation, it was ground in an agate mortar first as shown in Figure 19. Figure 18 shows the provided hydrochar materials from HTC of microalgae which conducted at 200°C for 2h. As KOH activation is conducted at the same impregnation ratio, so the KOH/hydrochar mixture was prepared at once for the two samples. Impregnation method was carried out by adding 1g of hydrochar with 40% (w/w) of the KOH solution under KOH/hydrochar mass ratio at 4:1 and stirred for 5h. Magnetic stirrer/hotplate was used to stir the KOH/hydrochar mixture continuously as shown in Figure 20. Sufficient mixing time is needed to allow the hydrochar and the solvents to diffuse into pore structure to create active sites for adsorption. An extra step for evaporation of water at low temperature is essential when impregnation method is implemented. The KOH/hydrochar mixture was then dried at 105°C for 48h before activation. The resulting dried mixture as shown in Figure 21 then was split into two portions equally and put into a porcelain crucible each as there were two samples needs to activate at different temperatures which are at 800°C and 900°C. Hereafter, the samples were ready for activation in the quartz tube furnace.
4.1.2 PREPARATION IN FURNACE

The porcelain crucible containing the sample was placed inside the quartz basket, then hung in the vertical quartz tube furnace. Quenching procedure of the sample inside the furnace is briefly described in section 3.2 as well as in Appendix B.
Figure 22 shows the physical setup of activation procedure. $N_2$ source is required to ensure the furnace cleaned for air and continuously needed during activation occur. Flowmeter is required to monitor the flowrate of $N_2$ and a valve to cut off the gas supply. Gas flow regime check-up is fully described in section 3.3. Plus, the furnace is required to activate the samples at the desired temperature.

![Physical setup of activation](image)

After hanging the sample inside the furnace, the furnace was then cleared of air using $N_2$ for 20mins. After 20mins, the flowrate of $N_2$ is reduced to the desired flow which is 2LPM. Then, set point temperature and heating rate was programmed. The desired temperature depended on the sample. Figure 23 and Figure 24 shows the temperature control program at 820°C and 920°C with several segments for AC1-4:1-800 sample and AC2-4:1-900 sample. Figure 23 shows that temperature control program is setup at 820°C for sample 1 to achieve desired activation temperature which is at 800°C because there was a temperature discrepancy, $T$ which is -20°C. This was briefly explained in section 3.1.3. Same goes to temperature control program for sample 2 as shown in Figure 24. Based on the graphs, both were kept for 1h of holding time at specified desired temperature and 10°C min⁻¹ of heating rate. Input data ($T05 = -121$), is programmed after 1h of holding time to let the program end and stop running. So that, the furnace is cooled naturally overnight until the furnace reached ambient temperature. The latch of the
furnace should not be opened while it was cooling down because this may damage the quartz tube. Turn N₂ off when the furnace reached ambient temperature. Hereafter, the sample is retrieved and ready for washing steps.

Sample mass is recorded before and after activation to give an idea about the activation process regarding mass loss. Table 5 shows the mass of the samples before and after activation. It is concluded that the percentage retained was approximately 50%.
Table 5: Mass of samples before and after activation

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC1-4:1-800</td>
<td>AC2-4:1-900</td>
</tr>
<tr>
<td>800°C</td>
<td>900°C</td>
</tr>
<tr>
<td>4:01</td>
<td>4:01</td>
</tr>
<tr>
<td>Before activation (g)</td>
<td>3.169</td>
</tr>
<tr>
<td>After activation (g)</td>
<td>1.572</td>
</tr>
<tr>
<td>Mass loss percentage (%)</td>
<td>50.404</td>
</tr>
</tbody>
</table>

4.1.3 Washing Steps

After the activation process, the samples can proceed to washing steps to remove remaining KOH as well as reaction products like salts and K. Once the samples have been washed, the expanded carbon lattices cannot return to their previous nonporous structure (Wang and Kaskel 2012). Vacuum filtration is adopted in washing steps for chemical separations instead of gravity filtration because it is a much faster process. Figure 25 shows the schematic overview of vacuum filtration setup. This figure shows that the setup for performing the washing steps contained a Buchner funnel and a vacuum aspirator assembly. A Buchner funnel is a circular porcelain bowl, porous and flat-bottomed. Type 4 of circular Whatman filter paper that has a diameter of 7cm is placed on the flat bottom and wetted to create a seal before starting the filtration. A diameter of a Buchner funnel is same as a diameter of filter paper. The stem of a Buchner funnel is fitted with a rubber bung and inserted into the mouth of a Buchner flask. Rubber tubing is attached the Buchner flask to a vacuum aspirator in the fume hood. Suction from aspirator creates a partial vacuum in a flask that pulls liquid through the filter and filter paper.
Figure 25: Schematic overview of vacuum filtration setup (Wikimedia Commons contributors 2018)

