Optimization and Modeling of Bio-oil Production from Palm Shell by Pyrolysis Using Response Surface Methodology

Faisal ABNISA, Wan Mohd Ashri WAN DAUD, JAYA NARAYAN Sahu
Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603, Kuala Lumpur, Malaysia
Presenting Author: faisal.abnisa@gmail.com, Tel: +60 162709281
Corresponding Author: jnsahu@um.edu.my, Tel: +60 379675295
ashri@um.edu.my

Abstract
Renewable energy is beneficial energy choice, more environmentally friendly, available in a wide variety of sources and capable regenerate within a short period of time. It is potential to replace fossil fuels as a dominant energy source. In this context, biomass appears as one important renewable source of energy. Biomass is the largest source in the world, available in several categories and easy to find in the surrounding environment. It is the only renewable energy source that can provide liquid fuels. In Malaysia, various types of biomass sources can be found easily, one of them is palm shell. Palm shell is one of the largest agriculture residues that can be categorized into the biomass. The objective of this work is to convert palm shell into bio-oil by using pyrolysis and to find the optimum condition to produce the highest yield of bio-oil. Several parameters which have effect to the process such as temperature, N_2 flow rate, reaction time and particle size is will be investigated in this study. The response surface methodology (RSM) in conjunction with the central composite design (CCD) was used to determine the optimum value of the operating factors for maximum yield of bio-oil. In addition, the bio-oil obtained under the optimum condition was characterized by Fourier Transform infra-red (FT-IR) spectroscopy and gas chromatography/mass spectrometry (GC-MS) techniques.

Keywords: optimization; bio-oil; biomass energy; palm shell; pyrolysis; response surface methodology

1. Introduction

Crisis of fossil fuel usage lead to increase research development of renewable energy technology. Renewable energy plays an important role in the supply of energy. When renewable energy sources are used, the demand for fossil fuels is reduced. In contrast to fossil fuels, renewable energy sources can be replenished in a short period of time and it is usually more environmentally friendly, especially with regard to air emissions [1]. However, most of the energy currently used in the world comes from non-renewable sources. Whereas, many kind of renewable energy source are widely available in the world and it has many potency to develop for the welfare of human life.

Today, several renewable energy technologies have been developed such as biomass energy, wind energy, solar energy and geothermal energy [2]. Each of these technologies provides a great significant contribution in lieu of non-renewable energy depends on several parameters such as geographical conditions, topography of the site, capacity and type of energy available in low cost, availability of local infrastructures (including electricity grid), plant size and feed water salinity [3]. Numerous studies shown that from four sources of renewable energy were mentioned above, energy that is derived from biomass is the largest source on earth. Theoretical biomass resources are potentially the world's largest sustainable energy source comprising about 220 billion oven dry tonne (odt) (or 4,500 EJ) of annual primary production

Copyright © 2010 ICAE Organising Committee

if the marine phytoplankton resource is included [4]. Currently, the modern use of biomass has increased rapidly in many parts of the world. Refers to targets implications for concentrations of greenhouse gases (GHG_S) balance and carbon accounting under the Kyoto Protocol, many countries have ambitious targets for further biomass utilization. Oil price increases have also increased the level of interest in biomass energy.

Accordingly, biomass for energy can play a pivotal role. Most countries have the abundant resources of biomass that can be developed as energy. Various categories of biomass can be easily found in the surrounding environment. Generally, biomass can be categorized into four groups: agriculture residues, wood residues, dedicated energy crops and municipal solid waste (MSW) [5]. Among the various categories of biomass, agriculture residues have been estimated to represent significant potential for the development of the bio-energy industry in numerous countries [6]. The main advantage of utilizing agriculture residues as biomass energy is that they generally have little or no market value and ready to be produced in large quantities and mainly managed by private entities with some potential market incentive. These residues are generated through the direct harvest of crops at the growing site (field residues), or as a byproduct of processing at a processing facility [7]. Several researchers have investigated the potency of agriculture residues for energy, and the results are very encouraging [8, 9, 10, 11].

One of the largest sources of biomass energy from agricultures residue in Malaysia is palm shell [12]. Palm shell waste is generated from oil palm milling process. There are more than 270 palm oil mills operate in the country. More than 2.4 million tones of palm shell waste are produced annually [13]. A study has been estimated that the amount of waste is equal to 45.84 PJ (peta joule) of energy unit which is important as renewable energy. The energy content of the palm shell varies based on the moisture, residual oil content and its high specific energy content [14]. In general, wastes of palm shell are not used and have to be disposed. Usually, to reduce amount of disposal, the waste of palm shell was burned without energy recovery or usually used to cover the surface of the roads in the plantation area. Whereas, the conversion of palm shell to bio-oil with thermal process provides more benefit and potency to be used as biomass energy to substitute fossil fuels.

