EXPERIMENTAL ON OXYGEN ADSORPTION STUDIES FOR STORAGE SYSTEM USING MODIFIED BURNT PADDY HUSK SORBENT

Nurul Shahiera Shafie[1], Nabilah Zaini[2], Noor Shawal Nasri[3]
[1,2]Department of Chemical Process Engineering, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, 54100 Wilayah Persekutuan, Kuala Lumpur, Malaysia.
[3]Sustainable Waste-To-Wealth Program, UTM-MPRC Institute for Oil and Gas, Resource Sustainability Research Alliance, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor, Malaysia

Abstract: A respirator is a device designed to protect the wearer from inhaling harmful substances such as dust, fumes, vapors, and/or gases. Generally, a respirator can be grouped into two categories which are air purified respirator (APR) and air supply respirator (ASR). Air purifying respirator removes contaminants from air by passing the ambient air through the air-purifying element before it reaches the user. Besides, the air supplying respirator supplies clean air to the users through an air-supply hose. Air supply respirator consists of the face mask, air cylinder, and regulator. By having air cylinder, air supply respirator can operates up to 45 minutes. However, there are few drawbacks associated in designing an appropriate air-supply respirator which are short duration of operation and not very practical to be used due to the heavy weight of air cylinder. In order to design a flexible and practical air-supply material, this research was conducted to modify the physical and structural properties of a low-cost green-based adsorbent for oxygen adsorption application. To complete the aim, paddy husk was modified using acid and alkaline-based activated carbon (AC) in order to improve the surface area and porosity volume of the modified sorbent. Then, the morphological and structural analysis were accomplished with the helped of variable pressure scanning electron microscopic, elemental dispersion x-ray analyzer, and Fourier Transform Infrared spectroscopy. The analysis shows that the acid and alkaline functionalized activated carbon burnt paddy husk affects the properties of the surface sorbent. The oxygen adsorption and desorption studies were conducted in a single cyclical operation. Results gained from this study revealed that the acid-AC burnt paddy husk sorbent recorded the highest oxygen adsorption capacity at 3 bar with the capacity is 38.1240 mmol/g, whilst the alkaline-AC burnt paddy husk sorbent adsorbs up to 31.6036 mmol/g oxygen at 5 bar. Thus, this study established that the surface chemistry modification done on the burnt paddy husk gives a reasonable effect to the oxygen adsorption capacity experimentally.
Keywords: Air Purified Respirator (APR); Air Supply Respirator (ASR); burnt paddy husk; chemistry modification; oxygen adsorption;

I. INTRODUCTION

A respirator is a device designed to protect the wearer from inhaling harmful substances such as dust, fumes, vapors, or gases [1]. Respirators are used wherever airborne contamination is a possible threat by personnel at home, industry, agriculture, mines, emergency first responses, medicine, and military. Gases, vapors, dust, and particulate of various sizes including aerosol are some examples of the threats that may be arisen. Respirators are designed in various types including popular filtering facepiece respirators (FFRs), filtering air-purifying respirators (APR), air-supplied respirators (ASR), blower powered air-purifying respirators (PAPR), and self-contained breathing apparatus (SCBA) [2]. Respirators can be divided into two categories which are air-purifying respirator (APR) and air-supplied respirator (ASR). Air purifying respirator also known as the gas mask respirator, full face mask, half face mask, and full-face respirator that has the same function to the disposable respirator and more versatile [3]. The APR type mask filters the air through the concept of negative pressure, where negative pressure is applied to the user when breathe using the respirator mask. This alteration is important since all the supplied air respirator and powered air respirator are intended to function under a positive pressure (ambient). Thus, through the filter, the air is blown into the respirator mask [3]. The other category is air-supplied respirator which also known as a self-contained breathing apparatus (SCBA) is worn by the firefighters, rescue workers, and other purposes that dealing with the oxygen-deficient atmosphere. The SCBA consists of three main components that are high-pressure tank, pressure regulator, and inhalation connection [3]. In Malaysia scenario, the military uses the APR-type, while the airlines use the ASR-type.

