CHEMICAL ENGINEERING TRANSACTIONS

VOL. 45, 2015

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216

DOI:10.3303/CET1545252

Effect of Process Variables on the Production of Biomass-Based Activated Carbons for Carbon Dioxide Capture and Sequestration

Nor Adilla Rashidi, Suzana Yusup*

Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Tronoh, Perak Malaysia.
drsuzana_yusuf@petronas.com.my

The mitigation of carbon dioxide (CO_2) from power plant generation using low-cost materials is a feasible technique to alleviate the global warming problems. In this present paper, CO_2 adsorptions at atmospheric pressure and temperature were investigated using the biomass-based activated carbons produced from various sources that include palm shell, palm mesocarp fibre, coconut shell, coconut fibre, as well as rice husk. The preparation variables which include nature of precursors, particle size, heating rate, flow rate of activation agent, activation temperature, and residence times were evaluated. The Taguchi L_{25} orthogonal arrays through analysis of variance (ANOVA) statistical approach with 95 % confidence limit had been used to study the effect of each operating variables at five levels each. Data analysis proved that both activation temperatures and types of starting materials were significant in producing activated carbons intended for CO_2 capture, since p-value was < 0.05. The operating variables i.e. particle sizes, heating rate, flow rate, and residence time were found to be insignificant. Although the maximum CO_2 adsorption capacity achieved by synthesised activated carbons were slightly lesser than the commercial activated carbon (1.79 mmol/g vs. 1.84 mmol/g), the proposed single-stage physical activation method in this study is an environmental-friendly approach to convert the massive agricultural wastes to value-added products, along with combating greenhouse problems caused by an uncontrolled release of greenhouse gases especially from electricity generation sectors.

1. Introduction

The vast demand of electricity in Malaysia had accelerated the carbon dioxide emission (CO_2) and hence, increasing the potential of global warming. Besides, Malaysia has been reported to be the second largest electricity consumers amongst the Asian countries (Tang, 2008), and demand for electricity is expected to increase by almost 4 - 5 % annually (Sunderan et al., 2011). With respect to high demand of the electricity, power generation is forecasted to be increased as well with more than 90 % of total energy production is from the fossil-fuel based, as shown in Table 1. According to Table 1, coals exploitation for the power and electricity generation are expected to increase due to wider availability and can be obtained at lower cost (Rashidi et al., 2013a). Nevertheless, coals are carbon intensive and will contribute to CO_2 emission.

Table 1: Forecasted electricity production in Malaysia from 2005-2030 (Tan et al., 2013)

Types of fuel	Electricity production (GWh)			Share of electricity generation (%)		
	2005	2010	2030	2005	2010	2030
Coal	23,134	49,675	154,686	26.5	41.6	49.1
Oil	2,489	2,855	3,107	2.9	2.4	1.0
Natural gas	55,899	55,700	139,025	64.0	46.6	44.1
Hydro	5,784	11,245	18,166	6.6	9.4	5.8
Total	87,306	119,475	314,984	100.0	100.0	100.0

Please cite this article as: Rashidi N.A., Yusup S., 2015, Effect of process variables on the production of biomass-based activated carbons for carbon dioxide capture and sequestration, Chemical Engineering Transactions, 45, 1507-1512 DOI:10.3303/CET1545252

Due to acceleration in coal consumption for electricity generation which result in global warming, researchers have developed several technologies intended for CO_2 capture prior to releasing clean gas to atmosphere. Some of these technologies are amine absorption, solid adsorption, membrane separation, and cryogenic distillation. Currently, amine absorption system has been extensively utilized due to its high selectivity absorptions ability. However, energy penalty and associated environmental problems caused by amine consumptions causes the researchers to shift to other technologies (Saiwan et al., 2013), such as adsorption by activated carbons that will be the focus point in this work. The inexpensive carbonaceous-based activated carbons are preferred due to their ability to capture CO_2 at low pressures, insensitiveness towards moisture that reduce temperature needed to remove CO_2, along with good CO_2 selectivity to other flue gas pollutants. In this work, effects of these variables in producing activated carbons have been investigated by using Taguchi optimization approach. Taguchi orthogonal array as a design of experiment is preferable since it minimizes the total number of experimental runs, and is a robust design (Kundu et al., 2014). The Taguchi method recommends the analysis of variance (ANOVA) analysis since the significance of the parameters towards the process can be determined. The calculations involved in ANOVA analysis are as in Eqs(1-9) (Roy, 2001). The ANOVA analysis which is predominant in the statistical method is due to the results obtained from the ANOVA analysis can assist users to make necessary decision, mainly referring to percent of contributions.

