Design Of Experiments: Production of CO_2 from *Aquilariella malaccensis* woods via pyrolysis-combustion process

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Abstract : - CO_2 is the main source used in conventional radiocarbon dating to estimate the age of the archaeological wood. However, the production of CO_2 by combustion for conventional radiocarbon dating normally produces minimal amounts of CO2,, making it difficult to proceed to subsequent processes. Thus, the objective of this paper is to introduce an integrated-combustion process on degraded wood that will maximize the production of CO_2. Karas or Aqualaria Malaccensis was taken as case study. 2^3 response surface central composite design method was successfully employed for design of experimental (DOE) and analysis of the results. The number of experimental runs was determined using the Design-Expert 6.10.0. Karas wood was studied at different temperatures in a horizontal laboratory tubular quartz reactor. The effect of temperature, concentration of inert gas supplied during pyrolysis reaction and residence time taken during the production of CO_2 from thermal and oxidative reactions were studied. The woods were pyrolysed in a thermogravimetry analyser (TGA) at different heating rates for the active pyrolysis occurrence. From the TGA results, it were observed that at lower temperature regime (less than 3000C) decompositon of wood, mainly H_2O, CO_2 and CO were evolved and at higher temperature regime, the main decomposition products were oil, H2O, hydrocarbon gases and lower concentration of CO and CO_2. The results indicated that the production of CO_2 increased with the continuous supply of oxygen at high temperature of pyrolysis and high flow rates of argon within a short period of residence time.

Keyword: Archaeological wood, Karas *(Aqualaria Malaccensis*), DOE, Integrated pyrolysis-combustion, ANOVA

1. 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. The samples retrieved will be pre-treated accordingly prior to radiocarbon system. The 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 its yield is to be used for the subsequent processes. Nevertheless, the weight % of carbon dioxide produced during combustion is unsatisfactorily and inconsistent with the amount of 60% from the existing carbon in the wood samples [3]. In this study, we will characterize the influence of argon as carrier gas onto the wood samples using pyrolysis-combustion approach. Thorough investigation and study will be emphasized onto the

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integrated pyrolysis- combustion system for its chemical characterization. The pyrolysis-combustion method will be introduced in this study to obtain the optimum amount of carbon dioxide with optimized parameters, which are temperature of pyrolysis, residence time and concentration of argon. Complete combustion produces carbon dioxide, water and char but the process are not controllable thus leading to inconsistent amount of carbon dioxide from the same amount of samples due to during combustion oxygen was consumed at the surface of semi-coke and negligibly diffused into its pore [3] and according to Browne (1958), wood does not burn directly but undergoes thermal degradation precedes the combustion.

Thermal treatments, both pyrolysis and combustion, are important reactions of depolymerization of volatiles and scission of carbon chain in the wood samples. The increased amount of the char formed at lower temperature during pyrolysis is due to the fact that slow heating will make the woods 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 [3]. The large amount of volatiles produced will be in direct contact with the excess oxygen so that all the volatiles are oxidized completely. Besides, the statistical design of experimental method was applied to predict the production of CO2 using pyrolysis-combustion technique. Central composite design and response surface methodology were applied to determine the best operating parameters for maximum yield of carbon dioxide production. Experimental results were analysed statistically by analysis of variance (ANOVA) using Fischer's F-ratio [1,2]. According to Bursali et al. the experimentation is to determine the effect of the independent variables on the dependent variables of a process and the relation between them

is illustrated by regression model by using experimental data.

2 Methodology

2.1 Preparation of sample

Karas woods were cut into smaller pieces and milled then washed with distilled water prior to oven dried. About 6-10g of sample underwent hot-solvent Soxhlet extraction to remove resins and wax. The ratio of 2:1 benzene and ethanol were used to eliminate wax and resin followed with 95% ethanol and distilled water respectively. Sample will be refluxed for 8 hours for each solvent and rinsed thoroughly with distilled water to eliminate any trace of benzene or ethanol before oven dried at $50^{o}C$.

2.2 Experiments in furnace

All the experiments were performed in a horizontal quartz tube-type reactor where the samples were put in the sampling boat, sealed and vacuumed (-90 to –100kPa) to avoid any contamination to the sample (Figure 1). This reactor was placed inside a furnace consisting of two independent heating zones. The first heating zone was at lower temperature ($265^{0}C$, $300^{0}C$,$350^{0}C$,$400^{0}C$,$434^{0}C$) where the pyrolysis reaction occurs while the second heating zone was at temperature higher than $600^{0}C$ for combustion. The argon was supplied at the inlet of quartz tube at designated flow rate (195, 400 ,700 , 1000, 1204 cm^{3}/min) for pyrolysis to occur and oxygen in excess was supplied at the end tip of quartz tube, hence the pyrolysis-combustion occurred simultaneously in the reactor. The residence times for pyrolysis reaction were fixed at 14, 20, 27.5, 35 and 40 minutes. All the designated parameters were obtained from Design-Expert 6.10.0 (State-Ease) software as shown in

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Table 1. Initially, the volatile matters released from pyrolysis were oxidized at second chamber at fixed residence time and the char remained after the reaction, was oxidized by switching the inlet from argon to oxygen supply.