The Fire and Rescue Department (FRD) and the Ministry of Health (MoH) are practicing the use of open-circuit SCBA. The open-circuit SCBA-type is filled with filtered and compressed air that passes through a regulator. An open-circuit SCBA is equipped with a full-mask, regulator, air cylinder, cylinder pressure gauge, and harness. The air cylinder holds the breathing air and completely equipped with the hand-operated shut-off valve. The regulator that functions to control the air flow harness are the strap and fastener to attach the SCBA to the firefighters. In fact, the use of SCBA is widely used for emergency cases during a rescue that lets the user mobilizes without the restriction of hose or air-line in an oxygen deficient atmosphere. A self-contained breathing apparatus (SCBA) is mainly used for an oxygen deficient atmosphere such as tanpal, tunnel, well, and sewer. SCBA is ordinarily utilized for a temporary routine and crisis work where the air is provided directly from the source conveyed by the users. In the case of the SCBA operated without the support of oxygen cylinder, the minimum time to sustain is only 30 minutes. However, if the SCBA is prepared with the airline operating that has a positive pressure mode, the air supply may last in excess in just 15 minutes for a normal work.

However, it can be less for escape use contingent on the cylinder size used. A self-contained breathing apparatus (SCBA) gives the air from a source conveyed by the user that some way or another limited due to the overwhelming weight and large in size that would lessen its practicability. In this study, the oxygen adsorption and storage studies were done using the modified green-based materials to determine the performance of the sustainable green-based material and storage system. This is to assess whether it can be used to be commercialized which will help the users to minimize the difficulties of wearing a respirator equipped with the heavy-weight air-supply storage system and changing to the intention towards the easier and practically use air-breathing system.

II. METHODOLOGY

For the preparation of samples, paddy husk was selected as a precursor in this study. This material underwent the physical modifications via carbonization and activation steps. After the modification was done, the samples were physically and structurally characterized using thermogravimetric analyzer (TGA), variable pressure scanning electron microscope (VPSEM), electron dispersive x-ray (EDX), and Fourier Transform Infrared (FTIR) spectroscopy. Afterwards, the prepared samples underwent the adsorption process in the oxygen adsorption system. These samples were compressed by varying the pressures at 3 bars and 5 bars, respectively.

III. RESULTS AND DISCUSSION

3.1 Thermo-gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) was used to determine the degradation of samples of weight loss with respect to the increasing temperature [4]. Figure 1 shows the TGA curve for the raw material of burned paddy husk (PH). The y-axis represents the percentage of weight loss, while x-axis signifies the temperature (℃). The temperature range for this analysis was 30℃ to 1000℃. Three degradation steps are recorded that weight loss due to removal of moisture content, weight loss due to removal of celluloses and hemicelluloses contents, and weight loss due to the formation of char [5].

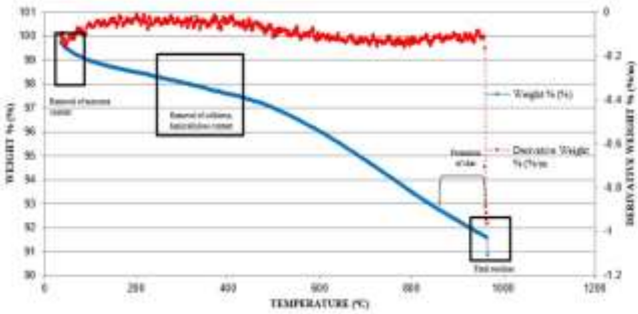

Figure 1: TGA curve for burned paddy husk. Thermo-gravimetric analysis result offers the important data in identifying the kinetic characteristics medium. Palm kernel shell and paddy husk are the examples of biomass containing celluloses, hemicelluloses, and lignin components. There are three phases involve in this TGA graph. The first degradation occurs at temperature range between 30℃ to 150℃ indicates the removal of moisture and some extractive. For paddy husk, it recorded of 1% of the weight loss. The second degradation range for paddy husk is occurred at 250℃ to 450℃ where the weight loss recorded is 3%. The second degradation range can be explicated by the degradation of hemicellulose, lignin, and celluloses. The third degradation range represents for the char production. At this range, a paddy husk loss another 9% from the second degradation stage.