Biomass is widely accepted as a potential source of energy and it is the only renewable energy source that can provide liquid fuels. Biomass can be converted into liquid fuels by thermal, biological and physical process. In thermal conversion process; combustion, gasification, liquefaction, pyrolysis and carbonization are general applications processes that were used for converting biomass into liquid fuels. Among the processes, pyrolysis is the most popular thermal conversion process. Currently, pyrolysis technique of biomass is getting more attention because it is promising the highest liquid yield up to 75% wt on a dry-feed basis [15, 16]. The characteristics of this liquid, also known as bio-oil, depend on the composition of biomass feedstock and the type of pyrolysis process used to form it.

The production of bio-oil from biomass is the first step in a multi-faceted process. In general, bio-oil was utilized for the fuel or a feedstock for many commodity chemicals depending on the raw material and process conditions. Bio-oil products from biomass pyrolyzed have benefits for transport, storage, combustion, retrofitting and flexibility in production and marketing [17]. Bio-oil has many names such as pyrolysis oil, pyrolysis liquid, bio-crude-oil, bio-fuel-oil, wood liquids, wood oil, liquid smoke, wood distillates, pyrolytic oil, pyroligneous tar, pyroligneous acid and liquid wood [18, 19]. Special characteristic of bio-oil is a dark-brown organic liquid and free flowing with a strong acrid smell [19, 20, 21]. The

bio-oil is a mixture of hundred types of organic compounds and this can be used as a source of some pure chemicals such as alcohol, phenol, aldehyde, organic acids, etc [22]. In short, the pyrolysis of biomass into bio-oil has a great potential to be developed by considering that the product of the process is able to enhance the economic value.

Converting biomass into a bio-oil eliminates many problems and makes the use of more efficient systems for possibility to substitute the fossil fuels. Therefore, optimization of the process by maximizing the desired product quality and quantity is an important issue for engineers while paying attention to minimizing costs and environmental concerns. Several techniques have been made to optimize the bio-oil product from biomass by pyrolysis process. In practice, up to 75 wt % of the biomass (on dry basis) is converted into bio-oil by using fast pyrolysis [15, 16]. Fast pyrolysis is mainly used for maximizing the yield of liquid product at the processing conditions of very high heating rate and heat transfer rate, finely ground biomass feed (around 2 mm in the case of fluid bed reactors to minimize the water in the product liquid oil), carefully controlled temperature (around 500 °C), short vapor residence time (less than 2 seconds) and rapid cooling of the pyrolysis vapors to give the bio-oil products [18, 23, 24].

The most important optimization in this study is to obtain the highest amount (quantity) of bio-oil by pyrolysis process. Referring to the target, the use of an adequate experimental design is particularly important. Response surface methodology (RSM) has been found to be a useful tool to study the interactions of two or more factors [25]. RSM is a collection of mathematical and statistical techniques that are useful for modeling and problems analysis in which a response of interest is influenced by several factors [26]. It is suitable for dealing with multivariant experimental design strategies, statistical modeling and optimization process. Several previous researchers have proved that RSM was a powerful statistical tool in process optimization [27].

Bio-oil production by pyrolysis process from palm shell is attractive product, at least for the present, but they are too expensive to seriously compete with fossil fuels because of the high production costs of the high heat energy consumption during the process. The purpose of this study was to reduce these negative impacts by finding the best formula of optimization from various effects that affect to bio-oil product under intense investigation. The main aim of this study is to analyze the behavior of various effects in the pyrolysis process such as temperature, flow rate of N_2, particle size of palm shell and reaction time by using the statistical application approach of response surface methodology in order to generate the best formulation in which produce the highest yield of bio-oil. The bio-oil obtained under optimum conditions was used for characterization by Fourier Transform infra-red (FT-IR) spectroscopy and gas chromatography/mass spectrometry (GC-MS) techniques.

2. Experimental technique

2.1 Material and sample preparation

Palm shell waste was obtained from local company and the sample was grinded and then screened to give fractions with $0.5 < dp < 0.85$, $0.85 < dp < 1.4$, $1.4 < dp < 1.7$, $1.7 < dp < 2$ mm and $dp > 2$. Then the samples were dried for 24 hr at 105 °C. The ligninocellulosic contents of palm shell were determined by using gravimetric method in order to determine the content of cellulose, hemicellulose and lignin, respectively. Ash, moisture and fixed carbon contains were determined according to ASTM Standards (D-1102-84 for ash, D-2016-74 for moisture and D-3174-89 for fixed carbon). The ultimate analysis for carbon, hydrogen and

nitrogen were determined by using TruSpec CHN, LECO Cooperation; Saint Joseph, Michigan USA. The main characteristics of palm shell are given in Table 1.

Table 1
Main characteristics of palm shell.