2.3 Recovery of carbon dioxide

The volatile and semi-volatile released from the Karas woods during pyrolysis were oxidized and produced desirable amount of carbon dioxide. At this time, the substantial amount of gases evolved was CO, CO_2, methane, formaldehyde, formation of carbonyl and carboxyl groups [4,5]. The char formed during low temperature pyrolysis was then oxidized at higher temperature (600^0C) with excess oxygen so that all the solid carbonaceous residues were fully converted to carbon dioxide. The carbon dioxide produced then passed through the purification system consisted of KI/I_2 solution for oxidation and decomposition of phosporus, nitrogen and sulfur, 0.1N $AgNO_3$ to precipitate chloride, halide and volatile acids and $K_2Cr_2O_7/H_2SO_4$ for final oxidation of any trace of carbon monoxide and trapped SO_3 [6]. Subsequently, the gases produced passed through the dry ice or the mixture of acetone and ethanol (-40^0C until -60^0C) to remove water molecules. The purified carbon dioxide was trapped in high-pressure tank (LP Gas Australia) cryogenically using liquid nitrogen and weighted. The difference of tank before and after carbon dioxide collection was calculated. The collected carbon dioxide was then transferred in Supelco 250ml sampling bulb.
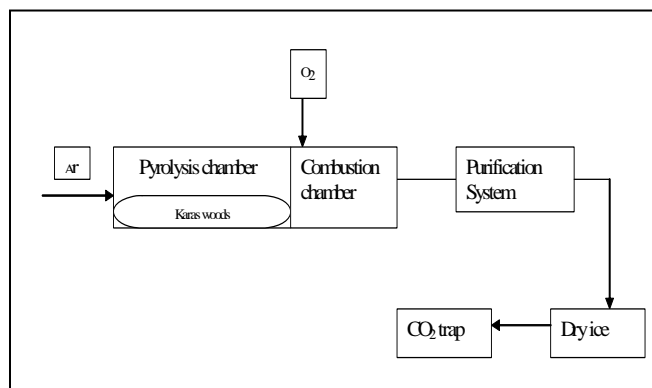
Figure 1. Schematic of pyrolysis-combustio

Table 1: Computer output from Design-Expert for completed design layout

Std	Run	Block	Factor 1 Temperature C	Factor 2 Time minute	Factor 3 Flow rates cm^3/m	Response CO_2 wt (%)
6	1	Block 1	400	20	1000	71.08
12	2	Block 1	350	27.5	700	73.49
8	3	Block 1	400	35	1000	59.04
11	4	Block 1	350	27.5	700	73.49
9	5	Block 1	350	27.5	700	75.05
7	6	Block 1	300	35	1000	75.9
4	7	Block 1	400	35	400	54.22
2	8	Block 1	400	20	400	73.49
1	9	Block 1	300	20	400	79.52
3	10	Block 1	300	35	400	67.47
10	11	Block 1	350	27.5	700	69.88
5	12	Block 1	300	20	1000	83.13
19	13	Block 2	350	27.5	700	71.08
14	14	Block 2	434.09	27.5	700	55.19
17	15	Block 2	350	27.5	195.46	58.19
13	16	Block 2	265.91	27.5	700	79.52
16	17	Block 2	350	40.11	700	61.42
15	18	Block 2	350	14.89	700	67.47
18	19	Block 2	350	27.5	1204.538	74.7
20	20	Block 2	350	27.5	700	72.29

2.4 Analysis

The analysis of carbon dioxide from Supelco sampling bulb was carried out in a Shimadzu Model Q5050A gas chromatography equipped with a Supelco capillary tube SPB-624 (30m x 0.25mm ID, thickness 1.4μm).Interfacial and injection temperature were fixed at 230^0C and 300^0C respectively. Helium acted as a carrier gas and the 10μl CO_2 was injected in the GC-MS. The CO_2 spectrum appeared at retention time 1.3minute and the system was left for 10 minutes and no other peaks observed during that period.

3.0 Results and discussions

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3.1 Ultimate and Proximate Analysis

Table 1 showed the chemical composition of Karas woods analysed by elemental analysis with LECO CHNS-932 for ultimate analysis. Determination of volatile matter, fixed carbon and ash were analysed using ASTM for proximate analysis [9].

