

CHARACTERIZATION OF ACTIVATED CARBON FROM AUTOMOTIVE PAINT SLUDGE VIA MICROWAVE PYROLYSIS AND ITS POTENTIAL IN SUPERCAPACITOR APPLICATION

Kevin Hosea anak Krisber and Dr. Siti Shawalliah Idris,

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—Industrial wastes such as automotive paint sludge has been an environmental problem for quite some time. With methods such as microwave assisted pyrolysis, it is possible to reduce the waste to be put to better use. Due to the high moisture content of the sludge, pyrolysis via microwave radiation is an added advantage as it will act as the heating medium. From this process, the automotive paint sludge is reduced to a solid char, liquid oil and gas. This research is focus on the producing the solid form with prior chemical activation. Radiation time and microwave power level are the parameters being applied in this research. It was concluded that through this method, the samples produced very low surface areas and is not suitable in producing activated carbon to be used as supercapacitors.

Keywords—Activated carbon, automotive paint sludge, microwave assisted pyrolysis, supercapacitor.

I. INTRODUCTION

Every year, millions of vehicles be it land, air or sea, are built all over the world. It is a known fact that this industry keeps on increasing in size every year due to the high and increasing demand for vehicles worldwide. For the purpose of this research, the automotive industries are focused on. These are the industries that focus on the manufacturing of cars and its processes. Shown in Figure 1.1, the growth of global car sales almost doubled since the 90's. With billion dollar revenues every year, it is not surprising that the amount of cars sold in the distant future will keep on increasing.

In this industry, the manufacturing of cars undergoes various processes with tweaks and fixes before being put out on the market. One of the process that relates to the topic is the painting process of the car as the finishing touches once the car has been fully manufactured. The results of this procedure are production of waste which are referred to as automotive paint sludge (APS). The sludge formed is very viscous and becomes problematic in handling the waste. Since the production of vehicles increase every year, it is inevitable that the sludge increases accordingly as well.

Automotive paint sludge is a waste that contains high amounts of organic and inorganic substance. The conversion of APS to solid char, fuel and biogas can be obtained via pyrolysis. By far, there hasn't been that many discoveries on the applications of APS char and how it can be fully utilized to optimize its potential. Based on the characteristics of APS char, it is known to contain high amounts of carbon. This fits well in the purpose of studying the possibility of converting the char into a supercapacitor. Supercapacitors can be produce if the char can be made into a

good activated carbon. Production of activated carbons from other types of char have been researched before this thus proving that there is a capability for a carbonaceous char to be used the same way. However, char that have been pre-treated with chemicals to produce the activated carbon before being converted into char has not been researched for the automated paint sludge. Thus, it is vital to study the potential of this pre-treated char in terms of whether it can produce the same or better supercapacitor compared to its predecessor.

In the automotive industry, many types of waste are produced. One of which is the automotive paint sludge (APS). APS are produced in the painting process of an automotive industry usually in a paint spray booth. As the parts are being sprayed in this section of the industry, a small amount of the excess paint which are unable to stick to the multiple layers of paint are then washed with the help of continuously circulating water curtains collecting the paint in a sludge pit underneath the floors of the paint booth [1].

The common painting process for the spray booth includes the coverage of three layers. Traditionally, both the metal and plastic surfaces will be covered with layers of primer, base and clear (varnish) as discussed by [2]. Some research has been done to reduce the production of waste from integrated painting methods. This requires extensive study as different plants will consume different raw material and have different conditions to fulfil. Such research includes studying the life cycle of different painting materials which includes solvent-base and powder primers, solvent-based and powder clear coats, and water-based basecoat as in [3].

Supercapacitors are part of an electrical storage device which are capable of storing electrical energy in a confined space. It is an electrochemical capacitor with a high capacitance value compared to conventional capacitors. It is also known as supercondensers, ultracapacitors, and pseudocapacitors. Basically, a supercapacitor consists of the electrodes separated by electrolytes, the applied voltage which is the power source and a load resistance to control the electrical intake. This is the basic concept of the There are many types of supercapacitors available.

Activated carbon is a material that consist of pure carbon produced by highly carbonaceous substance. Most carbonaceous material with low organic volatility, have enough strength and high in elementary carbon can be used to produce activated carbon [4]. Carbon is known to be a good conductor of electricity. This characteristic makes it a suitable in the application of supercapacitors where it can be used to develop the electrodes.