Ligninocellulosic analysis	Value (%)	Proximate analysis	Value (wt %)	Ultimate analysis	Value (wt %)
Cellulose	27.7	Moisture	11	C	49.74
Hemi cellulose	21.6	Ash	2.1	H	5.32
Lignin	44	Fixed carbon	19.7	N	0.08
		Volatile [a]	67.2	O [a]	44.86
				S	0.16

[a] by difference

Elemental analysis results were used for calculating the heating value. In general, heating values can be reported as higher and lower heating value, HHV (gross) and LHV (net), respectively. The difference between HHV and LHV is equal to the heat of vaporization of water formed by combustion of the fuel. The high heating value in this study was obtained from calculation by Dulong and the low heating value was calculated by the following equation proposed by Oasmaa [28]:

$$\mathrm{HHV\,(MJ/kg)} = \frac{338.2\times \mathrm{C} + 1442.8\times\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right)}{1000} \quad (1)$$

$$\mathrm{LHV\,(MJ/kg)} = \mathrm{HHV} - (0.218\times \mathrm{H}) \quad (2)$$

2.2 Experimental Procedure

The pyrolysis experiments were performed on 150 g of palm shell in a 304 stainless steel tubular reactor with a length of 127 cm and an internal diameter of 2.5 cm, with a sweep gas (nitrogen) connection. The reactor was heated externally by an electric vertical furnace, with the temperature being controlled by a K-type thermocouple inside the reactor. Fig. 1 shows more detail descriptions of the pyrolysis set up. The experiments were carried out as many as 30 times, according to the number given by the statistical software. Several effects such as temperature, N_2 flow rate, reaction time and particle size were chosen to investigation in this study. The temperature was maintained at 400, 500, 600, 700 and 800 °C, the sweep gas flow rates of N_2 were conducted at 1, 2, 3, 4 and 5 L/min, the reaction times were arranged at 30, 60, 90, 120 and 150 min and the particle size of samples varied in a range of 0.5, 1, 1.5, 2, 2.5 mm. Following pyrolysis, the condensable products (liquid) were collected and weighed in a series of condenser maintained at 0.5 °C. After pyrolysis, the solid char was removed from inside reactor and weighed. The gas was weighed by difference. The yields product is calculated as follows:

$$\mathrm{Yield\,(Wt\,\%)} = \frac{\mathrm{Desired\,product\,(g)}}{\mathrm{Palm\,shell\,feed\,(g)}}\times 100\,\% \quad (3)$$

2.3 Response surface methodology

It is important to evaluate the performance of the systems and to increase the yield of the processes without increasing the cost. The method used for this purpose is called optimization. The optimization could be either a maximum or a minimum of a function of the design parameters. One of the methodologies for obtaining the optimum results is response surface methodology (RSM). This method was introduced by Box and wilson in 1951 which is a regression method of exploring the relationship between some explanatory factors and one or more response [29]. The parameters that affect the production of bio-oil were studied

with a standard of RSM design using central composite design (CCD). The experiments were conducted with one response in CCD; it is a yield of bio-oil (Y_{OB}). Temperature, N_2 flow rate, reaction time and particle size were chosen as factors, each considered at five levels namely; -1, +1, 0, -α and +α. The value (α) is depending on the number of factors in the factorial part of design. Determining of alpha in CCD is following the Eq. 4.

$$\alpha = [2^n]^{1/4} \quad (4)$$

where *n* is the number of factors [29]. Hereby the value of alpha was presented at -2 and +2.

Table 2
Experimental design matrix and results

Run	Actual level of factors				Coded level of factors				Responses
	Temp. (°C)	N_2 Flow Rate (L/min)	Reaction Time (min)	Particle size (mm)	A	B	C	D	Experimental Y_{OB}
1	600	3	90	2.5	0	0	0	2	38.9
2	500	4	120	2	-1	1	1	1	33.1
3	600	3	90	1.5	0	0	0	0	40.4
4	700	2	120	2	1	-1	1	1	36
5	600	1	90	1.5	0	-2	0	0	40.4
6	600	3	150	1.5	0	0	2	0	34.9
7	600	3	90	1.5	0	0	0	0	40.4
8	400	3	90	1.5	-2	0	0	0	39.9
9	600	3	90	1.5	0	0	0	0	40.2
10	500	2	120	2	-1	-1	1	1	39.3
11	600	5	90	1.5	0	2	0	0	35.5
12	600	3	90	1.5	0	0	0	0	40.4
13	700	4	60	2	1	1	-1	1	33.9
14	500	2	60	2	-1	-1	-1	1	46.3
15	800	3	90	1.5	2	0	0	0	35
16	600	3	30	1.5	0	0	-2	0	35.5
17	500	4	60	1	-1	1	-1	-1	34.7
18	700	4	60	1	1	1	-1	-1	30
19	600	3	90	1.5	0	0	0	0	40.2
20	600	3	90	0.5	0	0	0	-2	33.3
21	500	2	120	1	-1	-1	1	-1	38.3
22	700	2	60	1	1	-1	-1	-1	33
23	700	4	120	1	1	1	1	-1	37.3
24	700	4	120	2	1	1	1	1	32.9
25	700	2	120	1	1	-1	1	-1	36.4
26	700	2	60	2	1	-1	-1	1	38.7
27	600	3	90	1.5	0	0	0	0	40.3
28	500	4	120	1	-1	1	1	-1	38.9
29	500	2	60	1	-1	-1	-1	-1	42.1
30	500	4	60	2	-1	1	-1	1	34.2

