Methane Adsorption on Hybrid and Non Hybrid Activated Carbon Synthesized from Coconut Shells and Poly Ether Ether Ketone

Umar Sidik Hayatu*
Federal Polytechnic Mubi, Department of Chemical Engineering Technology,
P.M.B 35 Mubi, Adamawa State, Nigeria, hayatusiddiki@yahoo.com

Abstract

The shorter driving range is the challenge of compressed natural gas (CNG) as a vehicular fuel. In this study, adsorbents were prepared from coconut shells and Poly Ether Ether Ketone (PEEK) using KOH microwave activation to overcome the challenge of CNG storage system. The CNG storage system has some disadvantages which include high-pressure operation with less safety guard, and heavy storage cylinders. The adsorbents were used as a potential Sorbents for methane (CH4) storage at different pressures. The coconut shell and PEEK were carbonized from ambient temperature to 700 ± 20 oC at 10 oC min-1 heating rate with 1 L min-1 N2 flow rate. The carbonization temperature of the precursor was determined using thermo-gravimetric and derivative thermogravimetric (TG/DTG) analysis. The activation was achieved with well modified microwave equipment operated at 500 W and 5 minutes. The adsorbents were characterized by Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption and scanning electron microscopy (SEM). The CH4 adsorption characteristics were conducted using volumetric adsorption equipment at an ambient temperature and pressures of 5-17 bar. The highest CH4 uptake achieved from hybrid adsorbent at 5, 7.5, 11 and 17 bar are 2.35, 3.04, 4.80 and 7.15 mmol/g respectively. The experimental data simulated using three common adsorption models: Langmuir, Freundlich and Sips. The Freundlich, had high correlation coefficient up to 0.9989 and lower root mean square deviation (RMSD) which fitted our data better than others. The findings revealed the potential of coconut shell-PEEK as sorbents for CH4 adsorption applications and isotherm models equations used in adsorption applications.

Keywords: Hybrid; Non hybrid; Activated carbon; Adsorption; Isotherm

Article history: Received: August 20, 2020; Accepted: December 24, 2020

1. Introduction

With the recent concern about the emissions from diesel engines, in addition to the increasing demand for energy coupled with instability of conventional fuel prices, has influenced interest towards sourcing alternative fuel [1]. Many countries want to reduce their dependency on the imported fuels (diesel and gasoline) due to the aforementioned issues. These issues could be solve by initiating a reliable and visible technology that can accommodate the demands in the energy application sectors. Works by [2] stated that the available and reliable energy that can secure sustainability in environmental delivery with minimal Green House Gases (GHGs) emission is Natural Gas (NG) [1]. NG is used

in industries, for transportation vehicles, and for households. For industries application, where there is no pipelines system, it sometimes has to be transported to the location using transportation systems (vehicles). For it to be transported it has to be stored in heavy tanks with pressure ranges between 200-250 bar at room temperature [2]. Compression and liquefaction methods were earlier adopted to increase the fuel density to meet up with several applications. However, they were found to be attributed to high-pressure applications and the high cost of processing respectively. To overcome these deficits, the gas stored by adsorption onto the surface of porous carbon at relatively lower pressure to that of compression and at a lower cost to both [3]. The gas stored at ambient temperature and moderate pressure range between 35-40 bar which reduces the processing cost and increases the storage capacity.

Various methods reported for the de-pollution of environments such as neutralization, precipitation, adsorption and filtration [18]. Adsorption is reported as the most reliable at the current situation, due to its enormous advantages such as easy handling, low cost and high efficiency [22] In a general perspective, conversion of non-living wastes into activated carbon for mitigation of waste or environmental pollution is a very good option [19] The readily available agro-wastes in Malaysia for the production of activated carbon includes coconut shells [12], palm kernel shells [10], rice husk, Kenaf, nut shells, tobacco stems and sugarcane bagasse [12.

The coconut was selected for this research work due to its availability and impact on environmental pollution in this region. It is estimated that in Malaysia about 142,000 hectares of land for coconut plantation [12]. A lot of solid waste (shells) generated annually [20] Therefore, channeling the wastes for adsorption application is compulsory due to the current environmental problem [21] Zeolites and commercial activated carbon are very popular in adsorption applications, but the process is expensive. However, activated carbons can be derived from readily available agricultural solid waste with an easier tailoring it textural and surface properties [12] Thus, there is an increase in demand for readily available adsorbent, less expensive for methane adsorption, particularly if the substrate is derived from waste materials. Conversion of coconut shells into activated carbon (waste-to wealth) which can be used as an adsorbent for CH4 could add value to this agricultural waste, help to reduce the cost of its disposal, and provide sustainable, reliable and cheap activated carbon that can serve the same purpose as the expensive commercial porous carbons.

