ISSN: 0128-7680
Pertanika J. Sci. & Technol. **17 (2)**: 355 – 362 (2009)

Production of Carbon Dioxide Using Direct Pyrolysis-Combustion from *Aquilariella malaccensis* or Karas Woods Under Argon Atmosphere

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ABSTRACT

The production of carbon dioxide from *Karas* woods under argon atmosphere was investigated using a direct pyrolysis-combustion approach. Direct burning was used in this study, using argon for pyrolysis and oxygen during combustion to look at the yield of carbon dioxide, produced at different parameters, such as the temperature, retention time and flow rate of argon, as the carrier gas. In this study, a new methodology, 2^3 response surface central composite design was successfully employed for the experimental design and analysis of results. Central composite experimental design and response surface method were utilized to determine the best operating condition for a maximum carbon dioxide production. Appropriate predictable empirical linear model was developed by incorporating interaction effects of all the variables involved. The results of the analysis revealed that linear equation models fitted well with the experimental for carbon dioxide yield. Nevertheless, the R-Squared obtained using the direct pyrolysis-combustion was 0.7118, indicating that the regression line was not at the best-fitted line.

Keywords: **Argon, carbon dioxide production, direct pyrolysis-combustion, *Karas*, response surface method**

ABBREVIATIONS

ANOVA- Analysis of variance
CO_2 - Carbon dioxide

INTRODUCTION

Nuclear Malaysia Radiocarbon Dating Laboratory has been equipped by conventional radiometric method in order to determine the age of archaeological, hydrological and environmental samples. This conventional technique encompasses production of carbon dioxide, production of acetylene and trimerization, respectively. The yield of the carbon dioxide using combustion technique is a prominent stage since it determines the yield of the subsequent process. The sufficient amount of CO_2 will determine the scientific age of the archaeological samples found. A complete combustion produces carbon dioxide, water and char, but the process is not controllable and this

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Received: 14 April 2008
Accepted: 16 May 2008
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leads to inconsistent amount of carbon dioxide produced from the same amount of samples due the consumption of oxygen at the surface of semi-coke during combustion, which negligibly diffused into its pore, causing the wood not to burn directly but undergo thermal degradation precedes the combustion (Browne, 1958). Joel (1994) and Fang *et al*. (2006) used a direct burning of biomass for CO_2 production, and found that the yield was unsatisfactorily inconsistent with the amount of 63% and 60%, respectively from the existing carbon in the samples. Browne (1958), and Wen and Stanley (1979) reported that the pyrolysis of wood would introduce more evolved gases compared to combustion, but this was most preferred because it is a controlled process, in which the desired yield could be determined accordingly. Besides, the yield of products would also be the same although the wood components such as cellulose, hemicelluloses and lignin were separately pyrolyzed. The increased amount of the char, formed at lower temperature during pyrolysis, was due to the fact that slow heating would make the woods to decompose in an orderly manner, in which there is stepwise formation of increasingly stable molecules, richer in carbon and converging toward the hexagonal structure of graphitic carbon (Browne, 1958).

In this study, the influence of argon was characterized as carrier gas onto the wood samples using a direct pyrolysis-combustion by statistical approach. The pyrolysis-combustion method was introduced in this study to obtain the efficiency of the carbon dioxide with respect to several parameters, including the temperature of pyrolysis, residence time and concentration of argon in maximizing the amount of CO_2 from the same amount of samples. Statistical design of experiments (DOE) is a well-known efficient experimentation technique and has been applied in a wide range of disciplines, particularly in industries. In this paper, 2^3central composite design (CCD) was used to predict the optimum numerical conditions for a maximum CO_2 production by applying the response surface method (RSM) using the Design-Expert 6.10.0 (Minneapolis, Inc., USA). The RSM is a collection of mathematical and statistical techniques for empirical model building. The estimated mathematical model was examined using the analysis of variance (ANOVA) at 5% level of significance.

