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AN OPTIMISATION STUDY FOR CATALYTIC HYDROLYSIS OF OIL PALM SHELL USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Oil palm shell has great potential for conversion to biofuels because of its abundance and favourable composition. Catalytic hydrolysis of oil palm shell was performed using sodium hydroxide as a catalyst. The main objective of the study was to optimise the process parameters for yield percentage of bio-oil from catalytic hydrolysis of palm shell by means of response surface methodology with central composite design. The parameters investigated were reaction temperature (140°C-230°C), reaction time (10-30 min) and NaOH concentration (04 m-1.5 m). The main product (bio-oil) was characterised using Fourier transform infra-red spectroscopy and the bomb calorimeter to find the functional groups and higher heating value of bio-oil. Among all the three parameters, the NaOH concentration was found to be the most influencing factor for liquid yield percentage followed by reaction temperature and time, respectively. The R-squared value of the model was 0.9657 indicating an excellent match for values of liquid production in predicted and experimental results. The optimum conditions found were: temperature at 230°C, time at 10 min, and NaOH concentration at 1.5 M yielded 74.6 wt.% of product. The heating values determined for acetone and water-soluble products at optimum conditions were 22.4 MJ kg^{-1} and 14.3 MJ kg^{-1}.

Keywords: bio-oil production, oil palm shell, hydrolysis, optimisation, higher heating value.

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INTRODUCTION

Contemporary world is dependent on conventional petroleum energy resources (Mazaheri *et al*., 2010b; Tahir and Amin, 2013), which may deplete soon due to their continuous use over the years (Asadieraghi and Wan Daud, 2014; Liu *et al*., 2014; Mofijur *et al*., 2014). At the same time, petroleum energy promotes adverse environmental effects such as climate change, global warming and increase in carbon footprints (Al-Hamamre *et al*., 2014; Mazziotti di Celso *et al*., 2014; Tahir and Amin, 2013). To remain sustainable, the progress and improvement in utilising environmental- friendly energy is necessary. Over the last few decades, biomass has been the main focus as a renewable energy source for future energy (Akhtar and Amin, 2011). It is because of the benefits provided by biomass such as abundance, environmental-friendliness, sustainability and renewability (Balat, 2011; Demirbas, 2001; 2008; 2010; Sequeira *et al*., 2007; Twidell, 1998; Wang *et al*.,

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2010). Moreover, utilisation of biomass can boost the economies of countries containing abundant supply of biomass such as Indonesia, Thailand and Malaysia (Akhtar and Amin, 2011).

Oil palm industry is the main producer of biomass in Malaysia, generating large amount of wastes (Mazaheri *et al.,* 2013; Sumathi *et al.,* 2008). The driving force behind the oil palm biomass research is the usage of abundant quantities of oil palm by-products to produce environmental-friendly fuels (Basiron and Weng, 2004; May *et al.,* 2005). Palm shell, a waste of oil palm industry, was selected as a feed biomass because of its potential to produce bio-fuels and its availability in large quantity (Abnisa *et al.,* 2011; Mubarak *et al.,* 2014). Currently, it is used for production of heat through combustion where it is not completely utilised due to low efficiency of the combustion process. Thus, it is important to utilise the oil palm shell effectively in order to get full benefits; this can be achieved by converting it to bio-fuels. Bio-fuels may be defined as gaseous, liquid or solid fuels produced from biomass resources (Demirbas, 2010; Nigam and Singh, 2011).

A variety of thermo-chemical processes such as pyrolysis, supercritical fluid extraction, liquefaction, gasification, carbonisation, supercritical and subcritical liquefaction (Asadieraghi and Wan Daud, 2014; Balat, 2011; Demirbas, 2010; Parshetti *et al.,* 2014; Reddy *et al.,* 2014) are widely used to produce bio-fuels from biomass resources. At present, many researchers are focusing on hydrolysis in hot compressed water at subcritical conditions. Subcritical water is non-flammable, non-toxic, non-explosive and cheap medium that offers more benefits over any other medium (Zhu *et al.,* 2011). It is appropriate for different degradation and synthesis processes as well (Lu *et al.,* 2009; Mazaheri *et al.,* 2010a). Furthermore, it breaks down the highly rigid structure of lignocellulosic material and reduces them into smaller components (Mazaheri *et al.,* 2013; Sınağ *et al.,* 2010).

Hydrolysis process breaks up complex polymers such as cellulose and hemicellulose into small organic fragments. Some of those fragments dissolve in water and some are released as a gas whereas the residue forms char (Iryani *et al.,* 2013). Hydrolysis in hot compressed water has relatively high rate of reaction with low maintenance cost. Moreover, it is a technology in which there is no corrosion and environmental problems (Yu *et al.,* 2007). Additionally, operational and capital costs are low (Sakaki *et al.,* 1996). Water and oxygen contents in bio-oil are higher, and pH and HHV are lower compared to petroleum fuels. However, it has been investigated for applications in engines, turbines, and boilers (Demirbas, 2004; Zhang *et al.,* 2010).