Degree of freedom (f_{Total}) = Total number of experiment (N) - 1 (1)

f_{error} = f_{Total} - (total of all factors' DOF) (2)

Total sum of square (SS_T) = $\sum_{I=1}^{N} Y_i^2 - \frac{1}{N}\left(\sum_{i=1}^{N} Y_i\right)^2$ (3)

Y_i = Response at each run;
N = Total no. of run.

SS_i = $\sum_{j=1}^{t} \frac{(Y_{ij})^2}{t} - \frac{1}{N}\left(\sum_{i=1}^{N} Y_i\right)^2$ (4)

t = level no. of each factor i;
Y_{ij} = sum of Y_i (response) of this factor and level j.

$SS_{E\ (\text{error/residual})}$ = $S_T - (S_A + S_B + S_C + S_D + S_E + S_F)$ (5)

Variance (mean square; V_i) = SS_i / f_i; whereby f_i is the DOF of each factor (6)

F-ratio = V_i / V_E ; whereby V_E is variance for error (7)

Pure sum of squares (SS'_i) = $SS_i - (V_E \cdot f_i)$ (8)

Percentage of contribution = SS'_i / SS_T (9)

In this present work, the carbonaceous solid activated carbons were produced from various raw precursors including the palm waste, coconut waste, and paddy waste materials. The extensive availability of these wastes were significant to be utilized since it eliminates environmental problems resulted from open burning or disposal in the dumpsite. In addition, a single stage physical activation method is adopted in this work, as the usual practice of chemical treatments as undesirable and has potential risk of water pollution resulted from the formation of acidic wastes (De Filippis et al., 2013). Evaluations of the operating variables in producing activated carbons through Taguchi optimization approach will be further discussed, to aid understanding of these parameters towards the adsorption characteristics.

2. Experimental

2.1 Preparation of activated carbons

The different types of agricultural waste materials (palm shell, palm mesocarp fibre, coconut shell, coconut fiber, rice husk) were collected from local market. These materials were oven-dried at 120 °C for at least 12 h. The dried materials were ground and sieved to particle size of 0.25-1.00 mm. These small particles were activated under purified CO_2 flow (100 - 300 mL/min) at temperatures between 500 - 900 °C, heating rate of 5 - 25 °C/min, and residence time of 15 - 90 min. The parameters that involved in the production of the activated carbon were optimized using Taguchi L_{25} orthogonal array design, as described by Rashidi et al. (2013b).

Table 2: Factors and levels studied by Taguchi orthogonal array (Rashidi et al., 2013b)

Factors / Levels	Precursors	Particle size (mm)	Heating rate (°C/min)	CO_2 flow rate (mL/min)	Temperature (°C)	Residence time (min)
Level 1	Palm fiber	0.250	5	100	500	15
Level 2	Palm shell	0.355	10	150	600	30
Level 3	Rice husk	0.500	15	200	700	45
Level 4	Coconut shell	0.710	20	250	800	60
Level 5	Coconut fiber	1.000	25	300	900	90

2.2 Adsorption tests

A batch CO_2 adsorption process was performed using thermal-gravimetric analyser at temperature of 25 °C and pressure of 100 kPa. During adsorption, the adsorbate gas flow at 50 mL/min and the adsorption was maintained for 120 min to ensure an equilibrium condition. Prior of the adsorption, the samples were degassed at 120 °C for 12 h. The equilibrium adsorption capacity (Y_i) in mg CO_2/g activated carbon was then recorded.