3.2 Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared (FTIR) spectroscopy was applied to distinguish the shrinking, appearing, and disappearing of the chemical structural in the form of spectra [6]. Figure 2 shows the FTIR spectra for paddy husk by comparing the raw, char, and activated carbon samples, respectively.

Figure 2: FTIR spectra for paddy husk, paddy husk char, and activated paddy husk samples.

As indicated in Figure 2, peak at 3446.34 cm^{-1} represents the hydrogen bond (-OH groups) which belongs to the cellulose compounds [7]. After the preparation of char and activated paddy husk, the peak has been disappeared that explained that the celluloses compounds had been entirely burned off. Then, the peak at 1646.24 cm^{-1} addresses the carbonyl stretching of C=O for acetyl and ester groups in hemicelluloses. The sharp peak at 797.30 cm^{-}1 is correlated to the (=C-H) bond from the alkene group which addresses to the lignin compound.

3.3 Variable Pressure Scanning Electron Microscope (VPSEM)

Variable pressure scanning electron microscope (VPSEM) was used to visualize the topographical of the prepared samples by scanning it with the focused beam of electrons Figure 3 shows the cross-sectional image of paddy husk in the forms of raw, chars, and activated carbon at the magnification of 500x, respectively.

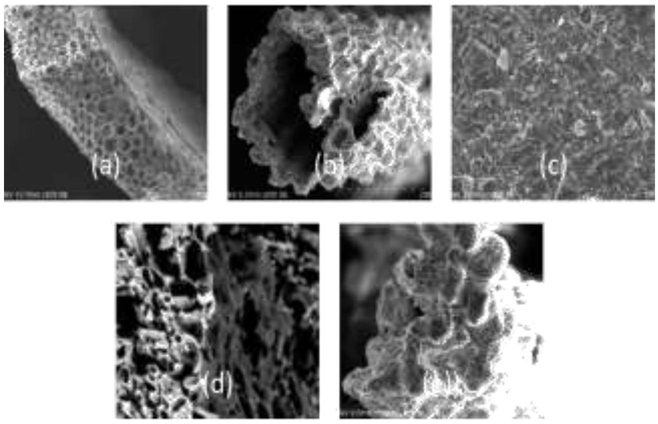

Figure 3: Cross-sectional area of (a) raw paddy husk, (b) burnt paddy husk, (c) char paddy husk, (d) 1M KOH paddy husk activated carbon, (e) 1M HNO3 paddy husk activated carbon.

From Figure 3, paddy husk formed a sturdy structure which is suitable for the gas adsorption process. The gaps that can be seen is suitable to interact with the higher amounts of sorbates during the adsorption process. After underwent carbonization step followed by activated carbon using 1 M of KOH and 1 M of HNO_3, the porosity and structure had shown some changes. The cross-sectional of the structure appear to be much clearer and circular holes can be observed apparently. The activated carbon porous surface is developed by the isolation of volatile matters in char and the gasification that was done which led to the meso porosity inside the carbon structure [8]. The pores can be classified into three categories which are micro-pores (< 2 nanometer diameter), meso-pores (2-50 nanometer), and macro-pores (>50 nanometer) [13].

3.4 Energy Dispersive X-Ray Spectroscopy (EDX)

Energy Dispersive X-Ray Spectroscopy (EDX) was applied to identify the elemental compositions of the prepared sample Table 1 shows the element compositions of paddy husk in different properties which are raw, carbonized, and activated carbon. The elemental composition was taken at the particular cross-sectional area of the sorbent surfaces. The elements that had been detected are carbon, oxygen, sodium, magnesium, potassium, as well as calcium.

Table 1: Elemental composition of paddy husk.

Sample	Paddy Husk (PH)				
Elemental Composition (%)	Raw	Burned	Char	1M KOH AC	1M HNO_3 AC
Carbon (C)	43.42	5.23	57.99	53.79	7.45
Oxygen (O)	52.43	68.09	41.74	31.33	90.1
Sodium (Na)	-	2.86	-	0.68	1.13
Magnesium (Mg)	0.27	8.43	0.17	1.55	0.65
Potassium (K)	2.02	9.38	0.08	12.66	-
Calcium (Ca)	0.86	6.02	0.02	-	-

From Table 1, the amounts of carbon for raw and burnt paddy husk are 43.42% and 5.23%, respectively. Through pyrolysis process, celluloses was burnt and decomposed into char [10]. There is an increment of 52.21% for carbon content of paddy husk which correlated to the increment of carbon content in the char samples. Since the carbonization took placed in the presence of inert gas, the carbon composition is improved after char production [8]. After the impregnation of chemical, the amount of carbon and potassium are increased that proves the successful of the preparation of activated carbon.