The main objective of this study was to investigate optimum process parameters for maximum yield percentage of liquid products from hydrolysis of oil palm shell with sodium hydroxide (NaOH) as a catalyst. A central composite design (CCD) in response surface methodology (RSM) was used to investigate optimisation of yield percentage of liquid product. The combined effects of reaction parameters, including reaction temperature, reaction time, and concentration of NaOH as catalyst were investigated. The composition of both water-soluble and acetone-soluble products obtained at optimum conditions was analysed by Fourier transform infra-red (FTIR) spectroscopy and gas chromatography and mass spectroscopy (GC-MS) analysis. The higher heating value (HHV) was also investigated to find its suitability for applications as a fuel.

MATERIALS AND METHODS

Raw Palm Shell

The raw palm shell was collected from Seri Ulu Langat Palm Oil Mill, Dengkil, Selangor, Malaysia. Initially, the raw palm shell was washed several times with tap water and finally with distilled water in order to get rid of dirt and impurities. The washed palm shell was kept in an oven for drying at 105ºC for 24 hr. The dried palm shell was ground and separated into different sizes through sieving. The size distribution is given in *Table 1*. The weight of a particular feed sample for each experiment was prepared based on weight distribution percentage.

Bio-oil Production Using Hydrolysis Process

The hydrolysis experiments were conducted in a high-pressure stainless steel batch reactor. The reactor was made of SS 316 to withstand high temperature and pressure of 500ºC and 100 bars, respectively. A turbine stirrer with 100-1450 rpm was used to mix the reactants uniformly. The prepared feed sample and solution of NaOH with specific molarities were mixed at 0.3 of biomass to water ratio in the high-pressure autoclave batch reactor. The reactor was closed and purged with N_2 gas with purity of 99.99% for 5 min at 3 bars to assure that the reactor

TABLE 1. SIZE DISTRIBUTION OF PALM SHELL USED FOR HYDROLYSIS PROCESS

Particle size (μm)	Weight distribution (%)
x<500	6.1
500<x<1 000	5.5
1 000<x<1 400	4.8
1 400<x<2 000	8.9
2 000<x<2 500	5.9
x>2 500	68.8

was closed tightly. After that, N_2 gas was purged at 10 bars to make sure that the solution remained in liquid phase during reaction and to avoid the vaporisation of water throughout the reaction. Then, the mixture of palm shell and solution of water and NaOH was stirred at 400 rpm for 5 min to mix the solution and the feed completely.

The reactor was heated to the required temperature at a 10ºC increase per minute. The reaction was maintained at preset values of reaction time and temperature. The starting point of the reaction time was when the reactor achieved the preset temperature value. When the reaction duration was completed, both the stirrer and heater were switched off. The reactor was cooled down to 25±1ºC with the help of a cooling coil by circulating water through the joints of the reactor. When the reactor achieved 25±1ºC, the slurry of solid residue and bio-oil were removed from the reactor manually, the gaseous product was insignificant and hence vented. After collecting the slurry from the reactor, it was filtered by using Fioroni filter paper grade 601 to separate water-soluble product and solid residue. Then, the bio-char filtrate was further washed repetitively with distilled water to make certain that all the water-soluble products were eliminated. After removal of water-soluble products, the solid residue was washed with acetone for several times to extract the acetone-soluble products.

The acetone-soluble mixture, water-soluble mixture and solid residue were kept in an oven at 105ºC for 24 hr to ensure complete drying. The products were then taken out of the oven, weighed and further characterised. The schematic diagram for overall process is shown in *Figure 1.*

Yield Percentage

The dried solid residue, acetone-soluble and water-soluble products were weighed and conversion of palm shell was calculated by the following equations.

$$\text{Yield of WS product (wt. \%)} = \left(W_{WS}/W_f\right) \text{x } 100\% \quad (1)$$

$$\text{Yield of AS product (wt. \%)} = \left(W_{AS}/W_f\right) \text{x } 100\% \quad (2)$$

$$\text{Bio-char yield (wt. \%)} = \left(W_{bc}/W_f\right) \text{ x } 100\% \quad (3)$$

$$\text{Total liquid product yield (wt. \%)} = \left((W_{WS} + W_{AS})/W_f\right) \text{x } 100\% \quad (4)$$

where f = feed, WS = water-soluble product and AS = acetone-soluble product, bc = bio-char.

Design of Experiment

RSM with CCD from Design Expert Version 8.0.7.1 (Stat-Ease, Inc., Minneapolis, USA) was used to find out the optimum operational conditions for maximum yield of bio-oil product from hydrolysis of palm shell. RSM is a statistical technique used to find appropriate design of experiment for the process optimisation by using software (Sidik *et al.*, 2013). Twenty experimental tests were suggested and conducted at temperatures (140ºC to 230ºC), time durations (10 to 30 min), and NaOH concentrations (0.4 M to 1.5 M). The RSM comprises of eight factorial points, six axial points, six central replicates and the axial points were located at a distance, α, of 1.682.