2.3 Analysis of Variance (ANOVA)

The quantitative analysis of the parameters involved in the activated carbon productions was analysed via the ANOVA analysis. The ANOVA analysis is significant to determine the importance of these parameters. Throughout ANOVA analysis, set of sum of squares, degree of freedom, variance, pure sum of squares, F-ratio, and percentage contribution were calculated using the Design Expert® version 8.0.

3. Results and Discussions

The ANOVA analysis is significant to be performed, as it determines the quantitative measurement of each parameter involved in the process. In Table 3, the operating temperature gives the highest percentage of contribution which means that this factor has significant influence to the particular response i.e. CO_2 adsorption capacity. The following factors that influence the quality of activated carbon in adsorbing CO_2 is the different type of precursors and residence time, whilst others are relatively lower (2 - 4 %). Since the calculated error in Table 3 is zero, then the F-ratio is incapable to be calculated. Therefore, in order to calculate the F-ratio of these parameters, another analysis is conducted by pooling the insignificant factors to error. The pooling can be described as a process to disregard the unimportance factors and re-adjust the contribution of the other factors. The pooled ANOVA analysis is as shown in Table 4, whereby the insignificant factors that include particle size, heating rate, and flow rate are disregard.

Table 3: ANOVA analysis

Factors	Degree of freedom	Sum of square	Variance	F-ratio	Pure sum of square	Percent (%)
Precursors	4	1,250.50	312.63	-	1,250.50	17.26
Particle size	4	279.04	69.76	-	279.04	3.85
Heating rate	4	209.46	52.36	-	209.46	2.89
Gas flow rate	4	149.83	37.46	-	149.83	2.07
Temperature	4	4,915.34	1,228.83	-	4,915.34	67.86
Residence time	4	438.96	109.74	-	438.96	6.06
Residual/error	0	0.00	0.00			-
Total	24	7,243.13				100.00

Based on the pooled ANOVA shown in Table 4, it revealed that the temperature significantly contributes to the adsorptive properties of activated carbons, as its percentage of contribution is 64.92 % and followed by the different precursors with 14.33 %. Aside from percentage of contribution, the contribution of individual parameter can also be evaluated by F-value and *p*-value (at confidence level of 95 %). Yusup et al. (2014) reported that the *p*-value is the probability of getting results closer to an actual experimental data and thus, lower *p*-value (<0.05) indicates that the parameter is significant in the process. On the other hand, *p*-value which is greater than 0.10 describes that the model term is insignificant for the process. On this basis, both temperature and type of precursors with corresponding *p*-value of < 0.0001 and 0.0074 is significant. Meanwhile, F-ratio is described as a test to compare the variance of that term with the variance of residual, and large F-ratio values imply that there are more variability accounted for the corresponding model term. Hence, temperature is expected to be the most influential parameters, as its F-ratio (23.10) is the largest amongst all. In addition, the precision of the model towards the actual data can be evaluated by the value of regression coefficients (R^2). The value of R^2 for the pooled ANOVA (Table 4) is estimated to be 0.9119, which is almost close to unity and it implies that the model gives good prediction towards the experimental values, and the corresponding standard deviation is 7.29.

Table 4: Pooled ANOVA analysis

Factors	Degree of freedom	Sum of square	Variance	F-ratio	Pure sum of square	Percent (%)	*p*-value
Precursors	4	1,250.50	312.63	5.88	1,037.74	14.33	0.0074
Temperature	4	4,915.34	1,228.84	23.10	4,702.58	64.92	< 0.0001
Residence time	4	438.96	109.74	2.06	226.20	3.12	0.1491
Residual/error	12	638.33	53.19			17.63	
Total	24	7,243.13				100.00	