MATERIALS AND METHODS

Sample Pre-treatment

Karas woods were taken from Nuclear Malaysia Reserved Forest as degraded woods cum archaeological samples. Karas woods are among the oldest species found in the rainforest of Asian countries like Malaysia and Indonesia. Karas woods were cut into smaller pieces, milled and then washed with distilled water prior to oven drying. About 50g of the sample underwent the hot-solvent Soxhlet extraction to get rid of resins and wax. Benzene and ethanol, with the ratio of 2:1, were used to eliminate wax and resin, followed by 95% ethanol and distilled water, respectively (Gupta and Polach, 1985). The sample was then refluxed for 8 hours for each solvent before it was oven dried at 50ºC for 3 days so that the samples would have totally dried prior to the pyrolysis-combustion process.

Direct Pyrolysis-combustion Reaction

About 5g of the milled Karas wood was spread in the 20cm length of the sample boat and inserted into a 50cm length quartz chamber. The schematic set up of the direct pyrolysis-combustion is shown in *Fig. 1*. It consists of a quartz chamber inserted with thermocouple Type-K integrated with temperature controller and monitor, while purification system, water and carbon dioxide traps were laid out in series and should be vacuumed before the experiment could be started. The quartz tube was heated up at designated temperatures (265, 300, 350, 400, 434ºC) using the flames from

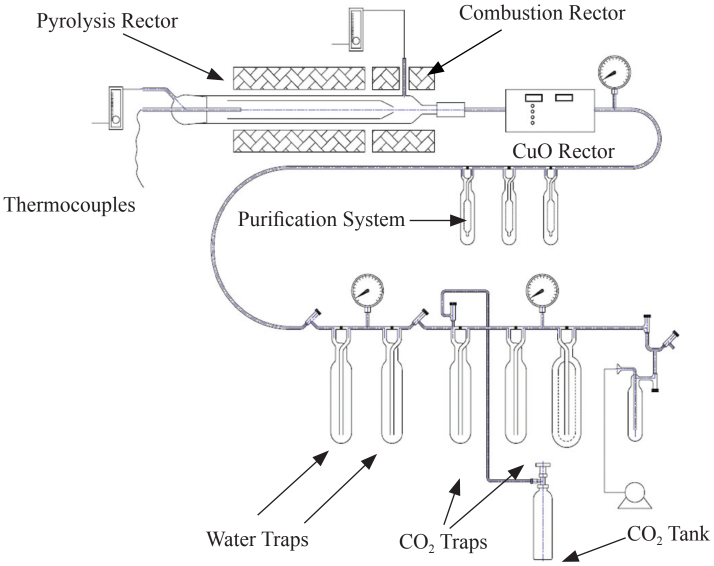

Fig. 1: Schematic diagram of pyrolysis-combustion set up in radiocarbon dating laboratory

TABLE 1
Experimental ranges and levels of process variables for wt% CO_2

Independent variables	Unit	Ranges and Levels				
Coded levels		-1.68179	1	0	1	+1.68179
temperature	°C	266	300	350	400	434
Time	Minutes	15	20	27.5	35	40
Flow rates	cm^3/min	195	400	700	1000	1204

the burners and the temperature monitor indicating the intended temperature; all the traps were fixed at their places. Finally, liquid nitrogen was used to trap the incoming carbon dioxide since the freezing point of liquid nitrogen is –196°C, and dry ice was also used to trap water produced during the experiment.

Initially, the argon was supplied at the inlet of quartz tube at selected flow rates (195,400,700, 1000, 1204 cm^3/min) for the pyrolysis to occur, and the oxygen in excess was supplied at the end tip of the quartz tube simultaneously; hence, the reactor experienced integrated pyrolysis and combustion reaction. After experiencing the integrated pyrolysis-combustion, at the designated retention times of 14, 20, 27.5, 35 and 40 minutes, the remaining char in the sample boat was combusted using oxygen, and the argon supply was automatically ceased. The purified carbon dioxide was cryogenically collected for further synthesis. In this study, the system should be free from any leakages so that it would not contaminate the results yielded. All the nominated parameters were obtained from the Design-Expert 6.10.0 (State-Ease, Minneapolis, USA) software layout as illustrated in Tables 1 and 2. Generally, the volatile matters released during pyrolysis reaction were oxidized at intended