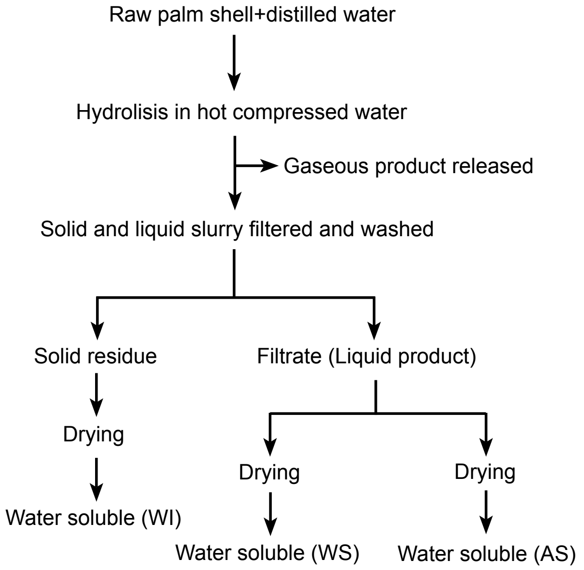


Figure 1. Schematic for experimental procedure of hydrolysis of palm shell for bio-oil production.

Characterisation of Bio-oil Product

The functional groups of both acetone-soluble and water-soluble liquid products obtained at optimum conditions were analysed by FTIR spectroscopy analysis by using model IFS66v/S, Bruker whereas the spectra were recorded by Bruker Optic GmBH 1997-2000 OPUS software, 3.1 Version. The HHV for the bio-oil product was also measured by using bomb calorimeter IKA C2000 basic.

RESULTS AND DISCUSSION

Effect of Operating Parameters

Reaction time, reaction temperature and concentration of NaOH solution were the main parameters investigated in this study. The NaOH concentration was observed to be the most influencing factor in liquid yield from hydrolysis of palm shell due to the highest Fistcher variance ratio ('F' value = 286.7 as shown in *Table* 2) followed by reaction temperature and time respectively. F-value is the ratio of mean square due to regression, divided by the mean square due to error (Deyhimi *et al.*,

TABLE 2. REDUCED MODEL OF ANALYSIS OF VARIANCE (ANOVA) FOR BIO-OIL

Source	Sum of squares	DF	Mean square	F-value	Prob > F	Comments
Quadratic	6 054.32	7	864.90	48.299	< 0.0001	Significant
A	586.86	1	586.86	32.773	< 0.0001	-
B	192.97	1	192.97	10.776	0.0065	-
C	5 134.08	1	5 134.08	286.705	< 0.0001	-
A^2	125.30	1	125.30	6.997	0.0214	-
AB	2.89	1	2.89	0.162	0.6948	-
AC	3.96	1	3.96	0.221	0.6465	-
BC	8.26	1	8.26	0.4614	0.5099	-
Residual	214.89	12	17.91	-	-	-
Lack of fit	167.43	7	23.92	2.520	0.1631	Not significant
Pure error	47.45	5	9.49	-	-	-
Cor total	6 269.21	19	-	-	-	-

Note: R-squared: 0.9657; adjusted R-squared: 0.9457; predicted R-squared: 0.8709; adequate precision: 24.368.

2006). The result was justified by previous research study (Akhtar and Amin, 2011).

Effect of catalyst. Catalyst has a major influence on the yield percentage of liquid product because it has the ability to decompose the feed biomass significantly. In this study, two sets of experiments were conducted: with catalyst and without catalyst to find the effects of catalyst on yield of hydrolysis. The results showed that higher amount of liquid product (48.8 wt. %) was formed in the presence of catalyst (0.95 M NaOH solution) while in the absence of catalyst only 16.5% of liquid yield was obtained as shown in *Figure 2*. It is either because of cracking reaction or reduction reaction was taking place during hydrolysis process in presence of NaOH catalyst (Mazaheri *et al.*, 2013). The large difference in liquid yield percentage confirms the compatibility and advantages of using catalysts in hydrolysis process.

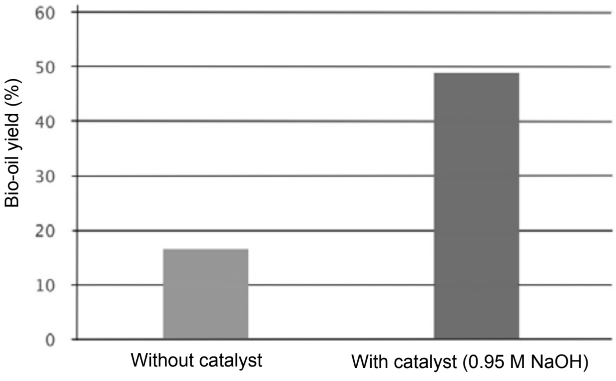


Figure 2. Comparison between bio-oil yield % with and without catalyst.