3.1 Effect of temperature towards CO_2 adsorptive properties on activated carbons

Based on ANOVA analysis, the activation is proven to be the most influential factor towards the adsorptive properties. As shown in Figure 1, there is a linear correlation between the activation temperatures and CO_2 adsorption capacity irrespective of the precursors used for the activated carbon productions. According to Fathy et al. (2012), an enhancement in terms of activation temperatures result in an evolution of micropore and pore volumes. In addition, the developments of carbons' porosity can be attributed to the released of volatiles and impurities from the carbonaceous materials during thermal decomposition process, as well as carbon monoxide emission from CO_2 and carbon reaction. Meanwhile, the least CO_2 adsorption capacity at 500 °C may be related to inadequate porosity developments, most probably due to lower energy to drive the devolatilization process, apart from insufficient carbon and CO_2 reaction. In addition, linear relationship between the activation temperatures and adsorptive properties is related to the endothermic nature of the activation process (Wang et al., 2010). Thus, high activation is favoured for activated carbon productions that further promote micropore development for gas storage. Nevertheless, when activation temperature is excessively high, the widening of micropores and development of mesopores will take place. In addition, severe activation temperature has the potential to disrupt the functional groups and reduce the micropores fraction, and lead to reduction in adsorption capacity (Chowdhury et al., 2012). Overall, it is significant to optimise activation temperatures as it determines the pore size distribution that affect adsorption process, as inappropriate pore size are unable to retain the small CO_2 gas molecules. Besides, Chowdhury et al. (2012) in their work also found out that activation temperature has the greatest impact on the adsorptive properties, whilst residence time and impregnation ratio give lesser impacts.

3.2 Effect of precursors towards CO_2 adsorptive properties on activated carbons

Based on the pooled ANOVA analysis shown in Table 4, types of precursors is the second most influential factor on the adsorptive properties of the synthesised activated carbon. According to Figure 1, the variation of the adsorption capacity between the coconut shell and rice husk can be justified in terms of their physio-chemicals. The average carbon contents of the coconut shell-based activated carbons is about 83.01 wt%, whereas the average carbon content of the synthesised activated carbons from rice husk is approximately 53.70 wt%. Paethanom and Yoshikawa (2012) suggested that the carbon content plays an important role in the adsorption process, as the carbon surface will hold the adsorbate molecule by the weak van der Waals intermolecular force. Accordingly, large carbon contents in carbonaceous materials imply that there will be more carbon surface for CO_2 molecules to be adsorbed. Apart from carbon content, low adsorption capacity exhibited by rice husk materials is related to their significantly high ash content. The ash contents of raw rice husk (≈ 12.35 wt%) affect the adsorption as these ashes tend to block the pores and thus, inhibit the porosity developments and adsorptive properties. In addition, similar work had been performed by Boonpoke et al. (2011), by investigating the comparison of two precursors which are rice husk (RHAC) and bagasse activated carbons (BAC) towards the CO_2 adsorption capacity at 30 - 150 °C. Based on their findings, it is revealed that RHAC gives lower adsorption capacity than bagasse-based activated carbons at any adsorption temperature. Despite of having comparable surface areas and pore volumes, BAC which has lower ash contents (1.90 wt%) than RHAC (25.40 wt%) justify the differences in their CO_2 adsorptive properties, since RHAC may consists of mineral elements that have potential to reduce the CO_2 adsorption capacity. Meanwhile, the BAC which has carbon contents of 84.5 wt% has higher CO_2 adsorption capacity since these carbons assist in inter-particle interaction between CO_2 molecules and adsorbents through van der Waals forces.

3.3 Effect of residence time towards CO_2 adsorptive properties on activated carbons

The residence time of the activation agent flow at the final activation temperature is one of the parameters that affect the quality of the synthesised activated carbons and their adsorptive properties. The variations in CO_2 adsorption capacity with respect to the residence time (15-90 min) can be attributed to the changes in terms of the porosity and surface area development. If the activation process performed in a shorter time, an insufficient devolatilization reaction will take place and accordingly, the pores are not appropriately developed and will only adsorb small amount of adsorbates. Meanwhile, when the activation process takes place at above an optimum residence time, severe reactions between CO_2 and carbon surfaces may occur and widening of microporosity to mesopores will be the dominant reaction. Due to this widening, the activated carbons are unable to capture and retain small CO_2 molecules (CO_2 kinetic dimension is 0.33 nm) properly and lead to reduction in CO_2 adsorption capacity. Further, by increasing the residence time, it has possibility to form more ash residuals that block the existing pores and prevent the adsorbates from being adsorbed onto the carbon surface. Referring to Figure 2, the optimum residence time is at 60 min. Nevertheless, the differences between the adsorption capacity at 45 min and 60 min are not much. Thus, from the economic point of view, the optimum point for the holding time is taken at 45 min, as it can reduce the total operating time, increase the carbon yield, and simultaneously save the operating cost.