Table 2: Ranges and Levels for three process factors

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
Concentration	cm^3/min	195	400	700	1000	1204

3.2 Thermogravimetric analysis

Woods, which are the biomass, were composed of cellulose, hemicellulose and lignin [11]. Thermogravimetric analysis (TGA) was used to determine the thermal decomposition of the wood at process conditions the same as in the slow pyrolysis batch reactor and to look at the range of active pyrolysis to happen [5]. Figures 2 and 3 showed the TGA thermograms of the weight loss to give the rate of weight loss (DTG) for the wood at lower heating rates (5, 10 and 20^{0}C/min) and higher heating rates (20, 30 and 40^{0}C/min).

From the TGA data, the smooth curves produced for TG was due to the homogeneity of the samples. At lower and higher heating rates, the weight loss occurred right after the heating was commenced. The initial loss of about 6 to 10% weight loss was due to elimination of water content in the wood samples. There was no weight loss after water removal until heating reached approximately 300^{0}C. At any heating rates the decomposition started at approximately 220^{0}C followed by a major loss of weight where they became constant at around 600^{0}C where there was no further loss of weight. The sudden drop was due to devolatization of combustible gases and vapors notably carbon monoxide, methane, formaldehyde, formic and acetic acids, carbon dioxide and water vapor [3,6]. Nevertheless, poor handling of samples during pre-treatment caused heating rate at 5^{0}C/min resembled the results as higher heating rates. For higher heating rates, the carbonisation took place at temperature about 400 to 600^{0}C while for lower heating rates, the carbonisation occurred at a range of 600 to 800^{0}C. Ashing happened at temperature 800^{0}C and 600^{0}C for lower and higher heating rates respectively. Nevertheless, according to Paul T. William & Serpil Besler, (1996), there was a small effect of heating rate on product yields. Thus, the TGA results were mainly concerned to look at the range of temperature for active pyrolysis.

3.2 Product yield

Table 3 showed the weight % yield results of carbon dioxide for the wood samples pyrolysed to final temperature of 266^{0}C, 300^{0}C, 350^{0}C, 400^{0}C and 434^{0}C and integrated with combustion in which for each condition the yields were cumulative. As the temperature increased, there was a decrease in the yield of carbon dioxide and the yield decrease as the temperature was lower than 300^{0}C. Char amount increased when temperature is lower [3,4]. During the slow pyrolysis, hydrolysis and dehydration reactions can proceed in orderly manner to uncover the still macro-molecular cellulose and lignin fragments. Thus, there will be less interaction to carbon to carbon bonds in glucosan and aromatic rings, leaving time for the carbon residues to condense into charcoal. According to Q.Liu et al. (2005), cellulose pyrolysis between 300 to 400^{0}C involved depolymerization of glycosyl units to levoglucosan and decomposition of H_2O, CO, CO_2

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and char. In addition, since the slow pyrolysis reactor was purged with oxygen, the secondary reactions involved were oxidization of volatiles and char respectively.

Table 3: Response Surface method-Central composite design matrix of wt% CO_2

Std	Type	Factor 1 temperature C	Factor 2 time minute	Factor 3 flow rates cm3/m	Carbon dioxide (wt%) Actual Value	Predicted Value
1	Fact	-1	-1	-1	79.52	79.20
2	Fact	1	-1	-1	73.49	66.15
3	Fact	-1	1	-1	67.47	70.30
4	Fact	1	1	-1	54.22	57.25
5	Fact	-1	-1	1	83.13	85.38
6	Fact	1	-1	1	71.08	72.33
7	Fact	-1	1	1	75.9	76.48
8	Fact	1	1	1	59.04	63.43
9	Center	0	0	0	75.05	71.31
10	Center	0	0	0	69.88	71.31
11	Center	0	0	0	73.49	71.31
12	Center	0	0	0	73.49	71.31
13	Axial	1.68179	0	0	79.52	78.46
14	Axial	1.68179	0	0	55.19	56.51
15	Axial	0	-1.68179	0	67.47	74.97
16	Axial	0	1.68179	0	61.42	60.00
17	Axial	0	0	-1.68179	58.19	62.28
18	Axial	0	0	1.68179	74.7	72.68
19	Center	0	0	0	71.08	67.48
20	Center	0	0	0	72.29	67.48

The optimum condition parameters of pyrolysis which were shortening the residence time, decreasing the heating temperature and increasing the concentration of inert gas can increase the production of charcoal. The volatiles released from pyrolyzed matters will react with oxygen to produce carbon dioxide. Thus, integrating the pyrolysis-combustion will boost up the yield of carbon dioxide. According to X.H. Liang and J.A. Kozinski (2000), oxidation of char comes from this reaction