There are two types of process to activate the carbon one is through physical activation and the other is chemical [5]. In the physical activation process, raw material is heated in extreme temperature conditions using carbon gases. This is also known as the dry activation process. For the chemical activation process, the

raw material is subjected to chemical injection which are called the activating reagent. Known also as the wet activation process, the reagents used are usually a strong base, an acid or a salt. The activation process is commonly done together with the carbonization process. This means that the raw material undergoes both processes simultaneously. There are many different types of chemicals that can be used as the reagent. Each one has their own specific benefits with some only reacting with certain raw material. Based on [5], these chemicals include H_2SO_4 , NaOH , KOH , ZnCl_2 , K_2CO_3 , K_2HPO_4 and H_3PO_4 amongst others. In comparison, both methods of activation have their own advantages and disadvantages. However, the chemical method of activation is usually chosen as it has a lower temperature and shorter time requirement.

Pyrolysis is a method of heating at high temperatures without the presence of oxygen. It is also known as a thermal decomposition method of organic materials. Both the chemical composition and the phase of the raw material changes when undergoing pyrolysis. These changes occur simultaneously and the reaction is an irreversible one. In pyrolysis, sufficient heat is required in order for the process to work efficiently. The heating method must supply enough heat while also using up less energy to function. One method which fits both criteria is by using microwave radiation. Microwave pyrolysis is able to provide the needed temperature while reducing the energy supplied for the process itself. One of the reasons for this is because microwave uses radiation which is able to supply heat to the raw materials efficiently and thoroughly since there is no resistance in heat transfer as compared to convection and conduction. In the research of [6], biochar was produced with the aid of microwave heating and slow pyrolysis with various biochar to agents' ratio to analyze how the pyrolysis process influenced the results.

The scope of this research on the characteristics of the pre-treated automotive paint sludge char which is generated via microwave pyrolysis. The characterization of the char is specifically based on the criteria of a supercapacitor as the objective states. This is to determine whether it is suitable to be used as a supercapacitor. The characteristics to be determined is the micro structure, porosity and the surface area. The product will be evaluated on its performance as a supercapacitor in comparison with other supercapacitors that have been previously researched and marketed. This research is solely on the potential of the activated APS being applied in the production of a supercapacitor and does not cover other possible potential of it in any other application in terms of better waste management. It is noted that this is a one-step method meaning that it is a shortcut method as compared to the research of [6] in the sense that the APS is chemically activated prior to undergoing microwave pyrolysis. As such, the objective of this research is to identify the characterization of the APS activated product and its potential to be used in the application of a supercapacitor.

II. METHODOLOGY

A. Materials

The raw material, which is the automotive paint sludge, is collected. This is done manually and the source of the raw sample is from a local automotive industry. The chemicals used are potassium hydroxide (KOH) and sulphuric acid (H_2SO_4) which are both prepared in the chemical laboratory to obtain 5M and 1M respectively which similar to the works of [6].

B. Experimental Setup

A modified commercial microwave is used to provide the microwave assisted pyrolysis. Samples are placed in the quartz

reactor which is connected with a nitrogen gas tank to provide the necessary inert condition with flowrates up to 250 mL/min. Before the microwave is started, it is first tightly closed and the reactor is purged with nitrogen gas for 10 minutes. 200g of APS samples are weighed using an electronic balance and prepared for each run.