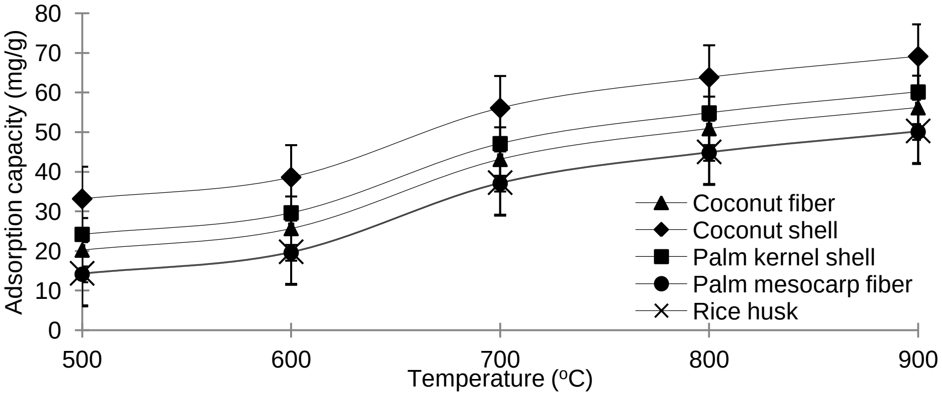

Figure 1: One-factor plot of effect of temperature towards CO_2 adsorptive properties with LSD ±8.1029 (at particle size = 0.25 mm; heating rate = 20 °C/min; flow rate = 150 mL/min; residence time = 45 min)

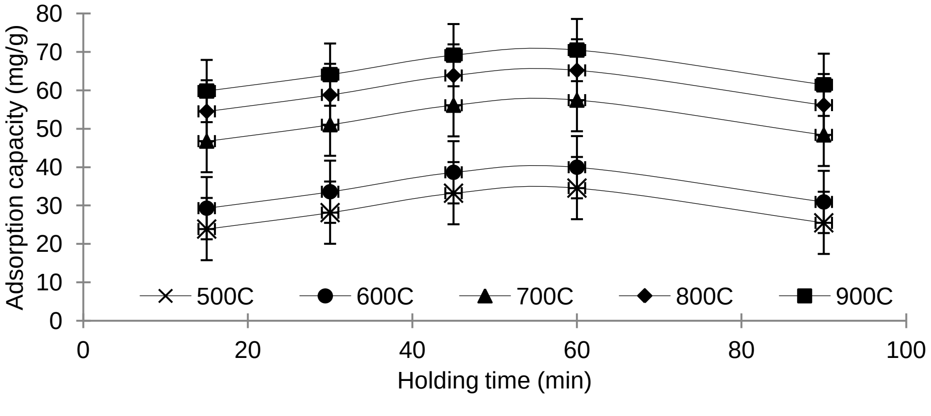

Figure 2: One factor plot of effect of residence time towards CO_2 adsorptive properties with LSD ±8.1029 (particle size = 0.25 mm; heating rate = 20 °C/min; flow rate = 150 mL/min; precursors = coconut shell)

4. Conclusions

In this work, activated carbons from the agricultural resources were produced. The Taguchi experimental design was employed, and the significant parameters analysed by ANOVA are the activation temperature, and followed by different types of starting materials. Meanwhile, other parameters including particle size, heating rate, flow rate, and residence time have no or little considerable effects towards the quality of the adsorbents. At an atmospheric pressure and room temperature, the maximum CO_2 adsorption capacity of 1.78 mmol/g had been obtained by coconut shell-based activated carbon of size 0.25 mm and activated at 900 °C, heating rate of 20 °C/min, CO_2 flow rates of 150 mL/min, and residence times of 45 min. Overall, the synthesised activated carbons from a single stage physical activation without N-doping had a comparable CO_2 adsorption capacity with the published data.