Figure 26 shows the front and top view of a physical experimental setup for vacuum filtration technique consisting of a Buchner funnel, the Buchner flask, and the vacuum aspirator. Vacuum aspirator should not fully open otherwise the filter paper can be damaged and the entire sample might suck into the Buchner flask due to high pressure.

Figure 26: Physical setup vacuum filtration setup (front & top views)

Firstly, the samples were transferred to a beaker containing hydrochloric acid (HCL) and washed by stirring continuously for 10mins. Then, the sample was sucked by vacuum filtration technique to filter out all the liquid. This process was repeated three times. Hereafter, the samples were washed with deionised water by left stirring for 10mins, then were sucked by vacuum filtration technique also. This process was repeated until the pH of the sample was neutral. At end suction of the samples, once the pH was neutral, the vacuum filtration was performed for 1h to ensure all the water is removed.
Then, resulting samples were transferred to a beaker and were dried for 3h at 120°C to remove remaining water. Figure 27 shows sample 1 (AC1-4:1-800) and sample 2 (AC2-4:1-900) after being washed and dried. Finally, the samples were ready for the analysis of the activated carbon which will be described in chapter 5 and 6.

![Figure 27: Samples after washing steps (AC1-4:1-800 & AC2-4:1-900 samples)](image)

5 ELECTROCHEMICAL CHARACTERIZATION

5.1 EXPERIMENTAL ASSEMBLY

Synthesized microalgae derived activated carbon material, which denotes as sample 1 and sample 2, and GRC22 of Calgon activated carbon, were used as working electrodes. These working electrodes will be tested in electrochemical characterization for energy storage capacity. GRC22 of Calgon activated carbon, which available in the market will be the reference electrode as they are good performance.

Firstly, the working surface of graphite bar is rubbed by sandpaper to remove any material from the surface and make them smoother. Graphite bar is used as it is an electric conductor and served as a current collector. Then, graphite bar is measured before coating. It needs to be measured before and after coating to identify the sample mass that will be used for the capacitance calculation. Electrodes were prepared by mixing 90% of activated carbon samples and 10% of polyvinylidene difluoride (PVDF) which dissolved
in 250ml of 1-Methyl-2-pyrrolidinone (NMP) by using an agate mortar to form a slurry mixture. PVDF is a standard binder material. PVDF is used because it does not react with the electrolyte and chemically inert. NMP is used as a solvent for electrode preparation due to its good solvency properties in the wide range of polymers. Resulting slurry mixture is cast onto a graphite bar by 1x1cm and heated to let NMP evaporated to form a paste electrode, which is only activated carbon left. Three times coating was done to ensure best possible thickness. The electrodes were heated on the magnetic hotplate for 5h to remove moisture as shown in Figure 28. Then, the electrode is measured again after coating once it cooled down. Sample mass is recorded. After that, the electrode is fully masked except at the end lead, and 1x1cm patch coated activated carbon as shown in Figure 29. 2M Sodium hydroxide (NaOH) was used as an electrolyte. Patch coated activated carbon which is an active material is fully immersed in the electrolyte.

![Figure 28: Activated carbon and samples electrodes were heated for 5h on magnetic hotplate](image)

![Figure 29: The electrode is masked (front & back views)](image)

Specific capacitance is often calculated for the capacitance of a single electrode, which is typically derived from a three-electrode laboratory test. The specific capacitance of a device is important in determining its electric charge storage. Then, energy density could
be identified regarding the total energy storage of activated carbon in supercapacitor applications. Figure 30 shows the three-electrode configuration. The figure shows that the active materials are tested in a three-electrode configuration for electrochemical characterization with the working electrode, reference electrode, and a counter electrode. Active materials were activated carbon, and sample 1 and sample 2 which were synthesized microalgae derived activated carbon. The working electrode is the materials to be tested and obtain information. The reference electrode acts as a set-point electrode that measures and regulates the potential of the working electrode without allowing any current to pass through it. The counter electrode varies its potential within the electrolyte to allow the required amount of current to be induced at the working electrode. (Taberna and Simon 2013) Figure 31 shows the physical setup of electrochemical characterization. Electrochemical testing was performed by using an SP-150 Potentiostat.