It was reported that Poly Ether Ether Ketone (PEEK) porous carbon has good properties for high compressive strength and gas storage applications [4]. This is due to the excellent textural properties of the PEEK porous carbon.

Adsorption isotherm models describe the behavior of absorbent and adsorbent towards their interaction and understanding

of their adsorption process [9]. Langmuir, Freundlich and Sips isotherm models have been used to study the interaction behaviors between adsorbent and adsorbent in this study.

In this study, the hybrid activated carbon prepared from coconut shells and PEEK was used to achieve the adsorption of methane at an ambient temperature and pressure up to 17 bar. The adsorption behavior of methane was detected using adsorption isotherm models. The experimental data were fitted using Freundlich, Langmuir, and Sips which were used to describe the experimental data and effective adsorptivity.

The objective of this research paper is to investigate the effect of PEEK toward the adsorption of methane on the surface of the activated carbon impregnated with potassium hydroxide and also to study the behavior of adsorption isotherm models, and equilibrium capacity. The novelty of this work tailored towards adsorbent preparation and adsorption models evaluation. Most studies on PEEK focus on thermal stability since it is one of the highest temperature (260 °C) resistance among all plastics [5], to the best of my knowledge the use of PEEK for this application has not been exploited.

2.Experimental Procedures

2.1 Adsorbent Synthesis and adsorption application

Raw coconut shells were washed, sun-dried, and then dehydrated at 105 oC for 24 hours using the oven. It was carbonized using the furnace to obtain char which were later sieved to 0.85-0.5 mm. the PEEKwas also carbonized and sieved to same size particle with coconut shells char. The PEEK char was blended with coconut shells char. The blended chars were chemically treated with KOH at a ratio of 1:1.5, and then activated using the microwave, the activated carbon denoted as ahybrid. The adsorption of CH4 initiated using the adopted procedure elsewhere [2].

2.2 Sample characterization

The two samples were named based on their preparation conditions. Preparation of hybrid activated carbon (M33P15) achieved at 300 Watt, 3 minutes irradiation time and 15% amount of PEEK. Non-hybrid activated carbon (M33P0) prepared at the same condition with (M33P15) but without the addition of PEEK. The samples were characterized by Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption and scanning electron microscopy (SEM).

2.3 Adsorption Isotherm

Methane adsorption isotherms show how the interaction between CH4 and the synthesized adsorbents occur.

2.4 Adsorption Isotherm Models

Adsorption isotherms are models used for identification of how adsorbent The CH4 adsorption isotherm shows how the interaction between CH4 and the synthesize adsorbents occur. Two parameters isotherm models (Langmuir and Freundlich) together with the three model parameters (Sips) were applied for this study. The detail of the aforementioned models is shown in

Table 1. Freundlich and Langmuir exhibit more satisfactory fit to the experimental data for both samples with R2 greater than 0.988 and lower RSMD (Table 1). The values of adsorption intensity (n) for the three models at all the samples were greater than 1, indicating favorable adsorption [16]. In general, the suitability of the three isotherm models predicting the interaction behavior of CH4 adsorption on the porous carbon synthesized is in order of Sips < Langmuir< Freundlich with the corresponding values as shown in Table 1. This shows that Freundlich gives a more accurate description of the interaction between CH4 and the porous carbon synthesized with high values of KLF indicating high adsorption capacity [17] and adsorbate interact to give a clear understanding of their behavior [9]. Langmuir, Freundlich, and Sips model equation are used for this application. Langmuir isotherm predicts the monolayer at the homogeneous surface, while Freundlich for a heterogeneous surface which describes non-ideal and reversible adsorption [10]. Sips is a model which combines the applications of both Langmuir and Freundlich. The nonlinear adsorption isotherm model equations (Langmuir, Freundlich, and Sips) were also shown in Equations 1, 2 and 3.

$$q = q_m \frac{k_1 p}{1 + k_1 p} \tag{1}$$

$$q_e = k_f p^{\frac{1}{n}} \tag{2}$$

$$q = \frac{q_m k_{lf} p^{\frac{1}{n_{lf}}}}{1 + k_{lf} p^{\frac{1}{n_{lf}}}} \tag{3}$$