3.5 Oxygen Adsorption Study

Figure 4 and Figure 5 present the oxygen adsorption capacity for 1M KOH burnt paddy husk and 1M HNO_3 burnt paddy husk against time, respectively. Moreover, Figure 6 shows the comparison of oxygen adsorption capacity of two adsorbents.

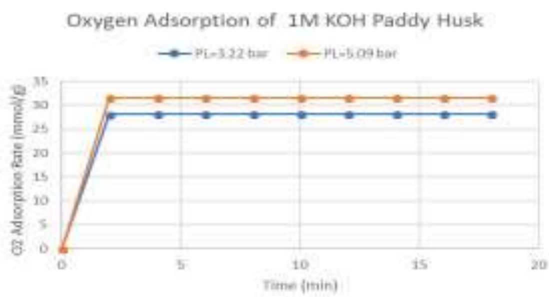

Figure 4: Adsorption capacity of 1M KOH burnt paddy husk against time.

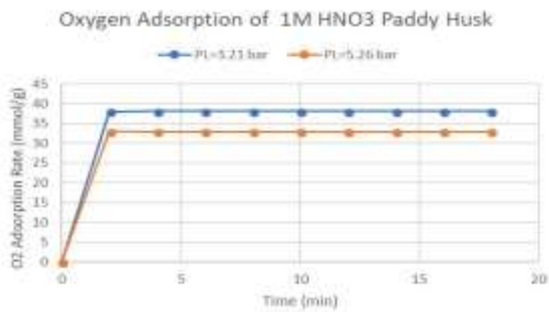

Figure 5: Adsorption capacity of 1M HNO3 burnt paddy husk against time.

Figure 4 and Figure 5 exhibit the adsorption capacity of 1M KOH paddy husk and 1M HNO3 paddy husk, respectively.

At the beginning, the increased pressure causes the increases of the adsorption capacity due to the increases of gas molecules striking on the surface of the adsorbent [11]. This correspond with the principal of adsorption that the increase of pressure is directly proportionally to the adsorption rate. From this result, it can be shown that the adsorption capacity remains constant after some time. This is because, the adsorption sites had been occupied and no more adsorption can be further happened. It can be concluded that the pressure does not have any effect on the adsorption anymore. At this point, the extent of adsorption is independent to the pressure.

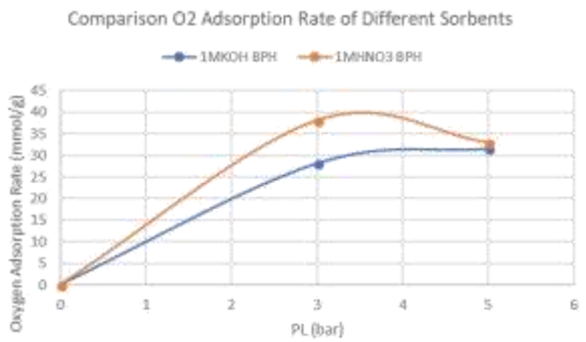

Figure 6: Comparison of adsorption capacity of each sorbent against pressure.

From Figure 6, it can be observed that 1M HNO_3 paddy husk adsorbent has higher adsorption capacity as compared to 1M KOH paddy husk. This proves that the chemical properties of adsorbent affects the oxygen adsorption capacity. It also have been proved that KOH impregnated activated carbon adsorption capacity could vividly reduce and block the pores due to accumulation of KOH molecules on the surface of the activated carbon [12]. Meanwhile, the pore and surface of the sorbent with acid is only partially destroyed or enlarged [13]. Tan et al. [13] also determined that due to the average pore diameter of acid larger than alkaline treated sorbent, alkaline produce the worse physical properties and adsorption results. Therefore, acid-based adsorbent have higher adsorption capacity than the alkaline-based sorbent.