Figure 30: Three-electrode configuration

Figure 31: Physical setup of electrochemical characterization
5.2 TESTING THE ELECTROCHEMICAL BEHAVIOURS

The electrochemical properties of activated carbon are studied by several measurement techniques such as cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) for performance evaluation of supercapacitor materials. CV allows in performing voltage window determination and kinetic analysis by scanning a wide range of sweep rates. Besides, CD enables in analysing cyclability, resistance and capacitance by applying wide range of constant current for measuring potential voltage. EIS is conducted for linearization of electrochemical system that allows the performance of usual electrical analysis. Hence, EIS helps to predict the behaviour of a system. (Taberna and Simon 2013)

After the activated carbon was studied, sample 1 and sample 2, which are microalgae derived activated carbon synthesized at different activation temperatures, were investigated and analysed for their electrochemical properties regarding suitability for electrochemical supercapacitors. Preliminary studies on the behaviour of activated carbon is to gain a basic knowledge and understanding of electrochemical behaviours. So then, the prepared samples can be easier analysed regarding their electrochemical properties of supercapacitor materials.

5.2.1 CYCLIC VOLTMETRY (CV)

![Graph showing cyclic voltammetry results for different scan rates.](image)
The activated carbon is studied for its electrochemical properties by cyclic voltammetry (CV) in 2M sodium hydroxide (NaOH) solution with a potential window of -1.0 to 0V vs. SCE using a three-electrode configuration system at room temperature. In Avinash's studies, the requirements for a material to be considered capacitive is the curves should be rectangular shape, as the capacitance is independent of potential (Avinash Balakrishnan 2014). Figure 32(a) shows the CV of the activated carbon at different sweep rates of 2 and 20mV/s. As expected, activated carbon electrode exhibits a shape like a rectangle on CV plots without obvious redox currents in the whole potential window of the investigation. Denote that the shape of CV plot is retained at a fast scan rate of 20mV/s, which determine good capacitive properties. This result considered a suitable supercapacitor material as it resembles the reported CV requirements of the
supercapacitor. Plus, the consistency of the adsorption and desorption of the ions species is preserved, as it presents a symmetrical shape even at a higher scan rate. Additionally, the area under the curve increased when the scan rate increased, signifying that a higher scan rate stimulates higher ion concentration. Thus, the energy stored increases as the ion migration speed of the electrolyte increases inside the pores of the activated carbon.

Figure 32(b) and (c) show CV curves of microalgae derived activated carbon samples which denoted as AC1-4:1-800 and AC2-4:1-900 that were synthesized at two different temperatures, 800°C and 900°C at the same impregnation ratio of KOH/hydrochar being 4:1 under N2 flow. CV was carried out over the potential range of -1.0 to 0V vs. SCE, at the scan rate of 2 and 20mV/s.

From Figure 32(b) and (c), AC1-4:1-800 exhibit a non-rectangular shape on CV plots because there is a capacitance dependence on potential while AC2-4:1-900 showed a rectangular shape and even retained at fast scan rate which reveals the good capacitive behaviour of the supercapacitor. The CV of a typical capacitor is a rectangular shape, as the capacitance is independent of potential. Besides that, clearly seen on the graph that AC1-4:1-800 present a non-stable redox current in the whole potential window at lower scan rate which not achieve the requirement for that material to be considered capacitive by cyclic voltammetry while AC2-4:1-900 showed a stable redox current and showed symmetrical shape even at higher scan rate, as consistency of the adsorption and desorption of the ions species is preserved.