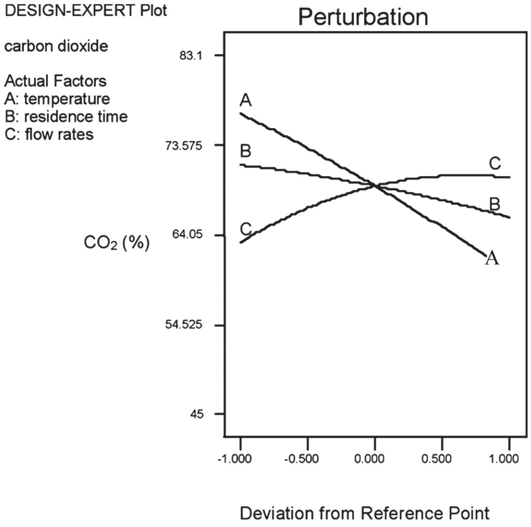

Fig. 2: Effect of temperature, time and flow rates with respect to carbon dioxide production

TABLE 2
Central composite design matrix of wt% CO_2

Run	Factor 1 T	Factor 2 time	Factor 3 flow rates	Response CO_2
	ºC	minute	cm^3/m	%
1	350	27.5	700	73.5
2	300	20	1000	83.1
3	350	27.5	700	67.5
4	400	20	1000	67
5	400	20	400	73.5
6	350	27.5	700	73
7	350	27.5	700	69.9
8	300	35	1000	75.9
9	300	35	400	68.7
10	300	20	400	79.5
11	400	35	1000	59
12	400	35	400	52
13	350	27.5	700	70.1
14	350	27.5	195.46	47
15	350	40.11	700	66
16	350	14.89	700	60.2
17	434.09	27.5	700	45
18	350	27.5	1204.54	68
19	350	27.5	700	69
20	265.91	27.5	700	80

residence time, while the remaining char after the reaction was oxidized by switching the inlet from argon to oxygen supply.

RESULTS AND DISCUSSION

Experimental Design and Statistical Analysis

The results from the Design-Expert showed that the maximum CO_2 production was achieved when the temperature was set at 300ºC; meanwhile, the retention time was set at 20 minutes for the 1000ml/min argon supplied as shown in Table 2. Moreover, *Fig. 2* shows that the low temperature of the pyrolysis, short retention time and excess argon flow rates had caused the amount of CO_2 production from the Karas woods to increase. This results were also supported by ANOVA, which gave the value $P<0.001$ for the low temperature, and $P< 0.0043$ for shorter residence time, respectively (Table 3). The small P value also indicated that the low temperature of pyrolysis and shorter residence time were the most significant effects of increasing the amount of CO_2 production as compared to the flow rate of argon, with $P<0.02$ (Chiang and Chang, 2006). The ANOVA also showed that the linear model chosen was less than 0.05 or was with 95% confidence, indicating that the model could be considered as statistically significant, and demonstrated that the terms in the model had a significant effect on the response (Chiang and Chang, 2006).

As the temperature increased, there was a decrease in the yield of carbon dioxide due to the decrease in the char yield, when the temperature was higher than 300ºC. According to Fang (2006), the amount of char would increase when the temperature was lower. Similarly, Fuwape (1996) and Lua *et al*. (2006) stated that the temperature higher than 300ºC would generate char which was less than 50%. During the slow pyrolysis, hydrolysis and dehydration reactions could proceed in an orderly manner to uncover the still macro-molecular cellulose and lignin fragments. Thus, less interaction exists between carbon to carbon bonds in glucosan and aromatic rings, leaving time for the carbon residues to condense into charcoal. According to Qinfeng *et al*. (2005), the cellulose pyrolysis between 300 to 400ºC involved a depolymerization of the glycosyl units to levoglucosan, and H_2O, CO, CO_2 and char to decompose. In addition, the secondary reactions involved were oxidization of volatiles and char, respectively, since the slow pyrolysis reactor was purged with oxygen. Moreover, Robert and Todd (2001) also reported that the elemental carbon (i.e. char) produced the highest emission of CO_2 as compared to various solid fuels like biomass.