The yield percentage of liquid bio-oil in hydrolysis process was enhanced significantly in the presence of catalyst. The range of concentration of NaOH used was 0.4 M to 1.5 M. The results showed that liquid yield increased as the concentration of NaOH increased as shown in *Table 3*. It is because that NaOH has a capability to weaken the C-C bond, reducing the activation energy of the complex reaction. Additionally, it has the ability to increase the internal surface area of palm shell feed and endorses separation bonds between lignin and cellulose (Cağlar and Demirbas, 2001). Furthermore, the intermolecular interaction of polymeric chains could be weakened by NaOH catalyst (Sun *et al.*, 2010), resulting in higher degradation of palm shell.

Effect of temperature. Reaction temperature is a main parameter for enhancing liquid yield percentage in hydrolysis process. The selection of reaction temperature (140°C - 230°C) range was based on the findings on the decomposition of lignocellulosic materials. Lignin and hemicellulose are extracted from lignocellulosic materials in HCW up to 230°C as water-soluble fractions (Sasaki *et al.*, 2003) and hydrolysis of cellulose takes place at 230°C (Sanchez *et al.*, 2004). Another study suggests that a typical batch process operating at 230°C yields about 96% hydrolysis of oil and fats (Parekh *et al.*, 2011). Palm shell is a lignocellulosic biomass with the following composition: lignin, 49%; cellulose, 31%; and hemicellulose, 20% (Salema and Ani, 2012).

It was predicted that at higher temperature, the rate of liquid yield production will be higher

TABLE 3. EXPERIMENTAL DESIGN MATRIX OF 'CCD' IN ACTUAL AND CODED UNIT WITH CORRESPONDING RESULTS

Run	Actual level of factors			Coded level of factors			Response
	Temp (°C)	Time (min)	Concentration M (mol litre^{-1})	A	B	C	Liquid product yield wt. (%)
1	109.3	20	0.95	1.68	0	0	27.1
2	185	36.8	0.95	0	1.68	0	32.7
3	230	20	0.95	1.68	0	0	48.8
4	230	10	0.40	1	-1	-1	29.2
5	140	30	0.40	-1	1	-1	17.4
6	140	30	1.50	-1	1	1	54.3
7	185	20	0.95	0	0	0	46.2
8	185	20	0.40	0	0	-1.68	17.4
9	140	10	1.50	-1	-1	1	59.7
10	185	20	0.95	0	0	0	50.9
11	230	30	1.50	1	1	1	70.3
12	230	10	1.50	1	-1	1	73.0
13	185	20	0.95	0	0	0	46.4
14	140	10	0.40	-1	-1	-1	18.4
15	185	20	0.95	0	0	0	42.1
16	185	3.18	0.95	0	1.68	0	58.4
17	185	20	0.95	0	0	0	48.3
18	185	20	1.87	0	0	1.68	78.4
19	185	20	0.95	0	0	0	44.2
20	230	30	0.40	1	1	-1	30.2

(Sidik *et al.,* 2013). However, the rate of liquid yield production may decline after achieving a specific temperature range where liquid product is converted into gaseous product (Akhtar and Amin, 2011). At the same time, the free radical reactions can take place at higher temperature leading towards the char formation. It is because that bonds are sufficiently broken in the structure of palm shell at higher temperatures (Akhtar and Amin, 2011). Similar behaviour was observed in this study as well as shown in *Table 3*. The lower bio-oil yield percentage was observed at 140°C, whereas higher bio-oil yield percentage was observed at higher temperatures (185°C and 230°C).

Effect of reaction time. The effect of reaction time is reverse to that of reaction temperature and catalyst. The result showed that as the interval of reaction increased, yield percentage of liquid product decreased. The results are justified by previous research work (Sahu *et al.,* 2010; Yin and Tan, 2012). Less amount of bio-oil is produced at higher reaction time. This is due to conversion of liquid to gaseous and other residues by secondary and tertiary reactions when the conversion process reaches the saturation point. To avoid the formation of lighter products, some reducing agents should be added. Furthermore, the reaction time has effect upon the composition of products (Akhtar and Amin, 2011). It is recommended that liquid product yield may be enhanced by shorter reaction time (Abnisa *et al.,* 2011).