Both the samples of AC1-4:1-800 and AC2-4:1-900 have a small area under the curve. It can be seen from the graph that the adsorption and desorption of AC1-4:1-800 is higher than AC2-4:1-900. However, the area under the curve is in accordance to specific capacitance obtained, which will reveal in Table 6 at section 5.3 (Cheng-Kim Sim 2015). From Figure 32, the activated carbon presents the higher redox current and larger area of rectangular shape on CV plots than that of sample 1 (AC1-4:1-800) and sample 2 (AC2-4:1-900).
5.2.2 GALVANOSTATIC CHARGE/DISCHARGE (CD)

Figure 33: Galvanostatic charge-discharge curves of porous carbons: (a) activated carbon at different current and microalgae derived activated carbon synthesized at (b) 800°C (AC1-4:1-800) and (c) 900°C (AC2-4:1-900) at 2mA.
Galvanostatic charge/discharge is also carried out at a different constant current of 1, 2, 5mA using three-electrode configuration system at room temperature. Galvanostatic charge/discharge measurement can analyse the electrochemical properties of electrode materials and provide the best representation of the real operation of a supercapacitor, indicating its specific capacitance as well as energy density. Figure 33(a) shows the charge-discharge (CD) curves of activated carbon with a different constant current of 1, 2, 5mA. As expected from the studies, the CD curves of activated carbon present a uniform and triangular shape, which reveals the good capacitive properties of the supercapacitor. In Avinash’s studies, the requirements for a material to be considered capacitive is the curves should be symmetric between charging and discharging, preferably with linear slopes to specify constant capacitance as a function of potential (Avinash Balakrishnan 2014). Plus, it can be seen on the graph that the activated carbon presents a very long charging and discharging time at high and low constant current. This demonstrates that the carbon can withstand high reversibility and stability. The duration of the discharge process is approximately 850sec at a constant current of 2mA.

Figure 33(b) and (c) shows a CD curves of AC1-4:1-800 and AC2-4:1-900 at a constant current of 2mA. CD curves of AC1-4:1-800 shows a non-triangular shape which indicates poor capacitive properties while AC2-4:1-900 shows a symmetrical and triangular shape which indicate good capacitive properties. However, both samples present a very short discharging time: AC1-4:1-800 is approximately 18sec, while AC2-4:1-900 is approximately 7sec. It means that the samples are unstable and could not withstand high reversibility.
5.2.3 **Electrochemical Impedance Spectroscopy (EIS)**

For further analysis of electrochemical behaviour, electrochemical impedance spectroscopy (EIS) of sample electrodes has been conducted by using three-electrode configuration system at room temperature. EIS is performed to analyse the frequency response of different porous carbons to gain a clear and deep understandings into the different behaviour of different electrode materials, especially that microalgae derived activated carbon which is AC1-4:1-800 and AC2-4:1-900. Figure 34 shows a Nyquist plot of activated carbon and AC2-4:1-900 in the frequency range of 0.01Hz to 100kHz. Nyquist plot presents the imaginary component ($Z''$) as a function of real component ($Z'$) of the impedance, specifies the frequency response of the electrode/electrolyte system. The impedance is calculated from high frequencies on the left side of the plot to lower frequencies on the right. Nyquist plots exhibit two different regions that include a semicircle loop in the high-frequency region and a nearly vertical line in the low-frequency region. (Avinash Balakrishnan 2014) High-frequency region is described the low series or electrolyte resistance, which indicates the ionic resistance of the electrolyte,
intrinsic resistance of carbon active materials, and contact resistance with the current collector (Li, Akhtar, et al. 2017).

From Figure 34, as expected from activated carbon, it exhibits a clear semicircle loop at high frequency which reflects charge transfer processes. It can be seen at the high frequency, activated carbon reveal a low series resistance of approximately 6Ω. It means that activated carbon has a large pore size, pore volume and a large surface area which promotes the ions diffusion and great penetration of electrolyte ions as well as reduce the ions diffusion distance. At low-frequency region, activated carbon is showed a less inclined vertical curves, signifying the good ion diffusion into the pore structures within electrode structure. The activated carbon is ideal capacitive properties for supercapacitor. Besides, it can be seen from the figure that AC2-4:1-900 also present a semicircle loop but has a high series resistance of approximately 8Ω. Somehow, at low-frequency region, AC2-4:1-900 exhibits a very inclined and long vertical curves that indicate a very poor ion diffusion into the pore structure compared to activated carbon. Therefore, AC2-4:1-900 is poor capacitive properties and not suitable for supercapacitor applications. EIS of AC1-4:1-800 has not been performed because its CV curves does not show a rectangular shape which do not meet the requirements of a material to be considered capacitive. The CV curves of AC1-4:1-800 is shown in Figure 32(b). There is no point to proceed EIS measurement techniques as the rough behaviour is recorded. However, the specific capacitance and energy density of the electrode materials will give a significance value that reflects the energy storage for supercapacitor applications. This will be briefly described in section 5.3.