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

While the oxidation of volatile matters are from this reaction

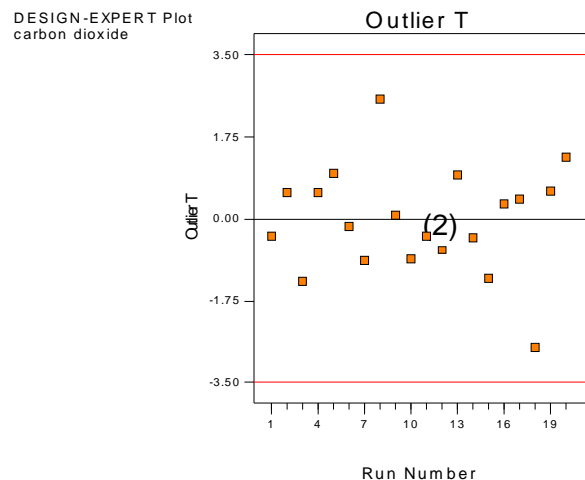$$CH_mO_n + O_2 \longrightarrow CO_2 + H_2O \qquad (2)$$

From Table 3, it showed that the losses of another 17 weight % of total mass balance at 300^0C, 20 minutes and $1000cm^3/min$ of nitrogen were most probably due to high vacuum suction throughout the experiment and the trace of oil observed during pyrolysis. The oil produced was considered as negligible since weighing out of oil was considered impractical for this study.

3.3 Analysis of variance (ANOVA)

The quality of fit of the linear model of response surface method was expressed by the coefficient of determination R^2 and is statistical significance was analyzed by Fisher's F-test and Student's t-test (ANOVA). According to ANOVA, the F values for all regressions were higher. The large value of F indicates that most of variation in the response can be explained by regression model equation [1,2]. Table 4 presented the results of the linear model for wt% CO_2 in the form of ANOVA. The value of "Prob>F" in the table is less than 0.05 (ie; 95% confidence). Thus, the linear model is considered to be statistically significant.

The "Lack of fit tests" table compared the residual error to the pure error from replicated design points. The table clearly showed that linear model is the best model due to the "Prob>F" fell below 0.05 for lack of fit tests.

Figure 4. The outliers vs run numbers

The predicted values (using model equations) were compared with experimental results for wt% carbon dioxide and the data are shown in Table 2 and also graphically represented in Fig.4.

Figure 5: Predicted Vs Actual results

The ANOVA confirmed the adequacy of the linear model (the Model Prob>F is less than 0.05).All terms with value "Prob>F"greater than 0.100 were eliminated [2]. Thus A,B and C were significant model terms. The test of lack-fit also displayed to be insignificant. proved that temperature, residence time of pyrolysis and conventration of argon were salient factors in carbon dioxide production respectively.Besides,the "Pred R-Squared" of 0.6226 is in reasonable agreement with the "Adj R-Squared" of 0.7637. Nevertheless, the R-Squared was very low. Thus, two points were identified outliers were removed from the graph (Fig.5). Table 5 showed the corrected value of "Pred R-Squared" and "Adj R-Squared".

Finally, the final response equation for wt% carbon dioxide is obtained in terms of coded factors and actual factors respectively, as follows,

Table 4: The Results Of The Linear Model For Wt% CO_2 In The Form Of ANOVA
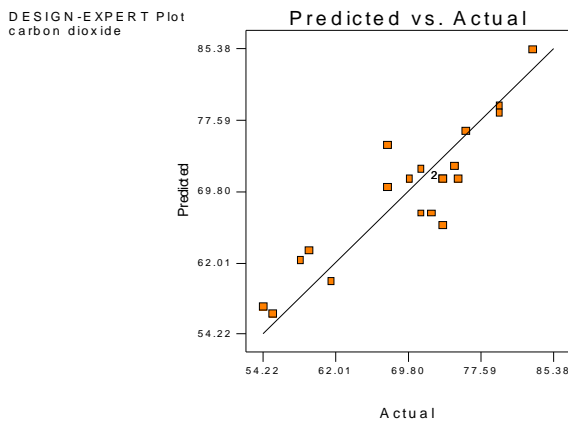
Sequential Model Sum of Squares						
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	97387.759	1.000	97387.759			
Block	70.441	1.000	70.441			
Linear	982.278	3.000	327.426	20.390	< 0.0001	Suggested
2FI	47.833	3.000	15.944	0.991	0.4299	
Quadratic	62.015	3.000	20.672	1.420	0.2998	
Cubic	105.317	4.000	26.329	5.121	0.0513	Aliased
Residual	25.709	5.000	5.142			
Total	98681.352	20.000	4934.068			