Thermal treatments, both pyrolysis and combustion, are important reactions of depolymerization of volatiles and scission of carbon chain in the wood samples. The large amount of volatiles produced, consisting of H_2O, CO_2, CO, C_2H_6, CH_4 and tar, would be in direct contact with the excess oxygen so that all the volatiles were completely oxidized. The volatiles released from the pyrolyzed matters react with oxygen to produce carbon dioxide. Thus, integrating the pyrolysis-combustion will boost up the yield of carbon dioxide. According to Liang and Kozinski (2000), oxidation of char comes from the following reaction:

$$\text{Char} + O_2 \longrightarrow CO_2 + \text{ash} \qquad (1)$$

While the oxidation of volatile matters are from this reaction:

$$CH_mO_n + O_2 \longrightarrow CO_2 + H_2O \qquad (2)$$

TABLE 3
Analysis of Variance (ANOVA) table

Source	Mean Square	F-Value	p-value	
Block	135.34			
Model	496.82	15.25	<0.0001	significant
A	902.20	27.70	<0.0001	
B	367.87	11.30	0.0043	
C	220.38	6.77	0.0200	
Residual	32.57			
Lack of fit	41.47	5.12	0.0643	Not significant

Fig. 2 shows that the time extension did not contribute in increasing the CO_2 yield based on the observation made; in this case, the smoke emitted was depleted after 15 minutes and totally ceased after 25 minutes. The smoke produced indicated that the volatiles were released, during the pyrolysis, and combusted after reacting with oxygen, as indicated by Equations 1 and 2. As time increased, other products produced CH_4, H_2 and C_2H_2 and secondary reaction could occur (Wen and Stanley, 1979). Secondary reaction could be very active due to the catalyzation from charcoal and this led to the formation of more highly combustible products. For example, carbon dioxide and water vapor react with carbon to form carbon monoxide, hydrogen and formaldehyde (Fang *et al.*, 2006).

A higher concentration of argon was needed to increase the production of $CO_{2,}$ as shown in *Fig. 2*. A higher concentration was also required to ensure that a complete degradation of woods occurred during the pyrolysis, with the complete cracking and splitting of C-O and C-C for high production of CO_2 and CO (Qinfeng *et al.*, 2005). *Fig. 3* illustrates that R^2 was 0.7531, indicating that 75.31% of the variability in the data was explained by this model and the regression line was not at the best fitted line. This effect might be due to the flaming process, which could not give consistent and optimum amount of carbon dioxide. The integrated process, using direct flaming as a tool of heating, led to a homogenous heating to the samples, and thus, caused the fluctuation in reading and produced non-reproducible result. In addition, *Fig. 4* shows that all the points fell in the allowable ranges between –3.50 to 3.50, showing that there were no significant influential factors during the experiments (Bursali *et al.*, 2006).

Mathematical model was built through regression, based on the coded experimental plan and the response results (Table 2). The following linear equation explains the experimental data for CO_2 production.

$$\text{(Actual factor)}Y= +134.57- 0.163T - 0.692t + 0.0133Q \tag{3}$$

$$\text{(Coded factor) } Y=+68.02 -8.13A -5.19B +4.02C \tag{4}$$

Where Y is CO_2 production in %, T is temperature in °C, t is retention time in minutes and Q is flow rate of argon in ml/min, similarly for the coded factor where A, B and C were for temperature, time and flow rate, respectively. In this study, all the three parameters gave significant effects to the CO_2 yield.