Accordingly, to support the RSM data, other 30 of experiments were conducted again. In the second aims of this study, the particle size were arranged in five categories of parables, which are $0.5 < dp < 0.85 \approx 0.5$ mm, $0.85 < dp < 1.4 \approx 1$ mm, $1.4 < dp < 1.7 \approx 1.5$ mm, $1.7 < dp < 2$ mm ≈ 2 mm and $dp > 2 \approx 2.5$ mm. The complete design matrixes of the experiments carried out, together with the results obtained, are shown in Table 2. Model terms were selected or rejected based on the P values with 95% confidence level. The results were completely analyzed using analysis of variance (ANOVA) by Design Expert software includes with the experimental design, data analysis, quadratic model buildings and graph (three-dimensional response surface). Three-dimensional response surface plots were obtained based on the effect of the four factors. From these three-dimensional plots, the simultaneous interaction of the four factors on the responses was studied.

2.4 Characterization of bio-oil

The bio-oil obtained under experimental conditions that gave maximum oil yield (pyrolysis temperature of 500 °C, reaction time of 60 min, N_2 flow rate of 2 L/min and particle size of 2

mm) was used for characterization. In order to evaluate the corrosive property of the oil products, the pH of the oil was measured by a Metrohm pH meter 827. The water content of the bio-oil was obtained by Karl Fischer titration. The density of the bio-oil was estimated with a 25 ml pycnometer. Viscosity of bio-oil was measured using a rotational viscometer equipped with NVst spindle (Haake model VT 550). The measurement was carried out by measuring the shear stress by varying the shear rate ranging from 16.23 to 3246 s^{-1}. The measurements were made at temperature of 50 °C.

The chemical compositions of the bio-oil from palm shell were determined by gas chromatography/mass spectroscopy. The gas chromatography/mass spectroscopy (GC/MS) analysis of the pyrolysis oil was performed with an Angilent HP 6890 N gas chromatograph equipped with an Agilent HP 5975 mass-selective detector (mass spectrometer), using a 30 m × 0.25 mm DB-5ms capillary column (0.25 µm film thickness). The injection port and detector were both operated at 300 °C. The GC oven was heated to 30 °C for 2 min then to 290 °C at a rate of 3 °C/min. The injection method was used for analysis of 1 µl samples. An elemental analysis was carried out using a TruSpec CHN, LECO Cooperation; Saint Joseph, Michigan USA. The functional group compositions of the bio-oil product were analyzed by FT-IR spectroscopy. The FT-IR instrument of model Perkin Elmer FT-IR Spectrometer Paragon 1000 was used to produce the IR-spectra of the derived liquids.

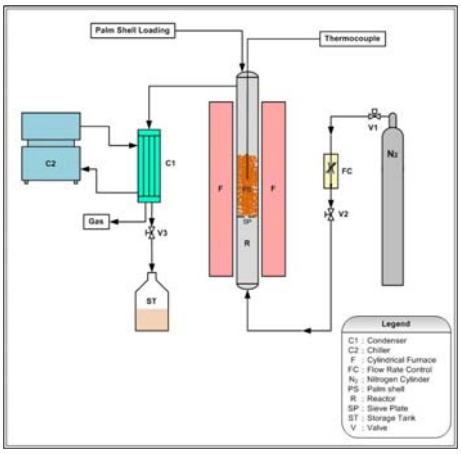

Fig. 1. Flow diagram of experimental set-up for bio-oil production.

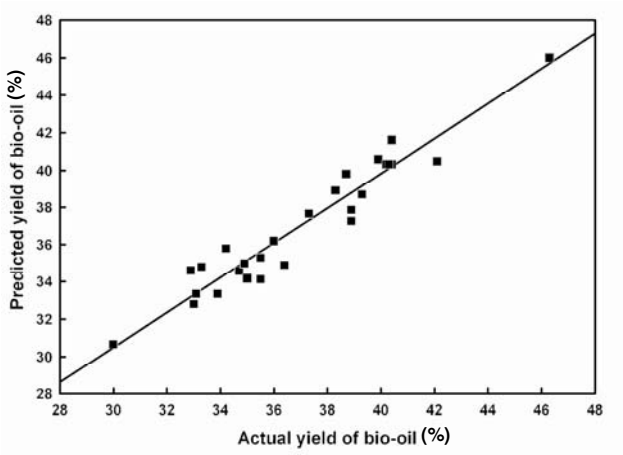

Fig. 2. Comparison plot between actual and predicted yield of bio-oil by using Eq. 5.