Lack of Fit Tests						
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Linear	225.726	11.000	20.521	5.419	0.0584	Suggested
2FI	177.894	8.000	22.237	5.872	0.0525	
Quadratic	115.878	5.000	23.176	6.120	0.0519	
Cubic	10.562	1.000	10.562	2.789	0.1702	Aliased
Pure Error	15.147	4.000	3.787			

Wt % CO_2 = 69.63 – 7.17 A- 4.98 B+ 3.74 C   (3)
Wt % CO_2= 129.383 –0.14344 Temperature – 0.66444 residence time + 0.012462 concentration (4)

3.4 Effects of temperature, retention time and flow rates on the production of CO_2

Figure 6(a-c) showed the effects of temperature, retention time and flow rates on the production of CO_2 for Karas wood. According to ultimate analysis, the carbon content in Karas wood is about 45%. Moreover, according to stoichiometric analysis, the CO_2 produced from each degraded wood was directly proportional to its initial carbon content.

Figure 6a shows that temperature had a significant effect on the production of CO_2. As the temperature increased, there was a decrease in the yield of carbon dioxide. During the slow pyrolysis, hydrolysis and dehydration reactions can proceed in an orderly
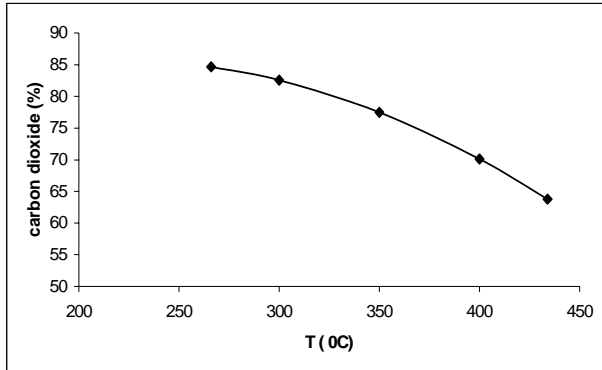

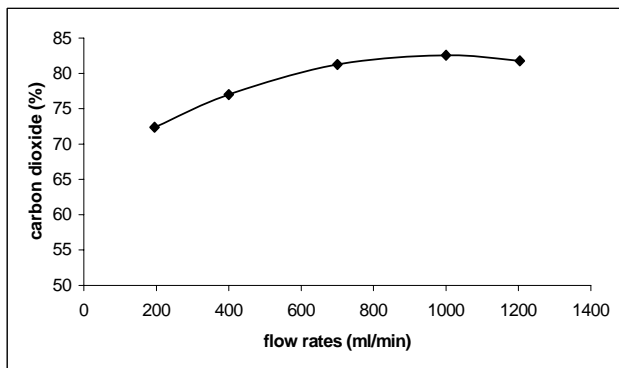Figure 6a. Effect of time with respect of carbon dioxide production

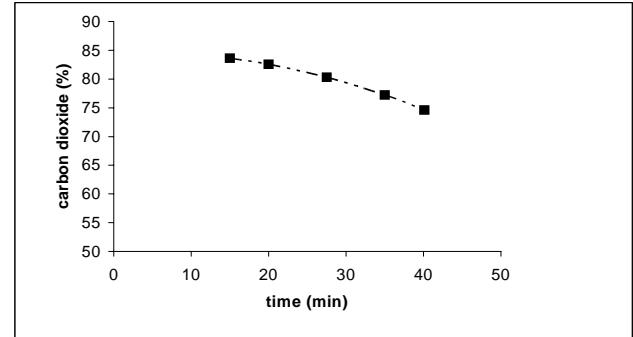Figure 6b. Effect of flow rate with respect of carbon dioxide production

Figure 6c. Effect of time with respect of carbon dioxide production

manner to uncover the remaining macro-molecular cellulose and lignin fragments [4]. Thus, there is less interaction between carbon-to-carbon bonds in glucosan and aromatic rings, leaving time for the carbon residues to condense into charcoal. Nevertheless, at temperatures below 300^0C, the result obtained was meaningless because the char produced was brown, indicating incomplete combustion [6]. High temperatures produced small amounts of CO_2 compared to low temperatures. As temperature increased, cellulose decomposition produced tar with major components consisting of laevoglucose, aldehyde, ketone, organic acids and small amounts of CO, CO_2, H_2 and char. Moreover, at temperatures greater than $500\ ^0C$, tar formation was dominant compared to char and gases. The tarry volatiles did not degrade easily and led to low amounts of produced CO_2, such that a higher temperature of 800-$900\ ^0C$ was needed to remove it [7].