IV. CONCLUSION

Paddy husk was chosen as precursor for this research due to its high potentials such as low-cost operation and has high porosity which led to large adsorption capacity. To enhance the adsorption process, paddy husk was physically modified through carbonization to obtain biochar that definitely increases the surface area of precursor. Surface textural analysis and structural analysis were used to characterize the samples through variable pressure scanning electron microscopy (VPSEM), energy dispersive x-ray spectroscopy (EDX), thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR). Based on the EDX results, the conversion of carbonized sample to the activated carbon is proven. VPSEM image gained also proves the highly porosity characteristics of the precursor. Based on the oxygen adsorption capacities achieved for each sorbent, 1M KOH burnt paddy husk shows a better adsorption capacity than the 1M HNO3 burnt paddy husk. This proves that the acid-based adsorbent is a promising adsorbent to be used for oxygen adsorption application.

Acknowledgement
The authors would like to dedicate a special appreciation to the financial supports and lab facilities provided by Universiti Teknologi Malaysia (UTM) through the University Research Grant (GUP) with the vote number is Q.K130000.2643.13J72 and Q.J130000.2546.18H81. An acknowledgement also goes to IISJ-UPEN Johor for grant vote, R.J130000.7346.4B282.

REFERENCES

[1] Georgia Institute of Technology. (2015, Sep 6). Respiratory Protection Environmental Health & Safety.website: https://www.ehs.gatech.edu/chemical/respiratory

[2] Johnson, A. (2016). Respirator masks protect health but impact performance: a review. Journal of Biological Engineering. 10(1).

[3] Mensch, A., & Bryner, N. (2011). Emergency first responder respirator thermal characteristics: workshop proceedings. US Department of Commerce, Engineering Laboratory, National Institute of Standards and Technology.

[4] Shahedifar, V. & Rezadoust, A. M. (2013). Thermal and mechanical behavior of cotton/vinyl ester composites: Effects of some flame retardants and fiber treatment. Journal of Reinforced Plastics and Composites. 32(10), 681-688.

[5] Sulaiman, F. & Abdullah, N. (2014). Pyrolytic product of washed and unwashed oil palm wastes by slow thermal conversion process. Journal of Physical Science. 25(2), 73.

[6] Munajad, A. S., Subroto, C., & Suwarno, S. (2018). Fourier Transform Infrared (FTIR) Spectroscopy Analysis of Transformer Paper in Mineral Oil-Paper Composite Insulation under Accelerated Thermal Aging. Energie. 11(2), 364.

[7] Zaini, N. (2016). Amine-Functionalized Kenaf as Carbon Dioxide Adsorbent in Pressure Swing Adsorption System. PhD Thesis. Universiti Teknologi Malaysia, Malaysia.

[8] Chowdhury, Z. Z., Hamid, S. B. A., Das, R., Hasan, M. R., Zain, S. M., Khalid, K., & Uddin, M. N. (2013). Preparation of carbonaceous adsorbents from lignocellulosic biomass and their use in removal of contaminants from aqueous solution. BioResources, 8(4), 6523-6555.

[9] Polini, A. & Yang, F. (2017). Physicochemical characterization of nanofiber composites. Nanofiber Composites for Biomedical Applications. 97-115.

[10] Yang, H. Y., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose,

cellulose and lignin pyrolysis. Fuel. 86(12-13), 1781-1788.

[11] Kamarudin, K. S. N., Mat, H., & Hamdan, H. (2007). Zeolite as natural gas adsorbents. University Technology Malaysia.

[12] Choo, H. S., Lau, L. C., Mohamed, A. R., & Lee, K. T. (2013). Hydrogen sulfide adsorption by alkaline impregnated coconut shell activated carbon. J. Eng. Sci. Technol. 8(6), 741-753.

[13] Tan, I. A., Abdullah, M. O., Lim, L. L. P., & Yeo, T. H. C. (2017). Surface Modification and Characterization of Coconut Shell-Based Activated Carbon Subjected to Acidic and Alkaline Treatments. Journal of Applied Science & Process Engineering. 4(2).