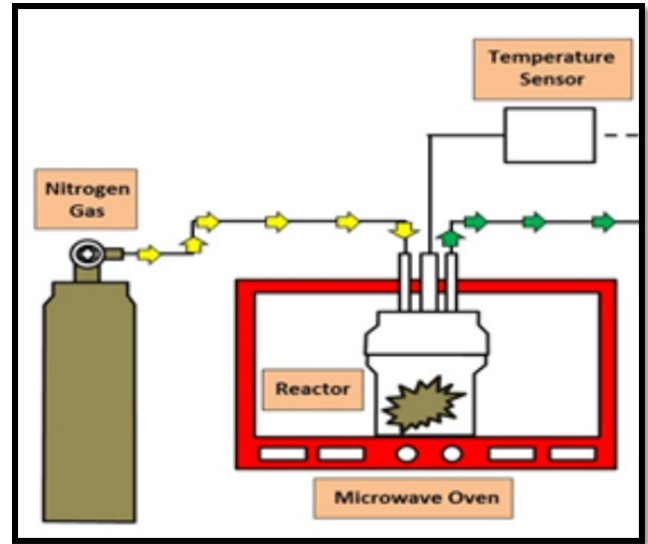


Fig. 1: Experimental setup of the microwave pyrolysis equipment

C. Experimental Procedure

An APS sample is taken and pre-treated with 5M KOH at a ratio of 4 parts APS to 1 part KOH which results in 200g of APS and 50g of KOH . This ratio is obtained based on the research of [7] where they discovered the higher chemical ratio leads to increased stripping of Hydrogen and Oxygen in the APS leading to higher weight loss and lower yield. It is then placed in the quartz reactor and left in the microwave to be purge for 10 minutes. In this research, two parameters are analyzed which are microwave power level and radiation time in the range of 300 W to 1000 W, and 20 minutes to 40 minutes respectively. The chemically activated sample is then taken out to be washed with 1M H_2SO_4 and filtered with filter papers. The filtered samples are then left to dry before being crushed into smaller particle size to be characterized using the Surface Area Analyzer BET (Brunauer-Emmett-Teller), 3Flex Micromeritics.

III. RESULTS AND DISCUSSION

A. Potassium hydroxide activation

For the first part of the experiment, the APS is added with potassium hydroxide (KOH) which acts as a chemical activator for the sludge before it is being placed inside a microwave pyrolysis equipment. The mass for the reactor, APS and KOH is taken before being each run to avoid any external factors that could manipulate the results.

After mixing the KOH with the APS, a pungent smell is produced due to the chemical reaction. The mixture is then placed inside the microwave to be applied with heat at a fixed amount of power and time. Post pyrolysis, the mixture is observed to be harden as in accordance to the mixture being heated to the point where moisture is loss from the substance due to evaporation.

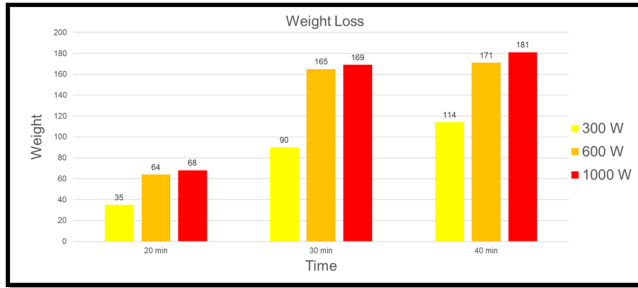


Fig. 2: Weight loss against radiation time after KOH activation

As shown in figure 2, the weight loss after KOH activation increases as the radiation time and also the radiation power increases. This is due to the sample being exposed to the radiating heat for a long period of time and at a higher frequency which increases the capability of the sample to lose its moisture. The amount of weight loss increases up to three times as much as the radiation time is increased from 20 minutes to 30 minutes. However, the increase in weight loss does not drastically increase when comparing 30 minutes of radiation time to 40 minutes. This shows that the effective weight loss of moisture is within the radiation times of 30 minutes to 40 minutes. This trend is also similar when comparing the difference in radiation power supply as the weight loss from 300 W about half the amount of weight loss at 600 W even at different radiation times. Still, the weight loss amount does not increase that much when comparing microwave power of 600 W than that of 1000 W. This also shows the maximum range in which the sample reaches its peak of moisture loss from microwave assisted pyrolysis. From the information of weight loss, the yield of the samples are able to be taken as shown in Table 1. The yield is observe to decrease as the radiation time and power is increased.

Table 1: Yield of sample after activation

Parameter	Initial Weight (g)	Final Weight (g)	Yield (%)
300 W / 20 min	250	215	86.0
600 W / 20 min	250	186	74.4
1000 W / 20 min	250	182	72.8
300 W / 30 min	250	160	64.0
600 W / 30 min	250	85	34.0
1000 W / 30 min	250	81	32.4
300 W / 40 min	250	136	54.4
Blank*	200	71	35.5
600 W / 40 min	250	79	31.6
1000 W / 40 min	250	69	27.6

*The blank sample is pure APS sample undergoing microwave pyrolysis at 1000 W for 30 minutes without the presence of any prior chemical activation.

When comparing to previous research, it is found that [7] obtained about 80% to 20% yeild with different temperatures. This proves that higher temperatures tend to increase the weight loss as the moisture is more prone to be dried up in the process.

B. Sulphuric acid washing

After being chemically activated, the samples are then washed down with sulphuric acid to neutralize the samples and dispose of any impurities and foreign particles. While washing, it is found that a very pungent smell is produced as the acid neutralizes the remainder of the potassium hydroxide trapped in the sample. The sample is of much darker form than before as the time goes by during washing.