Figure 6b indicates that retention time is another parameter with significant effect on the production of CO_2. It shows that the retention time with which pyrolysis occurred was inversely proportional to the production of CO_2. Shorter time was needed to produce large amounts of CO_2 using the integration of pyrolysis-combustion to limit the degree of reduction of CO_2 to CO [4]. The greater lengths of

time may cause the secondary reaction to occur and promote the formation of other products such as CH_4, H_2 and C_2H_2. The secondary reaction can be very active due to the cartelization by char, which causes the formation of flammable gases [8].

Figure 6c shows that a higher concentration of argon was needed to produce significant amount of CO_2. The argon excess was needed to ensure that complete degradation of woods occurred during pyrolysis, with the complete cracking and splitting of C-O and C-C for high production of CO_2 and CO [9]. Nevertheless, flow rate higher than 1000ml/min caused the sample to fly and scatter out of the sampling container in the reactor. This is because the reaction also occurs in a vacuum (-90 to –100kPa) as a prerequisite to the radiocarbon dating procedure. Moreover, the sample was ground prior to conducting the experiment. Thus, Figure 2c shows the drop of CO_2 production after 1000ml/min of argon was supplied. The continuous supply of argon and vacuum conditions during the process could increase char production to 35-40% as it has been reported that the use of vacuum will not adversely affect the char formed [10]. The analysis and identification of the CO_2 from integrated pyrolysis-combustion was done using gas chromatography –mass spectrometry (GC-MS) It shows the pure sole peak of carbon dioxide after injection into the GC-MS with a retention time of 1.3 minutes.

3.4 Confirmation of carbon dioxide using GC-MS

Fig.7, showed the peak of carbon dioxide after injection into the GC-MS with retention time at 1.3 minutes. The sole peak shown indicated that the CO_2 produced was pure.
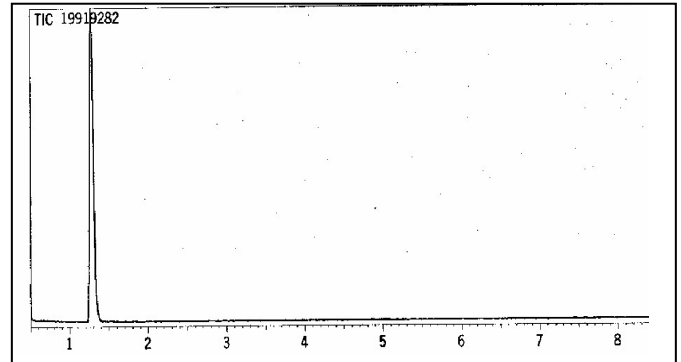

Figure 7 GCMS spectrum of carbon dioxide

3.3 Optimization of process parameters on production of CO_2

Optimization of process conditions using a statistical approach involved the selection of the experimental design, estimation of coefficients based on mathematical modeling and response prediction [11]. Based on model, the relationship between the response and the variables is visualized by a response surface or contour plot to see the relative influence of the parameters, to find an optimum parameter combination, and to predict experimental results for other parameter combinations. Numerical optimization was carried out with the help of Design-Expert 6.10.0 to determine the optimized parameters for an optimum yield of CO_2. Mathematical models were built through regression based on the coded experimental plan (Table 5) and results. The second order polynomial equations explain the experimentally determined relationship between significant factors and response after elimination of the non-significant terms. As a result, the dependence of response on the significant factors can be illustrated by Eqs. (2) as following :

Karas: $CO_2 = 15.63 + 0.36T + 0.582t + 0.043q - 0.0073t^2 - 0.004Tt$ (5)

According to the empirical models obtained, the three operating parameters (denoted as T for temperature, t for residence time and q for flow rates of argon), and interaction of temperature and time significantly affected the production of CO_2 for each type of wood. The analyses of the variances (ANOVAs) are presented in Table 2, which indicates the high significance of the model. Statistical analysis conducted on the data showed that all three operating parameters had significant quadratic effects on the model since "Prob >F" in Table 8 for this model is less than 0.05 (a=0.05, or 95% confidence). This indicates that the model is considered to be

Table 7   Analysis of variance (ANOVA) for the quadratic model

| | | "Prob>F" | |
Source of variation	Karas	Meranti	Setumpol
T	< 0.0001	< 0.0001	< 0.0001
t	< 0.0001	< 0.0001	0.0003
Q	< 0.0001	0.0029	0.0001
T^2	0.0019	0.1768	0.0120
t^2	0.1308	0.3621	0.2439
Q^2	0.5666	0.0373	0.0726
T.t	0.0627	0.3462	0.5895
T.Q	0.1424	0.2692	0.0025
t.Q	0.2302	0.1044	0.9134
Model	<0.0001	<0.0001	<0.0001
Lack-of-fit tests	Not significant	Not significant	Not significant
R^2	0.952	0.947	0.996