2.5 Validity of Fitting of Models

Root square mean deviation (RSMD) and regression coefficient (R2) values were used to validate the experimental data, as well as its fitness, the values were obtained using equations 4 and 5.

$$RMSD = \left[\frac{1}{n} \sum \left(q_{\exp} - q_p \right)^2 \right]^{\frac{1}{2}} \tag{4}$$

$$R^2 = 1 - \frac{\sum_{n-1}^{1} \left(q_{\exp} - q_p \right)^2}{\sum_{n-1}^{1} \left(q_{\exp} - \bar{q}_p \right)^2} \tag{5}$$

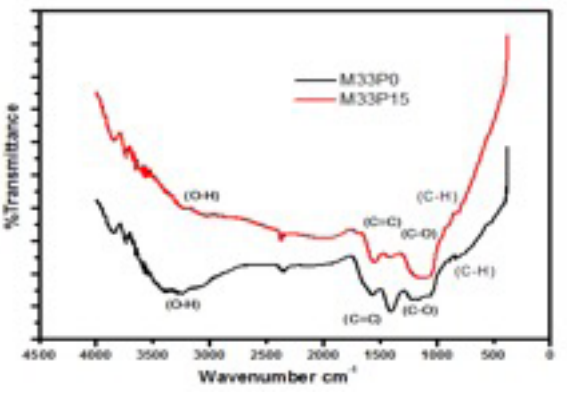
3. Results and Discussion

3.1 Samples Characterization

Fig.1 shows spectra of the porous carbon from coconut shell (M33P0) presents functional groups that depicted the following bands: (O-H) vibration in the hydroxyl groups were shown in peak 3609 cm-1 indicating the presence of alcohol and phenols [11]. It might be due to the activation with potassium hydroxide (KOH). Previous research conducted by [12] on coconut shell compared with the results obtained from this study showed the functional groups identified are same. The spectra of the coconut-PEEK porous carbon (M33P15) display belonging functional groups, which depicted the following bands. Vibration stretch of the C-H identified at the peak of 2920 cm-1. C=C bond stretching was identified at 1638 cm-1 shown in the benzene ring. Further, the activated carbon

displayed the following bands: 3500-3200, which indicates strong O-H stretch in alcohol and H-bond in moisture. This was obviously enhanced due to the treatment with KOH. Further investigation reveals that there is peak at 1600–1585 indicating the presence of C–C stretch (in–ring) in aromatics; this also assumes that it was enhanced by the treatment of CO2 during activation [3].

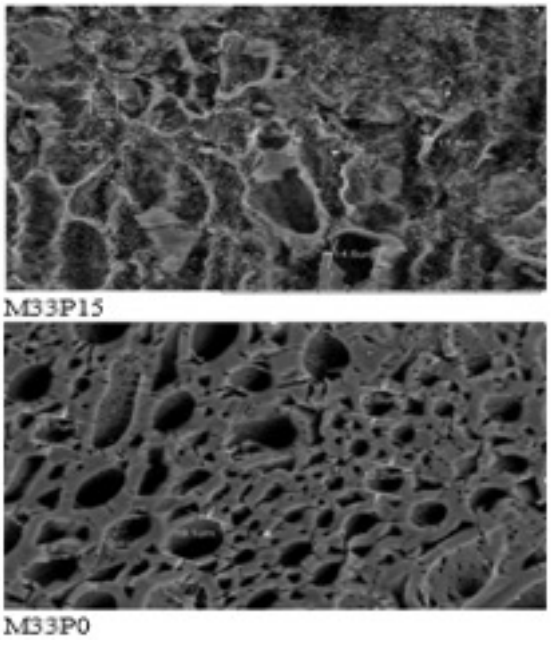
Fig.1: Fourier transforms infrared spectra of samples; M33P15 and M33P0



Scanning electron microscopy images of hybrid (M33P15) and non-hybrid (M33P0) activated carbon were presented in Fig.2. The surface morphology of the images displayed some cavities formation and rudimentary pores. These are created by the evaporation of impregnated KOH derived compounds and volatilization of the lignin, hemicellulose, cellulose and moisture content of the raw CNS after the heat treatment [2]. As seen in these pictures, coconut shell and PEEK (hybrid) form a matrix of porous carbon showing more compacted structures than non-hybrid activated carbon.