3. Results and discussion

3.1 Statistical analysis model

In this part of the study, the actual values of the independent factors and the response (30 experimental points) were used for prediction of model equations. Experimental data were fitted to higher degree polynomial equations, e.g. two factor interaction (2FI), quadratic and so on. ANOVA analysis showed that experimental data are best fitted into a quadratic equation. ANOVA for quadratic model was carried out to establish its significance. Therefore, the ANOVA was performed at 95% level of confidence for the designed experiments. The quadratic model for bio-oil conversion in terms of coded factors is represented as Eq. 5.

$$Y_{BO} = +40.32 - 1.60A - 1.87B - 0.079C + 0.62D + 0.94AB + 0.92AC + 0.37AD + 1.22BC - 1.08BD - 1.43CD - 0.73A^2 - 0.61B^2 - 1.30C^2 - 1.07D^2 \quad (5)$$

where Y_{BO} is the yield of bio-oil (%); A is the temperature (°C); B is the flow rate of N_2 (L/min), C is the reaction time (min) and D is the particle size (mm). The predicted bio-oil yield using Eq. 5 is given in Fig. 2 along with the experimental value.

The statistical model was checked by F-tests, and the ANOVA for the response surface quadratic model is summarized in Table 3. In Table 3, the Model F-value of 15.09 implies that model is significant. There is only a 0.01 % chance that a Model F-value this large could occur due to noise. There is a very low probability value (P model, F < 0.0001). Values of "Prob>F'' less than 0.0500 indicate that model terms are significant. Another of evidence is the lack-of-fit F-value. The lack-of-fit F-value of 246.25 implies the lack of fit is significant relative to the pure error. There is a 0.01 % chance that a lack-of-lit F-value this large could occur due to noise. Significant lack of fit is bad, and in this case, all the model coefficients, namely A, B, C, AB, AC, BC, BD, CD, A^2, B^2, C^2 and D^2 are significant.

Table 3
ANOVA for response surface quadratic model.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F-*Value*	p-value Probability > F	Remarks
Model	335.96	14	24.00	15.09	< 0.0001	Significant
A-Temperature	61.76	1	61.76	38.84	< 0.0001	Significant
B-N2 Flow rate	84.00	1	84.00	52.82	< 0.0001	Significant
C-Reaction Time	0.15	1	0.15	0.09	0.7626	-
D-Particle Size	9.25	1	9.25	5.82	0.0291	Significant
AB	14.25	1	14.25	8.96	0.0091	Significant
AC	13.51	1	13.51	8.49	0.0107	Significant
AD	2.18	1	2.18	1.37	0.2604	-
BC	23.77	1	23.77	14.95	0.0015	Significant
BD	18.71	1	18.71	11.76	0.0037	Significant
CD	32.78	1	32.78	20.61	0.0004	Significant
A^2	14.79	1	14.79	9.30	0.0081	Significant
B^2	10.19	1	10.19	6.41	0.0231	Significant
C^2	46.13	1	46.13	29.01	< 0.0001	Significant
D^2	31.51	1	31.51	19.82	0.0005	Significant
Residual	23.85	15	1.59			
Lack of Fit	23.80	10	2.38	246.25	< 0.0001	Significant
Pure Error	0.05	5	0.01			
Cor Total	359.81	29				

R^2 = 0.9337; adjusted-R^2 = 0.8718; predicted-R^2 = 0.6187 and adeq precision = 17.191

3.2 Effect of operating variables on the bio-oil products

The effects of the four factors on the yield of bio-oil were investigated by RSM using three-dimensional plots and contour plots. From Table 3 the response surface analysis it was found that all factors can influence directly or indirectly in order to increased the yield of bio-oil. Among all the significant factors, N_2 flow rate (B) was found to have the largest effect (due to the highest value of F). The maximum bio-oil production is essentially determined by the short residence times of vapor in reactor and N_2 flow rate is a determining factor. This effect is related with the reported by other researcher [30]. The reaction time (C) and interaction between the temperature and particle size (A and D) are not significant factors for maximized bio-oil production, this suggestion is due to the value of "Prob>F'' higher than 0.0500. The response surface graph for optimum yield of bio-oil was shown in Fig. 3. In Fig. 3 shows the interaction between the temperature and N_2 flow rate in three dimensional response surfaces plots (A and B). The combined effect of A and B factor on conversion of bio-oil maximum production was maintained at 500 °C and 2 L/min. The bio-oil is obtained maximum at 46.3 wt %, it was determined at 60 min of reaction time and 2 mm of particle size. All values of this figure are the real value from the experiment.