5.3 EVALUATION

The galvanostatic charge/discharge curves have been used to evaluate the overall performance of electrode samples by calculating the specific capacitance and energy density. A constant current of 2mA from CD curves is selected to evaluate the specific
capacitance. Specific capacitance (F g⁻¹) and energy density (Wh kg⁻¹) were calculated according to the equation below:

\[
\text{Specific capacitance (Cs)} = \frac{I \times t}{V \times m}
\]

**Equation 7: Specific capacitance**

\[
\text{Energy density (E)} = \frac{1}{2} \times Cs \times V^2
\]

**Equation 8: Energy density**

Where \(I\) (A) is the discharge current, \(t\) (s) is the discharge time, \(V\) (V) represents the voltage change after a full charge or discharge, and \(m\) (g) is the mass of active material.

Table 6: Performance as a capacitor of activated carbon and microalgae derived activated carbon, AC1-4:1-800 and AC2-4:1-900

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (g)</th>
<th>Specific Capacitance (F g⁻¹)</th>
<th>Energy Density (Wh kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>0.01377</td>
<td>124.436</td>
<td>62.218</td>
</tr>
<tr>
<td>Sample 1 (AC1-4:1-800)</td>
<td>0.0035</td>
<td>10.679</td>
<td>5.340</td>
</tr>
<tr>
<td>Sample 2 (AC2-4:1-900)</td>
<td>0.0155</td>
<td>0.939</td>
<td>0.470</td>
</tr>
</tbody>
</table>

Table 6 shows the performance comparison of activated carbon and two microalgae derived activated carbon samples, which are AC1-4:1-800 and AC2-4:1-900. The result showed a significant difference in capacitance and energy density value for both sample 1 and sample 2 compared with the activated carbon. From the table, the activated carbon exhibits high capacitance and energy density. It means that activated carbon can store a lot of energy, which good for supercapacitor applications. However, both sample 1 and sample 2 present low energy density and low capacitance value which reflect low area under the curve on CV plots. It means that both samples can only store a relatively small amount of energy, which makes them not suitable for supercapacitor applications compared with activated carbon. This poor result indicates poor KOH activation process.
of microalgal hydrochars. Activation parameters play a major role to ensure successful
activation of hydrochars. Significantly, the activation parameters and carbon sources
have a major influence on the pore microstructure and surface chemistry. Further studies
of various activation strategies on hydrochar from HTC are worth pursuing. It is because
HTC is an efficient wet lipid extraction technology that ensure the sustainable production
of microalgal biodiesel. Plus, its interest as a precursor of activated carbon materials for
high performance supercapacitor electrodes could enhance the economic performance of
algal biodiesel production. For further investigation, sample characterization is
performed to analyse the chemical structure, BET surface area, and pore size distribution
(PSD) of both sample 1 and sample 2.
6 SAMPLE CHARACTERIZATION

6.1 SCANNING ELECTRON MICROSCOPY (SEM)

Figure 35: A scanning electron microscopy (SEM) surface images showing typical particle morphology: (a and b) activated carbon and microalgae derived activated carbon with same impregnation ratios of KOH/char being 4:1 synthesized at different activation temperature (c and d) 800°C (AC1-4:1-800), and (e and f) 900°C (AC2-4:1-900)
The scanning electron microscopy (SEM) images were conducted to observe the surface morphology of activated carbon, and sample 1 (AC1-4:1-800) and sample 2 (AC2-4:1-900). SEM images are obtained on a Micromeritics instrument. SEM is useful to examine and analyse the microstructural morphology when using energy dispersive x-ray spectrometer (EDS) with the electron microscope. It utilizes a condensed and focused electron beam to scan a sample generating a variety of signals at the surface of solid specimen's surface, which produces images. Figure 35 shows the SEM images of the activated carbon, and microalgae derived activated carbon with same impregnation ratio of KOH/char being 4:1 synthesized at two different activation temperature, which is at 800°C (AC1-4:1-800) and 900°C (AC2-4:1-900). As seen in Figure 35(a and b), as expected for activated carbon, the material is composed of particles of irregular morphology with sharp corners and large conchoidal cavities. The SEM images reveal that activated carbon is composed of large sponge-like particles that are loose and porous. It shows a large number of pores. Figures 35(c and d) and (e and f) show the surface morphology of AC1-4:1-800 and AC2-4:1-900, respectively. AC1-4:1-800 exhibit an irregular shape with sharp edges as well, but the structure has a small number of pores developed on the surface compared with activated carbon (Figure 35(a and b)). On the other hand, AC2-4:1-900 exhibit a lumpy surface with round edges and the structure is tight and has few pores available on the surface. It seems like the structure is degrade. The different pore shapes result from the reaction between the carbon atoms and the KOH, and the impact of high temperature during KOH activation.
6.2 BRUNAUER-EMMETT-TELLER (BET) SURFACE AREA AND PORE SIZE DISTRIBUTION (PSD)