Interaction between Process Parameters

The interaction of reaction temperature and time at 1.5 M and 0.4 M solution of NaOH is discussed in *Figures 3a* and *3b*, respectively. The same trend in production of liquid yield is observed in both figures. More yield was produced at higher reaction temperature and lower reaction time. Similar trend was observed by Akalın *et al.* (2012). The highest amount of liquid yield was 74.6%, produced by 1.5 M solution of NaOH, 10 min and 230°C; whereas the amount of liquid product obtained at 0.4 M of NaOH, 10 min and 230°C was only 32.38%. These

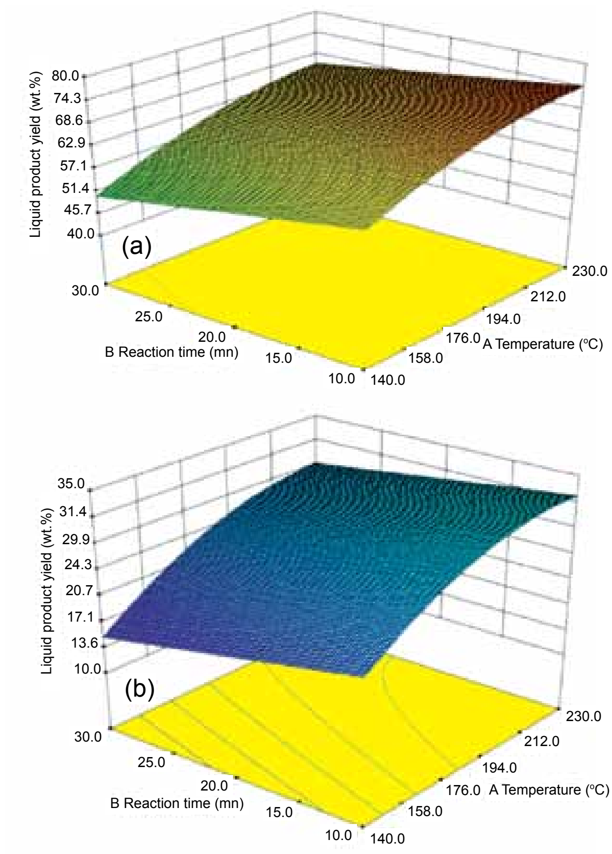


Figure 3. The effect of reaction time and temperature on the bio-oil product at: (a) 1.5 M solution of NaOH and (b) 0.4 M of NaOH solution.

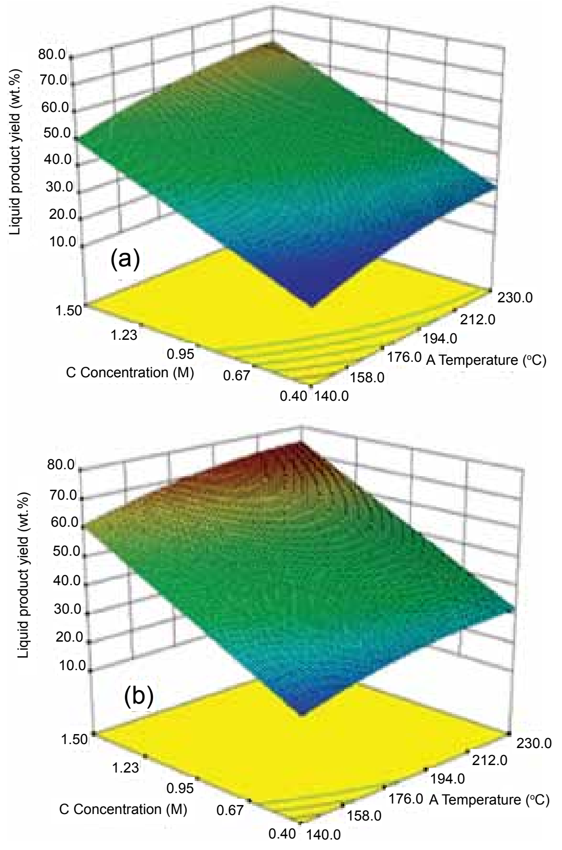


Figure 4. The effect of reaction temperature and concentration of NaOH solution on yield of bio-oil: (a) at 30 min and (b) at 10 min reaction time.

results suggest that NaOH concentration has a high influence on the conversion of oil palm shell into liquid yield. The interaction between reaction temperature and NaOH concentration is given in *Figures 4a* and *4b*. The results showed that the maximum liquid yield was obtained at the conditions of 30 min, 230°C and 1.5 M NaOH concentration. The liquid product obtained was 66.2%. The combined effect of reaction time and concentration of NaOH on the conversion of palm shell to liquid product is shown in *Figures 5a* and *5b*. The maximum amount of liquid yield was 61.2% produced at 1.5 M solution of NaOH, 10 min and 140°C. It was found that the linear effect of each parameter was considered to be significant and there was a slight interaction between process parameters.

Statistical Analysis of Bio-oil Production

The values of experimental design matrix and results obtained are listed in *Table 3*. The minimum and maximum liquid yield percentage obtained at different reaction conditions were 17.4 and 78.4 respectively. The model was evaluated through analysis of variance (ANOVA) to find adequacy of model and the obtained ANOVA results are listed in *Table 4*.