Nitrogen adsorption measurement parameters of the synthesized AC from co-

Fig.2: SEM image of (M33P15) hybrid activated carbon and non-hybrid (M33P0) activated carbon



conut shell and hybrid coconut shell and PEEK such as specific surface area, total pore volume (Vt), average pore diameter (DAvg) and average pore width (WAvg) were shown in Table 1. The surface area of sample M33P15 is higher than sample M33P0. The surface area plays a very good role in activated carbon application, high surface area translates to better adsorptivity. There was an improvement of pores and surface area by adding PEEK to coconut shells; this might be due to a high value of carbon content.

Table 1: Porosity parameters of the synthesized porous carbons obtained from nitrogen adsorption

Sample	Surface area (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	D_{avg} (nm)	W_{Avg} (nm)
M33P0	802	0.127	0.091	1.900	3.120
M33P15	1115	0.214	0.165	1.790	2.890

3.2 CH_4 Adsorption

Methane adsorption capacity on the surface of hybrid and non-hybrid activated

carbons for the higher pressure were presented in Table 2. The adsorption study was obtained with respect to time at isotherms of ambient temperature and pressures starting from 5 to 17 bar. The methane uptake was fast at the initial stage of the experiment, then, later decrease with increase in contact time. This is due to the increase in the concentration of gas stored in the pore volume of the adsorbent [10]. It was observed that the adsorption equilibrium increase with an increase of initial pressure from 5 - 17 bar. Increase in working pressure of the system lead to the increase in the methane adsorption uptake. As stated by [13] that increase in working pressure would increase the Van der Waal force of attraction between the adsorbent and adsorbate. The lowest amount of CH_4 uptake at an ambient temperature at pressures 5, 7.5, 11 and 17 bar depicted on non-hybrid sample was 2.06, 3.04, 4.30 and 6.96 mmol/g respectively. While the highest uptake was depicted on hybrid under the same condition with uptake 2.35, 3.04, 4.80 and 7.15 mmol/g respectively. This might be due to the higher surface area display in nitrogen adsorption analysis [3]. It was observed more than 60% of the CH_4 adsorbed achieved at the first 60 minutes in all the pressures. According to the functional relationship between the amount of uptake of adsorption and time, it can be seen that when time tends to infinity, the adsorption uptake is prone to a fixed value. This is the actual saturated adsorption uptake [14].

Table 2: Comparison of experimental methane uptake

Sample	Surface area (m^2/g)	Uptake (mmol/g)
Hybrid (M33P15)	1115	7.15
Non-hybrid (M33P0)	802	6.96

3.2 CH_4 Adsorption Isotherm

The CH_4 adsorption isotherm shows how the interaction between CH_4 and the synthesize adsorbents occur. Two parameters isotherm models (Langmuir and Freundlich) together with the three model parameters (Sips) were applied for this study. The detail of the aforementioned models is shown in Table 3. Freundlich and Langmuir exhibit more satisfactory fit to the experimental data for both samples with R2 greater than 0.988 and lower RSMD (Table 3). The values of adsorption intensity (n) for the three models at all the samples were greater than 1, indicating favorable adsorption [16]. In general, the suitability of the three isotherm models predicting the interaction behavior of CH_4 adsorption on the porous carbon synthesized is in order of Sips < Langmuir< Freundlich with the corresponding values as shown in Table 3. This shows that Freundlich gives a more accurate description of the interaction between CH^4 and the porous carbon synthesized with high values of KF indicating high adsorption capacity [17]

Table 3. Freudlich, Langmuir and Sips fitting parameters of CH4 adsorption on M33P15 and M49P0 porous carbon

Sample	Isotherm	n	KF	R^2	RSMD	
M33P15	Freud.	1.04	0.47	0.99	0.07	
M49P0	Freud.	1.01	0.41	0.99	0.03	
		q_m	K_L	R^2	RSMD	
M33P15	Lang.	136	0.01	0.99	0.07	

M49P0	Lang.	493	0.01	0.99	0.03	
		q_m	n	R^2	RSMD	K_{LF}
M33P15	Sips	137	1.04	0.95	0.22	0.1
M49P0	Sips	493	1.01	0.95	0.20	0.1

4. Conclusions

The study investigates both the experimental and modeling of CH_4 adsorption study on KOH microwave treated porous carbon. The CH_4 adsorption study was investigated using static volumetric equipment and method. The
fitness and interaction between the adsorbent and adsorbate were evaluated using the three common kinetics and the common adsorption isotherm models.The amount of CH_4 adsorption uptake increases with increase in pressure.

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