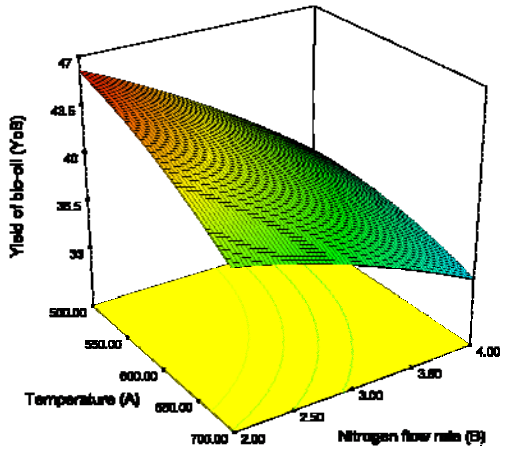

Fig. 3. Response surface plots showing the effect of temperature (A) and N_2 flow rate (B) for the yield of bio-oil (Y_{OB})

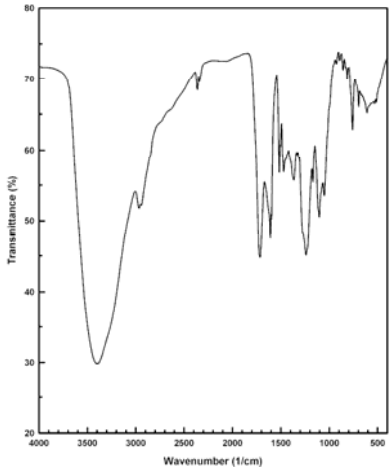

Fig. 4. FT-IR spectra of bio-oil derived from palm shell

3.3 Optimization by response surface modeling

The investigation to find the optimum process factors to maximize the conversion of palm shell for production of bio-oil by developing the mathematical model equation is one of the main aims of this study. The quadratic programming model was used as mathematical model equation to predict the maximum yield of bio-oil. The optimum values of temperature rate of 500 °C, N_2 flow rate of 2 L/min, particle size of 2 mm and reaction time of 60 min were obtained for maximum yield of bio-oil of 46.4 wt %. The yield of bio-oil from predicted was higher 0.3 wt % than the experimental result. The comparison of predicted and experimental was conducted in the same condition process. Several experiments were conducted at these optimum conditions in order to verify the accuracy of the model proposed. The experimental and predicted results are shown in Table 4.

Table 4
Comparison of optimization bio-oil product by experimental and prediction

	Factor				Yield of bio-oil	
	Temperature	N2 Flow rate	Reaction Time	Particle size	Experimental	Predicted
Term of coded	-1	-1	-1	1	46.1	46.4
Term of actual	500	2	60	2		

3.4 Physical and chemical characterization of bio-oil

3.4.1 Physical characterization of bio-oil

The typical properties of bio-oil derived from palm shell are given in Table 5. As can be seen from the Table 5, the density of the bio-oil at 24 °C was 1051 kg/m^3. It is denser than heavy fuel oil, which are typically about 855 kg/m^3. However, the density is much related to the liquid mass flow rate, which significantly affects the performance of fluid atomizers. Another property that has also given the affect to atomization quality is viscosity. The bio-oil on this experiment shown low viscous which has 3.2 cP at 50 °C. The low viscous is influenced by the high value of water content in bio-oil (53 %). The presence of water content in bio-oil is mainly consisting from lignin-derived materials. From this study, there are shows consist of palm shell mostly has a high percentage of lignin (53.4 %).

The pH at room temperature is 2.5, which is also consistent with the findings of previous studies. The low pH is attributed to the presence of acidic compounds in the aqueous portion of the bio-oil. It has been reported that bio-oils with low pH are very corrosive to aluminum, mild steel and nickel based materials.

Table 5
Physical and chemical properties of bio-oil.

Properties	Value	Properties	Value
Viscosity at 50 °C (cP)	3.2	H (wt %)	8.92
pH	2.5	N (wt %)	0.2
Density at 24 °C (kg/m^3)	1051	O[a] (wt %)	71.40
Water content (wt %)	53	S (wt %)	0.04
C (wt %)	19.48	HHV (MJ/kg)	6.58
		LHV (MJ/kg)	4.63

[a] by difference

3.4.2 Chemical characterization of bio-oil

The FT-IR spectra of the bio oil derived from palm shell is given in Fig. 4, representing functional group compositional analysis of bio-oil. The analysis was carried out on KBr pellet. The O-H stretching vibrations between 3200 and 3400 cm^{-1} of the bio-oils indicate the presence of phenols and alcohols; the C-H stretching vibrations between 2800 and 3000 cm^{-1} and C-H deformation vibrations between 1350 and 1450 cm^{-1} indicates the presence of alkane groups. The C=O stretching vibrations between 1680 and 1750 cm^{-1} is compatible with the presence of ketones, quinones, aldehyde groups, etc. The absorbance peaks between 1500 and 1645 cm^{-1} represent C=C stretching vibrations indicative of alkenes. Furthermore, mono and polycyclic and substituted aromatic groups are indicated by the absorption peaks between 690-900 and 1350-1450 cm^{-1}.