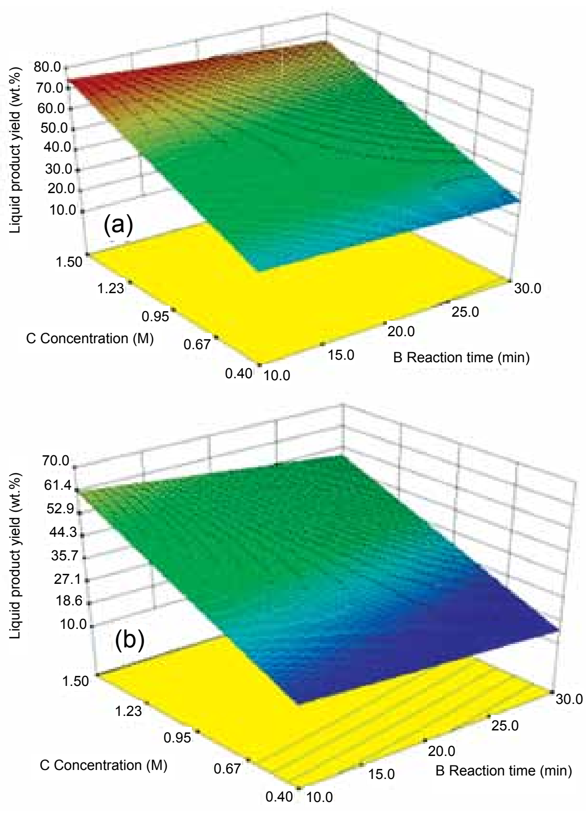


Figure 5. The effect of concentration of NaOH solution and reaction time on bio-oil yield: (a) at 230°C and (b) at 140°C.

TABLE 4. UNREDUCED MODEL OF ANALYSIS OF VARIANCE (ANOVA) FOR LIQUID YIELD

Source	Sum of squares	DF	Mean square	F-value	Prob > F	Comments
Quadratic	6 060.73	9	673.41	32.301	< 0.0001	Significant
A	586.86	1	586.86	28.150	0.0003	-
B	192.97	1	192.97	9.256	0.0124	-
C	5 134.08	1	5 134.08	246.262	< 0.0001	-
A^2	119.84	1	119.84	5.748	0.0375	-
B^2	0.53	1	0.53	0.025	0.8767	-
C^2	5.48	1	5.48	0.263	0.6194	-
AB	2.89	1	2.89	0.139	0.7173	-
AC	3.96	1	3.96	0.190	0.6721	-
BC	8.26	1	8.26	0.396	0.5431	-
Residual	208.48	10	20.85	-	-	-
Lack of fit	161.03	5	32.21	3.393	0.1030	Not significant
Pure error	47.45	5	9.49	-	-	-
Cor total	6 269.21	19	-	-	-	-

Note: R-squared: 0.9667; adjusted R-squared: 0.9368; predicted R-squared: 0.7940; adequate precision: 20.255.

By definition, the significance of every term at a specific level of assurance or confidence may be defined by its p-value (Prob) and F-value (Montgomery, 2008). The term is said to be significant when the p-value is less than 0.05 while in this study the p-values of B^2 and C^2 models are greater than 0.05, which are not found to be significant at confidence level of 95% as shown in the *Table 4*. As the design model was found to be insignificant, we need to perform a model reduction in order to improve overall model significance. Finally, it was decided to eliminate both B^2 and C^2 models to increase the adequacy of the model. AB, BC and AC models cannot be removed because the main purpose was to find the relationship between parameters A (reaction temperature), B (reaction duration) and C (concentration of NaOH solution). *Table 2* gives the new and reduced model after removal both B^2 and C^2 models. *Table 2* shows that the R-squared value for bio-oil yield of new reduced model was 0.9657, indicating excellent results for matching the predicted and experimental liquid product yield. Although the value (0.9657) obtained by the new model is less than the value (0.9667) of the previous R-squared quadratic model, the consideration is based on value of adjusted R-square (Ahmadi *et al.*, 2005) that defines the advancement where the adjusted R-squared value is 0.9457. The number of variables will increase R-squared value.

In this study, adjusted R-squared value was recommended for the reason that it is appropriate to be used in the reduced model where its value rises with elimination of unnecessary terms (Mazaheri *et al.*, 2010b). Moreover, the predicted value of R-squared model has been improved from previous value (0.7940) to new value (0.8709). The difference of predicted R-squared and adjusted R-squared was not greater than 0.2, which shows the reliability of model. *Table 2* shows that the adequate precision value is 24.368, which is higher than 4, indicating that an adequate signal was delivered by this model and noise was insignificant to the process. The model F-value of 48.3 further supported the significance of the model. It was concluded from the higher F-value with a very low p-value (< 0.0001) that the model is sufficient to respond to the tested variables. Additionally, the value of lack of fit is small and insignificant indicating the reliability of model.

The predicted response values of quadratic model and actual response values obtained from experimental results were compared and shown in *Figure 6*. The graph distribution confirms the ability of the model to cover all the range of experiments studied. The equation in terms of coded factors for this study from data analysis of ANOVA is:

$$\text{Yield}\ \% = 46.66+6.5A - 3.76B+19.39C - 2.92A^2 + 0.6AB+0.7AC - 1.02BC \quad (5)$$

where A = reaction temperature (°C), B = reaction interval (min), C = NaOH solution concentration (M), the negative (-) sign indicates the antagonistic effect and positive (+) sign shows the synergistic effect.