Nitrogen sorption isotherms of the both synthesized carbon samples and activated carbon were carried out to further analyse the surface area and porosity. Adsorptive capacity is plotted as a function of relative pressure. N₂ sorption is conducted by using a Micromeritics TriStar II. Figure 36 shows a N₂ sorption isotherm plots of activated carbon, and AC1-4:1-800 and AC2-4:1-900. Based on International Union of Pure and Applied Chemistry (IUPAC) classification, the activated carbon displays a type I adsorption isothermal curve with little hysteresis loop between the adsorption and desorption branches as characterized by typical of microporous materials. The activated carbon exhibits a large adsorption uptake, which reflects high surface area and pore volume (Table 7). Figure 36 also shows that both samples, AC1-4:1-800 and AC2-4:1-900 are demonstrated a type II adsorption isothermal curve according to IUPAC classification. In
this isotherm, it indicates the macroporous materials with strong and weak adsorbate-
adsorbent interactions. AC2-4:1-900 exhibit a lower adsorption uptake than AC1-4:1-800,
which reflects the lower surface area and pore volume (Table 7).

Table 7: Textural properties of activated carbon, and AC1-4:1-800 and AC2-4:1-900

<table>
<thead>
<tr>
<th>Textural Properties</th>
<th>Sample</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activated Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>1133.804</td>
<td>943.743</td>
<td>223.982</td>
</tr>
<tr>
<td>t-plot Micropore Volume (cm³ g⁻¹)</td>
<td>0.392</td>
<td>0.175</td>
<td>0.0338</td>
</tr>
<tr>
<td>t-plot Micropore Area (m² g⁻¹)</td>
<td>783.859</td>
<td>326.379</td>
<td>64.771</td>
</tr>
<tr>
<td>Total Pores Volume (cm³ g⁻¹)</td>
<td>0.483</td>
<td>0.375</td>
<td>0.0705</td>
</tr>
<tr>
<td>Total Pores Area (m² g⁻¹)</td>
<td>891.909</td>
<td>449.453</td>
<td>143.505</td>
</tr>
</tbody>
</table>

Table 7 summarizes the porosity characteristics of the samples, which are AC1-4:1-
800 and AC2-4:1-900 in comparison with the activated carbon. The resulting data of the
porosity characteristics were fitted to well-known adsorption models, which is the
Brunauer-Emmett-Teller (BET) model. The total surface area of the synthesized sample,
AC1-4:1-800 estimated using BET method is 943.743 m² g⁻¹. This surface area value is
close to the commercial GRC22 Activated Carbon (1133.804 m² g⁻¹). Micropore volume
and micropore area which determined by t-plot method of AC1-4:1-800 is 0.175 cm³ g⁻¹
and 326.379 m² g⁻¹, respectively. These micropore volume and micropore area are less
than half the present value of the activated carbon (0.392 cm³ g⁻¹ and 783.859 m² g⁻¹,
respectively). Density functional theory (DFT) method is believed to be among the most accurate for porosity distribution calculations. Thus, total pores volume and total pores area of AC1-4:1-800 measured using Origin DFT is 0.375 cm³ g⁻¹ and 449.453 m² g⁻¹, respectively, which the value is less than half the present value of the activated carbon (0.483 cm³ g⁻¹ and 891.909 m² g⁻¹, respectively). It shows contradiction measurement between t-plot method and Origin DFT techniques, anyhow the pores volume and pores area of AC1-4:1-800 is half lower than the activated carbon. Besides that, AC2-4:1-900 exhibits the lowest BET surface area, pores volume and pores area (223.982 m² g⁻¹, 0.0705 cm³ g⁻¹ and 143.505 m² g⁻¹, respectively) compared to AC1-4:1-800 and the activated carbon. The results recorded significant different which shows the influence of impact on activation temperature. The BET surface area, pores volume and pores area are reduced excessively, which leads to less suitable for supercapacitor electrodes. This overly reduced porosity property shows that too high activation temperature (900°C) may cause ablation or damage the pore structure of the electrode materials.
6.3 EVALUATION