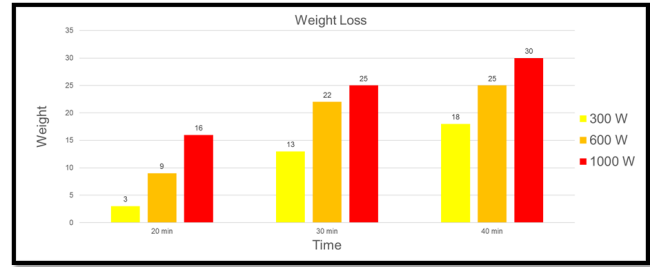


Fig. 3: Weight loss against radiation time after H₂SO₄ washing

The weight loss is noticed to be increasing as the radiation time and power increases. This trend is due to the increased radiation exposure and higher intensities of radiation which allows more excess weight to be washed away. The reason for this is because the chemical structure of the sludge is weakened thus allowing more excess amounts to be disposed of.

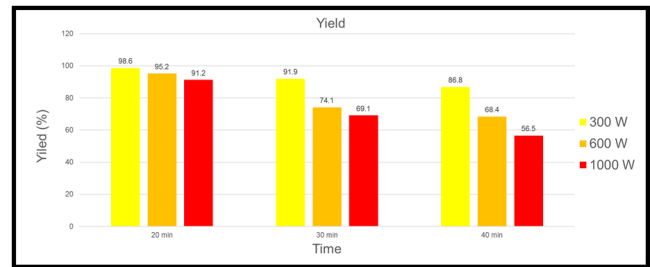


Fig. 4: Yield percentage of samples after washing

The percentage of yield of the sample is calculated after washing and clearly shows the difference in yield between different radiation time and power. The trend is not different when comparing 20 minutes to 30 minutes and 40 minutes as the initial weight is different for every single one. Shown in Figure 4, the decrease is not that significant for the 20 minutes' sample as in the other two as it shows the stability of the sample in the time region. However, due to increasing radiation time, the sample shows lower yield as the radiation time increases, and significantly decreases when comparing 300 W to 600 W and 1000 W signifying that the bonds of the sludge is much weaker when using 600 W and 1000 W thus decreasing the yield furthermore in the washing stage.

C. Surface area analyzer BET (Brunauer-Emmett-Teller), 3Flex Micromeritics

To analyze the surface area of the sample, a BET analyzer is used. As shown in Figure 5, the higher power and radiation time increases the surface area of the sample. At 1000 W, it continues to increase as the radiation exposure time is increased. However, when compared to various journals, the surface area obtain is far from the surface area of a standard activated carbon which is in the range of 500 m²/g to 3000 m²/g where even 600 m²/g is considered a low surface area in [8]. This shows the method of this research is not applicable in obtaining a proper activated carbon sample.

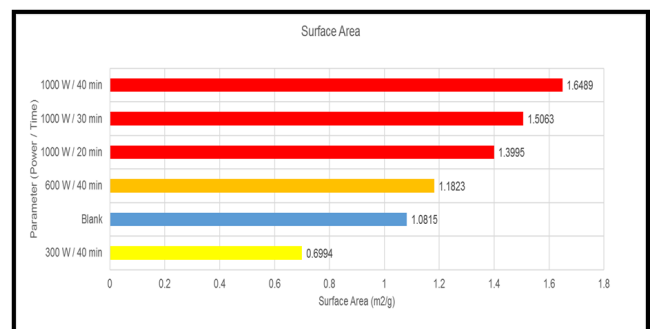


Fig. 5: Surface area of samples from BET analysis

IV. CONCLUSION

The characteristics of the samples were able to be obtained and the surface area is studied and compared with that in previous journals of the similar research. As for the purpose of producing activated carbons to be used as supercapacitors, it is found that this shortcut method to chemically activate the APS prior to undergoing microwave pyrolysis is not the most suitable as the results produced very small surface areas compared to the conventional method of producing biochar using microwave pyrolysis prior to chemical activation and then repeating the microwave pyrolysis process. It can be noted that using different chemical activation and parameters involve may increase the surface area but it will not be as significant as to obtain the surface area of an activated carbon. It is recommended to remain with the procedure of producing APS char prior to chemical activation and microwave pyrolysis in order for the activation to be fully utilized and decrease the moisture content of the sample to a significant amount.

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