Optimisation of Bio-oil Yield Percentage

The main objective of the study of optimisation was to find the finest combination value of the

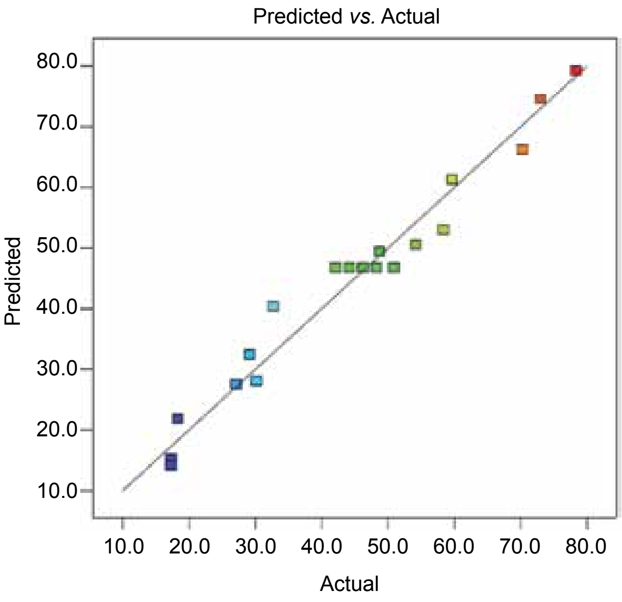


Figure 6. Comparison of predicted and actual yield of bio-oil.

all parameters (reaction temperature, interval of reaction and NaOH concentration) within their particular range in order to maximise the production of bio-oil yield percentage from palm shell. The lower and upper range of reaction parameters and liquid product yield are listed in *Table 5*.

Five possible optimum conditions for higher liquid yield production and their yield percentage are listed in *Table 6*. The higher desirability of predicted solution is 0.93, which confirms the sufficiency of the proposed model to predict the yield percentage of liquid product in proposed hydrolysis process in presence of catalyst. The optimum conditions of first row in *Table 6* were selected to validate the data with experimental results because it showed the highest rate of liquid production. The discrepancy value of 0.3 wt.% was shown by experimental results as compared to predicted value, hence justifying the adequacy of model.

Characterisation of Liquid Product

HHV of both acetone-soluble and water-soluble products obtained at optimum conditions was analysed using the bomb calorimeter. The HHV of water-soluble product was found to be 14.3±0.4 MJ kg^{-1} whereas that of the acetone-soluble product was 22.4±0.7 MJ kg^{-1}. The lower HHV of bio-oil is because of the oxygenated compounds present in it. The quality of bio-oil can be improved by total or partial removal of oxygenated functionalities present (Fisk *et al.*, 2009). Other reason for lower HHV of bio-oil might be due to the higher moisture content present in it. Higher moisture content present in bio-fuels causes ignition problems and reduces the combustion temperature. Furthermore, use of bio-fuels with higher moisture content leads to high fuel usage resulting in generation of large amount of flue gases (Demirbas, 2004; Khan *et al.*, 2009). Biomass and bio-fuels with lower HHV values cause flame stability problems which can be reduced by blending of biomass with coal (Demirbas, 2004). Co-firing with coal is also a possible solution for flame stability problems (Saidur *et al.*, 2011).

Comparing HHV of bio-oil (14.3 MJ kg^{-1} and 22.4 MJ kg^{-1}) from hydrolysis of oil palm shell to HHV of petroleum fuels (44 MJ kg^{-1}), it is advised that fuels produced from hydrolysis process should be upgraded to get similar performance to fossil fuels. Catalytic cracking, steam reforming and hydro-processing are widely applied methods to crude bio-oil to improve its quality (Peng *et al.*, 2009). Duan and Savage (2011) studied catalytic upgrading of crude bio-oil and found that it is an effective upgrading method for crude bio-oils to improve the quality of bio-oils. The heating value of upgraded bio-oil was 43 MJ kg^{-1}, which is comparable to that of petroleum fuels.

The FT-IR spectra of water-soluble and acetone-soluble products is shown in *Figures 7a* and *7b*, respectively. *Figure 7a* shows that a strong and broad peak is observed at 3393 cm^{-1} representing the possible presence of phenolic and alcoholic compounds in liquid product (Fierro *et al.*, 2007). The absorption peak of 1579 cm^{-1} recommends the occurrence of aromatics with C-C stretch (in ring) whereas the peak observed at 1043 cm^{-1} represents the presence of ether group. On the other hand, the peak observed at 664 cm^{-1} reveals that alkynes with C-H blends is present. In *Figure 7b*, the absorbance peaks of 1609 cm^{-1} and 1512 cm^{-1} might confirm the existence of aromatic compounds whereas the peak observed at 1220 cm^{-1} may show the C-O stretching