Both samples, AC1-4:1-800 and AC2-4:1-900 exhibited a low capacitance value, thus low energy density. Therefore, SEM, BET and porosity analysis were used for further investigation. In SEM analysis, sample 1 has a small number of pores developed on the surface while sample 2 has few pores available on the surface contrast to activated carbon. Besides that, both samples present a type II isotherm, which describes macroporous materials. In contrast, activated carbon presents a type 1 isotherm, which describes microporous materials. Plus, both samples exhibited low pores area, pores volume and low BET surface area which explains their low capacitance and energy density value. Thus, both samples can only store a relatively small amount of energy and are not suitable for supercapacitor applications. Ideal supercapacitor should store a large amount of power. It is because supercapacitor has advantages in applications where a bulk amount of power is required for a relatively short time.
7 CONCLUSION

In this study, microalgae derived activated carbon was successfully synthesized by employing KOH as an activating agent using two activation temperatures is the main variables of this process, which is at 800°C and 900°C. The procedure for KOH activation from microalgal hydrochar is shown. For the analysis of the activated carbon, the carbon materials indicate the large surface area, pore volume and large pores area which is 1133.8038 m² g⁻¹, 0.48348 cm³ g⁻¹ and 891.909 m² g⁻¹, respectively. The activated carbon presents an exclusively microporous structure. When tested in a three-electrode configuration for electrochemical characterization working with 2M NaOH electrolyte solution, the activated carbon exhibits excellent capacitance and energy density value which is 124.436 F g⁻¹ and 62.218 Wh kg⁻¹, respectively. The activated carbon summarizes that it can store a lot of energy which is good for supercapacitor applications. Two samples prepared at 800°C and 900°C with impregnation ratio of KOH/hydrochar is being 4:1 present low capacitance and thus low energy density value which sample 1 exhibited 10.679 F g⁻¹ and 5.34 Wh kg⁻¹, respectively, while sample 2 exhibit 0.939 F g⁻¹ and 0.47 Wh kg⁻¹, respectively. It was thought that increasing the activation temperature might increase the energy storage. Unfortunately, the 900°C did not perform well. BET and porosity analysis conclude that both samples have low BET surface area, pores volume and low pores area. Drastic reduced of porosity properties of sample 2 summarized that too high activation temperature (900°C) might degrade the pore structure of electrode materials. Both samples were not suitable for supercapacitor applications. It is too early to judge if the materials are suitable for the supercapacitor use or not. The experimental of the samples could be performed twice at least to ensure the validity of the results. Anyhow, the limited amount of hydrochar makes it impossible because they have to be carefully consumed for prepared samples to ensure the carbon yield.
8 Future Work

Future work would include the optimization of the process parameters on the KOH activation method for the productions of microalgae derived activated carbon with the best energy storage performance. There are several factors that influence the successful of chemical activation. It includes the activation temperature, holding time, activating agent-carbon mass ratio and nitrogen flow rate. Large-scale on many variables of the activation process has to be considered in order to optimize the productions of microalgae derived carbon with the best energy storage performance. Studies on KOH activation of carbon-based materials for energy storage suggests that the activation temperature is typically in the range from 650 to 950°C, the holding time ranges from 0.5 to 2 hr, and KOH-carbon mass ratio ranges from 2 to 5 (Wang and Kaskel 2012). In this study, thought of increasing the energy storage, the activation temperature should slightly decrease in the range from 650 to 800°C at the first start in future work.
# APPENDIX A–OTF-1200X-S-VT FEATURES AND SPECIFICATIONS

| Furnace Casing | • Double layer steel structure with air cooling  
| | • Split door design for easy installation of tube  
| | • High purity Al2O3 fibrous insulation designed for maximum energy saving  
| Power | 1200W  
| Voltage | AC 110V or 220V Single Phase, 50/60 Hz  
| Max. Temperature | 1100°C  
| Continuous Temperature | 1000°C  
| Max. Heating Rate | <= 20 °C/min  
| Tube Size and Materials | OD: 25mm (or 50mm); ID: 20mm (or 44mm); Length: 610mm, Quartz tube (included)  
| Heating Zone Length | 200mm (single zone)  
| Constant Heating Zone | 100mm (+/-2°C)  
| | • 30 programmable segments for precise control of heating rate, cooling rate and dwell time.  