Table 8 Optimum parameters for CO_2 production

Parameter	Goal	Lower limit	Upper limit
Temp (^{0}C)	is in range	300	400
time (min)	is in range	20	35
Flowrates (ml/min)	is in range	400	1000
CO_2 (%)	maximum	55.0	85.0

| Solutions | Parameters | | | | |
	Temp (^{0}C)	Time (min)	Flowrates (ml/min)	desirability	CO_2 (%)
Karas	300	20	982	0.981	82.57
Meranti	300	20	984	0.983	79.7
Setumpol	303.4	20.23	987.6	1.000	84

statistically significant as it demonstrates that the terms in the model have a significant effect on the response [12,13]. The high R^2 values (> 0.9) for all wood samples demonstrate that there is good agreement between the experimental results and the theoretical values predicted by the model [14].

The effects of operating temperature, residence time and inlet argon concentration on the production of CO_2 from Karas wood is depicted in the three-dimensional contour plots in Figures 3(a-c) for the yield of CO_2. Figure 8a shows the % of CO_2 production as a function of the pyrolysis temperature for Karas at different levels and for different retention times. The best maximum yield for CO_2 was 81.3% when temperature was low and the time was short. Williams & S. Besler [15] reported that the amount of char increased with decreased temperature. Fuwape and Lua et al [16,17] found that the increased amount of char formed at lower temperatures during pyrolysis is due to the fact that slow heating allows the wood to decompose in an orderly manner, from hemicellulose, cellulose and lignin, such that there is stepwise formation of increasingly stable molecules, each richer in carbon

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than the last, and converging toward the hexagonal structure of graphitic carbon. According to Fuwape and Lua et al.[16,17], at temperatures greater than 300^0C, the char produced was reduced to 30% compared to 50% at 300^0C. Robert & Todd [18] found that char that was mainly composed of carbon produced significant amounts of carbon dioxide compared to other lignocellulose materials.

Figure 8b shows the CO_2 production as a function of retention time of pyrolysis at different levels and flow rates of argon. As the retention time was shortened from 35 minutes to 20 minutes, the % of CO_2 was increased. This may be due to the fact that, during the experiment, the gases evolved started to recede at 15 minutes and ceased after 20 to 30 minutes. Leavitt et al. [19] reported that char produced at 35 minutes and 300^0C was 37% CO_2 compared to 39% at 35 minutes and 400^0C. Figure 3b also shows that at temperatures less than 300^0C, the production of CO_2 was high. Nevertheless, Leavitt et al [16] found that the char produced at temperatures less than 300^0C was rejected because the combustion was not complete. Fang et al. [20] reported that time extension can cause secondary reactions to occur and promote formation of products such as CH_4, H_2 and C_2H_2.

Figure 8c shows the production of CO_2 as a function of flow rate and pyrolysis temperature at different levels. The maximum yield of CO_2 was at 77.56%. The yield of CO_2 increased as the flow rate of argon increased. This due to the fact that excess argon is needed to ensure complete degradation of the wood during pyrolysis for the complete cracking and splitting of C-O and C-C needed for high production of CO and CO_2 [19].

Moreover, William & Susan [21] large amounts of volatiles produced from slow pyrolysis in direct contact with excess oxygen allows for complete oxidation of all the volatiles. Cellulose pyrolysis between 300 to 400^0C involved the depolymerization of glycosyl units to levoglucosan and decomposition of H_2O, CO, CO_2 and char [15]. The volatiles released from pyrolyzed matters will react with oxygen to produce carbon dioxide [21]. Thus, integrating the pyrolysis-combustion will boost the yield of carbon dioxide. According to Liang and Kozinski [10], oxidation of char comes from this reaction:

$$Char + O_2 \longrightarrow CO_2 + ash \qquad (7)$$

While the oxidation of volatile matter is from this reaction:

$$CH_mO_n + O_2 \longrightarrow CO_2 + H_2O \qquad (8)$$

Based on the aforementioned results, the optimum conditions for the production of CO_2 using integrated pyrolysis-combustion were determined to be 300^0C for the pyrolysis temperature, 20 minutes of retention time and 980ml/min for the argon flow rate.