Acknowledgement

The authors gratefully acknowledge the financial and technical supports from Top-Down Nanotechnology Research Grant (NND/NA/(1)/TD11-036) under the Ministry of Science, Technology & Innovation (MOSTI), and Universiti Teknologi PETRONAS.

References

Boonpoke A., Chiarakorn S., Laosiripojana N., Towprayoon S., Chidthaisong A., 2011, Synthesis of activated carbon and MCM-41 from bagasse and rice husk and their carbon dioxide adsorption capacity, Journal of Sustainable Energy & Environment, 2, 77-81.

Chowdhury Z.Z., Zain S.M., Khan R.A., Arami-Niya A., Khalid K., 2012, Process variables optimisation for preparation and characterization of novel adsorbent from lignocellulosic waste, Bioresources, 7, 3732-3754.

De Filippis P., Di Palma L., Petrucci E., Scarsella M., Verdone N., 2013, Production and characterization of adsorbent materials from sewage sludge by pyrolysis, Chemical Engineering Transactions, 32, 205-210.

Fathy N.A., Sayed Ahmed S.A., Abo El-Enin R.M., 2012, Effect of activation temperature on textural and adsorptive properties for activated carbon derived from local reed biomass: Removal of p-nitrophenol, Environmental Research, Engineering and Management, 59, 10-22.

Herawan S.G., Ahmad M., Putra A., Yusof A., 2013, Effect of flow rate on the Pinang frond-based activated carbon for methylene blue removal, The Scientific World Journal, 2013, 1-6.

Kundu A., Gupta B.S., Hashim M., Redzwan G., 2014, Taguchi optimisation approach for production of activated carbon from phosphoric acid impregnated palm kernel shell by microwave heating. Journal of Cleaner Production, 105, 420-427.

Paethanom A., Yoshikawa K., 2012, Influence of pyrolysis temperature on rice husk char characteristics and its tar adsorption capability, Energies, 5, 4941-4951.

Rashidi N.A., Yusup S., Hameed B.H., 2013a, Kinetic studies on carbon dioxide capture using lignocellulosic based activated carbon, Energy, 61, 440-446.

Rashidi N.A., Yusup S., Loong L.H., 2013b, Kinetic studies on carbon dioxide capture using activated carbon, Chemical Engineering Transactions, 35, 361-366.

Roy R.K., 2001. Design of Experiments Using the Taguchi Approach: 16 Steps to Product and Process Improvement, John Wiley & Sons, New York, USA.

Saiwan C., Srisuwanvichein S., Tontiwachwuthikul P., 2013, Biopolymer modified with piperazine-2-carboxylic acid for carbon dioxide adsorption, Chemical Engineering Transactions, 35, 397-402.

Sunderan P., Singh B., Mohamed N., Husain N., 2011, Sizing and designing a stand-alone photovoltaic electricity generation system using a customized simulation program, paper presented in International Conference on Business, Engineering and Industrial Applications (ICBEIA), Kuala Lumpur, 169-173, DOI: 10.1109/ICBEIA.2011.5994234

Tan C., Maragatham K., Leong Y., 2013, Electricity energy outlook in Malaysia, IOP Conference Series: Earth and Environmental Science 16, IOP Publishing, 1-4.

Tang C.F., 2008, A re-examination of the relationship between electricity consumption and economic growth in Malaysia, Energy Policy, 36, 3077-3085.

Wang X., Lee J.S., Tsouris C., Depaoli D.W., Dai S., 2010, Preparation of activated mesoporous carbons for electrosorption of ions from aqueous solutions, Journal of Materials Chemistry, 20, 4602-4608.

Yusup S., Khan Z., Ahmad M.M. Rashidi N.A., 2014, Optimisation of hydrogen production in in-situ catalytic adsorption (ICA) steam gasification based on Response Surface Methodology, Biomass and Bioenergy, 60, 98-07.