GC-MS analysis was carried out for the oil obtained at pyrolysis temperature of 500 °C, reaction time of 60 min, N_2 flow rate of 2 L/min and particle size of 2 mm to identity type of compounds, in order to establish the possible ways of treating and reusing them and the results are shown in Table 6. The most abundant products, which peak areas around or greater than 2 %, are phenol, 2,6-dimethoxy phenol, trimethylamine and 4-hydroxy benzoic acid. There are a great number of compounds but their peak areas are very low, they are not examined further in this study. Every compound in Table 6 has been classified as oxygenated aromatic (ArO) and non-aromatic (NAr). Oxygenated aromatic compounds such as phenols, acids and aldehyde (furfural) are dominated in bio-oil. The presence of these compounds may be explained by the thermal degradation of oxygenated components of the palm shell. Generally, the phenols and aldehyde are responsible to thermal instability in bio-oil. Furthermore, the highest of peak area was obtained by trimethylamine (47.14 %) a substance mainly responsible for the odor and high of water content in the bio-oil (53 wt %).

Table 6
Identification and quantification of chemical compounds in bio-oil by GC-MS analysis.

Chemical compounds	Molecular formula	Molecular weight (g/mol)	Type of compound	Peak Area (%)
Phenol	C_6H_5OH	94	ArO	13.41
2 –methoxy phenol	$C_7H_8O_2$	124	ArO	1.93
2,6-dimethoxy phenol	$C_8H_{10}O_3$	154	ArO	3.52
4-ethyl -2 methoxy-phenol	$C_9H_{12}O_2$	152	ArO	0.99
3,4-dimethoxy phenol	$C_8H_{10}O_3$	154	ArO	0.60
2 - methyl phenol (o-cresol)	C_7H_8O	108	ArO	0.45
4- methyl phenol (p-cresol)	C_7H_8O	108	ArO	0.60
Furfural	$C_5H_4O_2$	96	ArO	1.88
Trimethylamine	C_3H_9N	59	NAr	47.14
3-methoxy-1,2-Benzenediol	$C_7H_8O_3$	140	ArO	1.90
4-methyl-1,2-Benzenediol	$C_7H_8O_2$	124	ArO	1.24
4-hydroxy benzoic acid	$C_7H_6O_3$	138	ArO	2.84
3-hydroxy-4 methoxy benzoic acid	$C_8H_8O_4$	168	ArO	1.53
4-hydroxy -3-methoxy benzaldehyde	$C_8H_8O_3$	152	ArO	0.6
1,4-dimethoxy benzene	$C_8H_{10}O_2$	138	ArO	0.78
Methylparaben	$C_8H_8O_3$	152	ArO	0.95

The results Table 5 show the oxygenated contents in the bio-oil are obtained during of pyrolysis process. The oxygen content was obtained at high value (71.40 wt.%). The high oxygen content is not attractive for the production of transport fuels because it decreases heating value. In brief, the high oxygen from organic components and water content would need to be removed from the bio-oil by using methods such as hydrotreating–hydrocracking process in order to further raise their heating value and reduce the corrosiveness when they are used as a fuel.

4. Conclusion

The optimum condition processes of bio-oil derived from palm shell were determined using central composite design in RSM. Mathematical model equations were building by using sets of experimental data and ANOVA. The N_2 flow rate was founded as the largest of significant factor on optimization of bio-oil production. The reaction time and interaction between the temperature and particle size are not significant factors in this study. The optimum point ware obtained at temperature of 500 °C with a particle size of $1.7 < dp < 2$ mm, a reaction time of 60 min and a nitrogen flow rate of 2 L/min. Various organic compounds of carbon (C_3, C_5, C_6, C_7, C_8 and C_9) were founded in bio-oil, which is dominated by oxygenated aromatic (ArO). From FT-IR analysis also showed that the bio-oil composition was dominated by oxygenated species. In brief, the bio-oil derived from palm shell is contains a low pH (2.5), high water content (53 wt %) and high oxygen content (71.40 wt %).

Acknowledgments

The authors acknowledge financial support from the Postgraduate Research Fund (No. PS061/2009A), University of Malaya and appreciate the Department of Chemical Engineering for research facilities.