| **Temperature Controller** | • Built in PID Auto-Tune function with overheating & broken thermocouple protection.  
| | • Over temperature protection and alarm allows for operation without attendant(s).  
| | • +/- 1 ºC temperature accuracy.  
| **Heating Elements** | Fe-Cr-Al Alloy doped by Mo  
| **Vacuum Sealing** | • Two stainless steel flanges with vacuum gauge and valves included  
| | • A hook ring is welded inside of the top flange for hanging samples or crucibles by wire  
| **Fitting Ports** | □ You may order an optional 2” flange (for 50mm O.D. tubes only) with 1/4” feedthrough port for inserting a thermocouple or rod  
| | • Standard 1/4” Barbed fittings with needle valves.  
| | • For supplying high pressure gas, you may replace the standard barbed hose fitting with the 304SS 1/4” Swagelok® Tube Fitting, please click underlined to order.  
| | • Optional: In order to increase the throughput and achieve high vacuum, you may replace the standard barbed hose fitting with the KF25 adapter, please click the underlined to order.  
| | • Optional: You may also consider using the parts in below to increase the vacuum efficiency ○ Please click here to
**order digital vacuum gauge for precision vacuum control up to** $10^{-4}$**torr** (see picture below and click to enlarge)

- You may click here to order flow-meter and install in tube flange (see picture below)
- **KF25 Stainless steel Bellows**
- **KF25 Quick Clamps**

<table>
<thead>
<tr>
<th><strong>Vacuum Level</strong></th>
<th>0.1 Torr by mechanical pump</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dimensions</strong></td>
<td>340mm×300mm×1000mm (W x L x H)</td>
</tr>
<tr>
<td><strong>Net Weight</strong></td>
<td>about 20 Kg (excluding mobile cart)</td>
</tr>
<tr>
<td><strong>Shipping Weight</strong></td>
<td>200 lbs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Warranty</strong></th>
<th>□ One year limited warranty (Consumable parts such as heating elements, processing tubes and O-rings are not covered by the warranty, please order the replacement at related products below.)</th>
</tr>
</thead>
</table>
| **Compliance** | • **CE Certified**  
• UL / MET / CSA Certification is available upon request, additional charges will apply  
• Transformer is UL Certified |

| **Application Notes** | □ [Click here to learn how to use and maintain ceramic tubes in MTI high temperature tube furnaces](#)  
In order to obtain accurate temperature inside tube furnace, you need to calibrate temperature before use, please click [here to learn how](#)  
High temperature alloy wire is available at related products |

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APPENDIX B–SETTING UP THE TUBE AND VACUUM FLANGES

Properly setting up the tube and vacuum flanges prior to heating will ensure the furnace to work under the most ideal conditions. This will insulate the heat from the flanges while simultaneously preventing the dissipation of heat from the furnace chamber. The insulation of heat stabilizes the heating zone which in turn expends less energy and places less wear on the heating elements.

Please use the tips below for safe and proper handling of the furnace equipment.

1. Refractory tube blocks should **ALWAYS** be inserted inside the tube and placed on both ends of the furnace casing (shown in the picture below).

![Diagram of tube blocks inserted in furnace]

2. Install the vacuum sealing flanges on each side of the tube using the picture below as reference. Seal the flanges by tightening the screws to finish the assembly.

![Diagram of vacuum sealing flanges]

3. Limit the pressure regulator attached to the gas tank to below 1.1 atm before filling the tube with gas. Keep the vacuum valve(s) open during gas filling to avoid high pressure from building up inside tube.
WARNING:

- Tube furnaces are designed to be used under vacuum with low pressure gases. **NEVER** inject gas into the tube with pressure higher than 1.2 atm. Pressure build up inside the tube may cause the flange(s) to be catapulted which may cause injury or death.
- Use of vacuum on alumina tubes at temperatures over 1500 °C is strictly prohibited.

4. MTI will not be responsible for any equipment damage, physical injuries, or fatalities resulting from negligence, misuse and lack of proper knowledge of the end users. For further guidance on using the tube furnace, please contact MTI engineers at info@mtixtl.com for assistance.


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