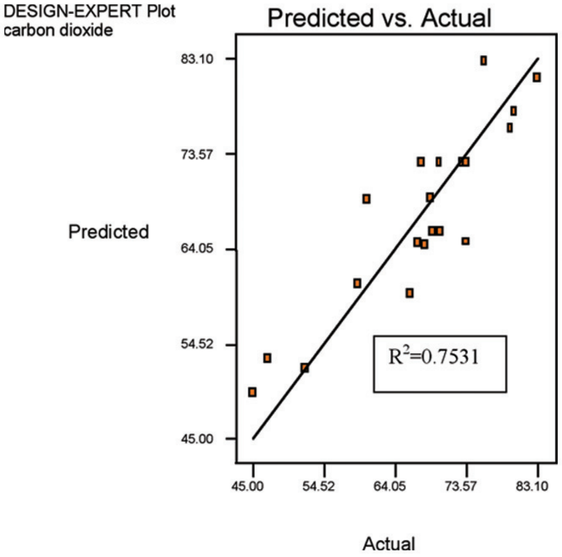

Fig. 3: Regression line of CO_2 production from Karas woods

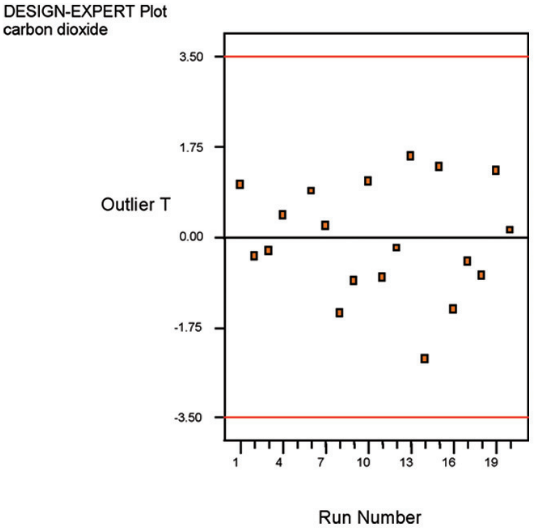

Fig 4: The outlier with respect to the run number of experiments

CONCLUSIONS

The objective of this study was to investigate the influence of temperature, residence time of pyrolysis and the concentration of argon on the production of carbon dioxide during direct pyrolysis-combustion process. The result from the Design-Expert showed that the maximum CO_2 production was achieved when the temperature was set at 300°C, and the retention time was at 20 minutes for 1000ml/min argon supplied. These show that the low temperature of pyrolysis, short retention time and excess argon flow rates will increase the amount of CO_2 production from the Karas woods.

The results were also supported by ANOVA using the central composite design by giving the value $P<0.001$ for the low temperature, and $P< 0.0043$ for shorter residence time, respectively. The small P value also indicated that the low temperature of pyrolysis and shorter residence time were the most significant effects which increased the amount of CO_2 production as compared to the flow rate of argon, in which $P<0.02$. The study also showed that the low temperature of pyrolysis at 300°C would increase the amount of char production, whereas the oxidization of the char during combustion would add up to another increment of CO_2.

ACKNOWLEDGEMENT

The work described above was fully supported by Nuclear Malaysia Agency through the grant Project No: NM-RND-07-07 from the Ministry of Science, Technology and Innovation Malaysia (MOSTI).

REFERENCES

Browne, F.L. (1958). *Theories on the combustion of wood and its control*. US forest Prod. Lab Report. 2136.

Bursali, N., Ertunc, S. and Akay, B. (2006). Process improvement approach to the saponification reaction by using statistical experimental design. *Chemical Engineering and Processing, 45*, 980-989.

Chiang, K.T. and Chang, F.P. (2006). Application of response surface methodology in the parametric optimization of a pin-fin type heat sink. *International Communications in Heat and Mass Transfer, 33*, 836-845.

Fang, M.X., Shen, D.K., Li, Y.X., Yu, C.J, Luo, Z.Y. and Cen, K.F. (2006). Kinetic study on pyrolysis and combustion of wood under different oxygen concentrations by using TG-FTIR analysis. *Journal of Analytical and Applied Pyrolysis, 77*, 22-27.

Fuwape, J.A. (1996). Effects of carbonization temperature on charcoal from some tropical trees. *Bioresource Technology, 57,* 91-94.

Gupta, S. and Polach, H. (1985). *Radiocarbon Dating Practices at ANU*. Handbook: Australia Publishing.

Joel, S.L. (ed.). (1994). *Biomass Burning and the Production of Greenhouse Gases*. New York: John Wiley and Sons.

Liang, X.H. and Kozinski, J.A. (2000). Numerical modelling of combustion and pyrolysis of cellulosic biomass in thermogravimetric systems. *Fuel, 79,* 1477- 1486.

Lua, A.C., Fong, Y.L. and Jia, G. (2006). Influence of pyrolysis conditions on pore development of oil-palm-shell activated carbons. *Journal of Analytical and Applied Pyrolysis,76,* 96-102.

Qinfeng, L., Chunxiang, L., Yonggang, Y., Fu, H. and Licheng, L. (2005). Study on the pyrolysis of wood-derived rayon fiber by thermogravimetry-mass spectrometry. *Journal of Molecular Structure, 733,* 193-302.

Robert, H. and Todd, L. (2001). Minimizing net carbon dioxide emissions by oxidative co-pyrolysis of coal/ blends. Technical report for research project (10/2000-3/2001).

Wen, C.Y. and Stanley, L.E. (1979). *Coal Conversion Technology, Advanced Book Program Reading*. Massachusetts: Addison-Wesley Publishing Company.