Table 4 presents the optimization condition limits for the yield of CO_2 production via integrated pyrolysis-combustion. Finally, Table 4 presents a comparison of the yield of CO_2 via integrated pyrolysis–combustion with other reactions like combustion and single pyrolysis as stand alone reactions. The table shows that the integrated pyrolysis-combustion reaction produced the highest percentage of CO_2, compared to the other reactions. This study proved that the sequencing integrated pyrolysis-combustion reaction is viable and reliable for estimating the age of archaeological wood.
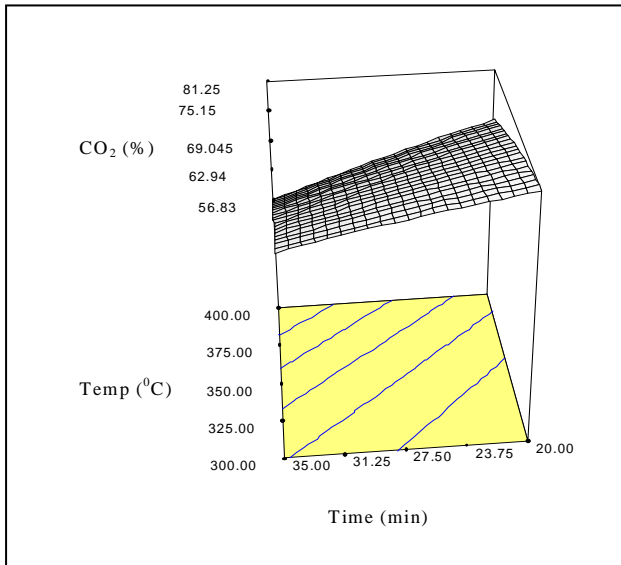
S. K. Kamarudin, A. Othman, Z. Yaakob,
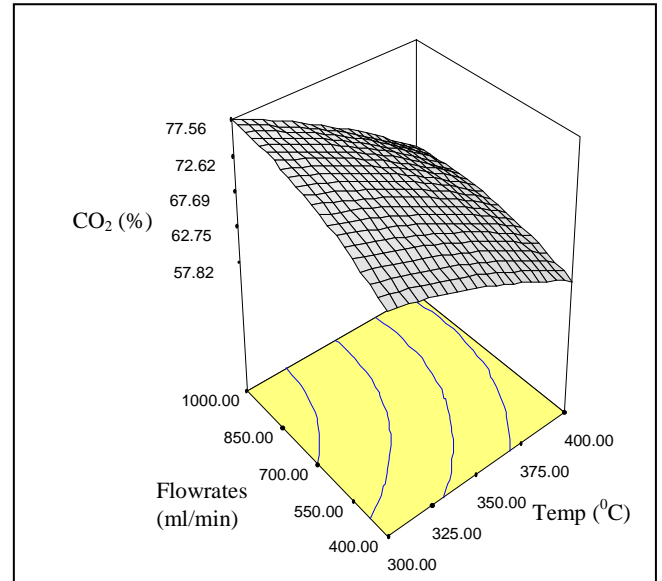S. R. S. Abdullah, A. Zaharim

Figure 3a. Temperature vs Time with respect to CO_2 production

4.0 Conclusions

The objective of this study was to investigate the influence of temperature, residence time of pyrolysis and concentration of argon on carbon dioxide production during pyrolysis-combustion process. A
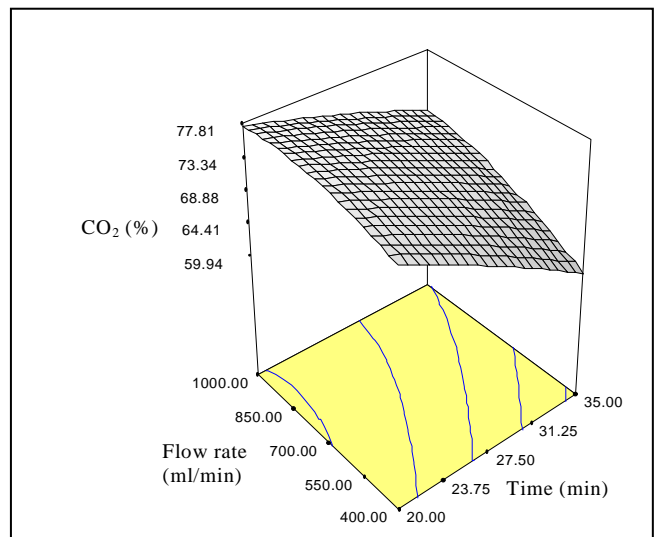

Figure 8b. Flow rates vs Temperature with respect to CO_2 production

Figure 8c. Flow rates vs Time with respect to CO_2 production

Table 9: Comparison on the % of CO_2 production with other reactions

Reaction	CO_2 (%)	Reference
Combustion	60	[1]
Pyrolysis	10-12	[3]
Pyrolysis-Combustion	83	This study

new methodology, 2^3 response surface central composite design was successfully employed for experimental design and analysis of results. The RSM technique really facilitate in constructing model and finding the significant interactions between parameters towards the output response. In this study, the linear model was developed and derived to estimate the wt% of carbon dioxide. Appropriate empirical model equations were developed either coded or actual factors for wt % of carbon dioxide using pyrolysis- combustion approach.

Acknowledgements

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