References

[1] Schroeder M, Utilizing the clean development mechanism for the deployment of renewable energies in China, Appl Energy 2009, 86: 237–242.
[2] Quaschning V, Understanding renewable energy systems, Earthscan, UK and USA, 2005.
[3] Eltawil MA, Zhengming Z, Yuan L, A review of renewable energy technologies integrated with desalination systems, Renew Sust Energy Rev 2009, 13: 2245–2262.
[4] Moreira JR, Global biomass energy potential, Mitigat Adapt Strat Glob Change 2006, 11: 313–342.
[5] Easterly JL, Burnham M, Overview of biomass and waste fuel resources for power production, Biomass Bioenergy 1996, 10: 79-92.
[6] Demirbas A, Pehlivan E, Altun T, Potential evolution of Turkish agricultural residues as bio-gas, bio-char and bio-oil sources, Inter J Hydro Energy 2006, 31: 613 – 620.
[7] Landry BM, Green hydrogen: site selection analysis for potential biomass hydrogen production facility in the Texas-Louisiana coastal region. Master Thesis, the Department of Geography and Anthropology, B.A., Louisiana State University, 1996.
[8] Perez LEB, Cortez LAB, Potential for the use of pyrolytic tar from bagasse in industry, Biomass Bioenergy 1997, 12: 363-366.
[9] Blasi CD, Signorelli G, Russo CD, Rea G, Product distribution from pyrolysis of wood and agricultural residues, Ind Eng Chem Res 1999, 38: 2216-2224.
[10] Li AM, Li SQ, Ren Y, Chi Y, Yan JH, Cen KF, Pyrolysis of solid waste in a rotary kiln: influence of final pyrolysis temperature on the pyrolysis products, J Anal Appl Pyrolysis 1999, 50: 149–162.

[11] Balat M, Mechanisms of thermochemical biomass conversion processes. Part 1: reactions of pyrolysis, Energy Sources 2008, 30: 620–635.
[12] Sumathi S, Chai SP, Mohamed AR, Utilization of oil palm as a source of renewable energy in Malaysia, Renew Sust Energy Rev 2008, 12: 2404–2421.
[13] Kawser M, Nash F, Oil palm shell as a source of phenol, J Oil Palm Research 2000, 12: 86-94.
[14] Hussain A, Ani FN, Darus AN, Ahmed Z, Thermogravimetric and thermochemical studies of Malaysian oil palm shell waste, Jurnal Teknologi 2006, 45(A): 43–53.
[15] Guillain M, Fairouz K, Mar SR, Monique F, Jacques L, Attrition-free pyrolysis to produce bio-oil and char, Bioresour Technol 2009, 100: 6069–6075.
[16] Bridgwater T, Review biomass for energy, J Sci Food Agric 2006, 86: 1755–1768.
[17] Asadullah M, Rahman MA, Ali MM, Motin MA, Sultan MB, Alam MR, Rahman MS, Jute stick pyrolysis for bio-oil production in fluidized bed reactor, Bioresour Technol 2008, 99: 44–50.
[18] Bridgwater AV, Biomass fast pyrolysis: review paper, Therm Sci 2004, 8 (No. 2): 21-49.
[19] Czernik S, Bridgwater AV, Overview of applications of biomass fast pyrolysis oil, Energy Fuels 2004, 18: 590-598.
[20] Ozbay N, Varol EA, Uzun BB, Pütün AE, Characterization of bio-oil obtained from pulp pyrolysis, Energy 2008, 33: 1233– 1240.
[21] Islam MR, Tushar MSHK, Haniu H, Production of liquid fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes, J Anal Appl Pyrolysis 2008, 82: 96–109.
[22] Perez MG, Chaala A, Pakdel H, Kretschmer D, Roy C, Characterization of bio-oils in chemical families, Biomass Bioenergy 2007, 31: 222–242.
[23] Mohan D, Pittman CUJr, Steele PH, Pyrolysis of wood/biomass for bio-oil: a critical review. Energy, Fuels 2006, 20: 848-889.
[24] Tsai WT, Lee MK, Chang YM, Fast pyrolysis of rice straw, surgacane bagasse and coconut shell in an induction-heating reactor, J Anal Appl Pyrolysis 2006, 76: 230–237.
[25] Karacan F, Ozden U, Karacan S, Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology, Appl Therm Eng 2007, 27: 1212–1218.
[26] Montgomery DC, Design and analysis of experiments, Fifth ed, Arizona State University, United States of America, 2001.
[27] Zhang Z, Peng J, Qu W, Zhang L, Zhang Z, Li W, Wan R, Regeneration of high-performance activated carbon from spent catalyst: Optimization using response surface methodology, J Taiwan Inst Chem Eng 2009, 40: 541–548.
[28] Mahfud FH, Exploratory studies on fast pyrolysis oil upgrading, PhD Thesis, University of Groningen, 2007.
[29] Box GEP, Wilson KB, On the experimental attainment of optimum conditions, J Roy Stat Soc Ser B Metho 1951, 13: 1-45.
[30] Bridgwater AV, Peacocke GVC, Fast pyrolysis processes for biomass, Renew Sust Energy Rev 2000, 4: 1-73.