TABLE 5. LOWER AND UPPER LIMIT OF HYDROLYSIS PARAMETERS FOR OPTIMISATION OF LIQUID YIELD

Type of variable	Temp (°C)	Time (min)	Conc. (M)	Yield (wt. %)
Lower limit	140	10	0.4	17.4
Upper limit	230	30	1.5	78.4

TABLE 6. OPTIMUM CONDITIONS FOR MAXIMUM YIELD PERCENTAGE OF LIQUID PRODUCT

No.	Temperature (°C)	Reaction time (min)	Concentration (M)	Liquid product yield (wt. %)	Desirability
1	230.0	10.0	1.5	74.5631	0.938
2	229.7	10.0	1.5	74.5567	0.938
3	229.2	10.0	1.5	74.5472	0.937
4	228.7	10.0	1.5	74.5366	0.937
5	228.3	10.0	1.5	74.5287	0.937

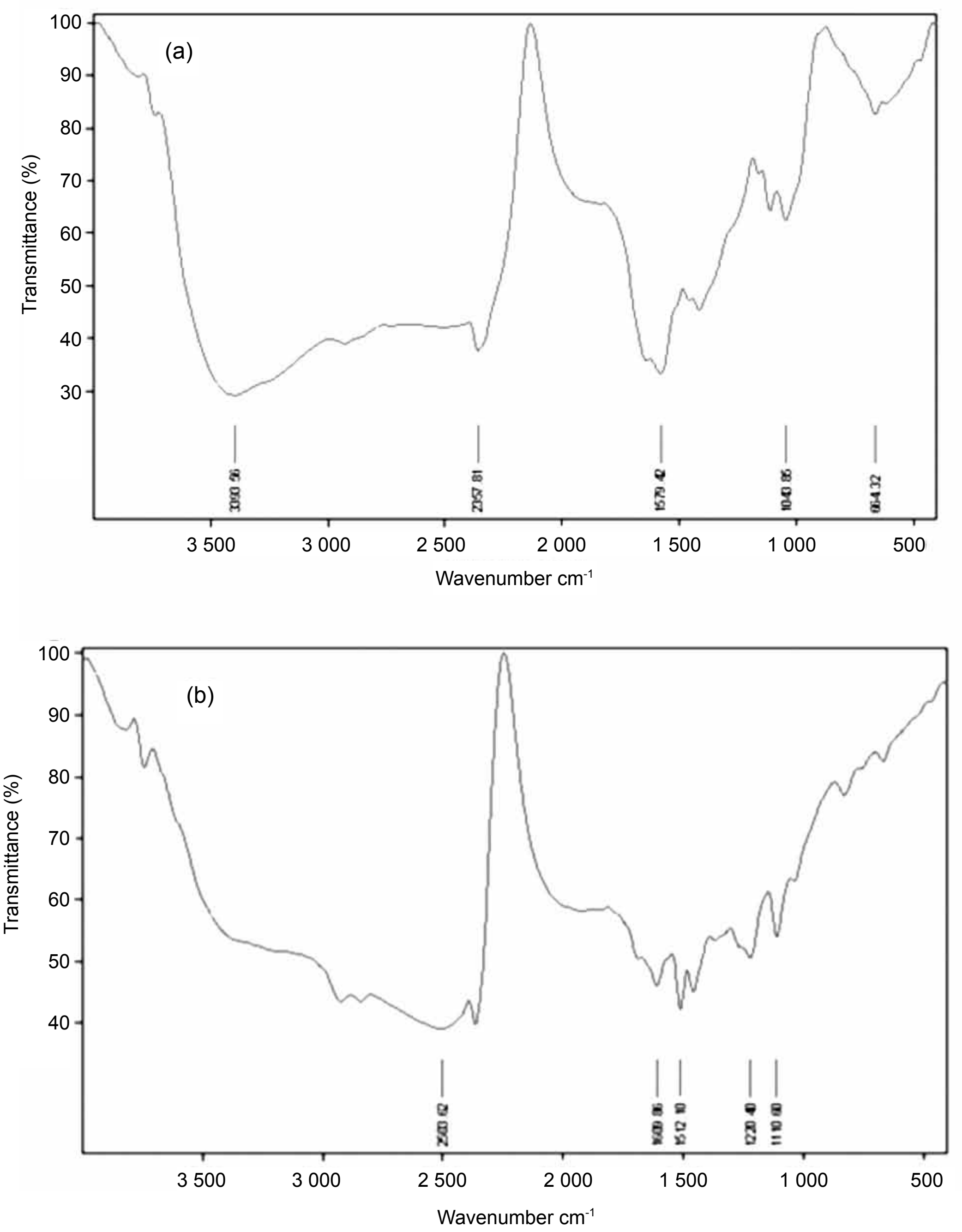
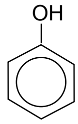
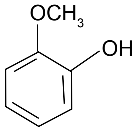
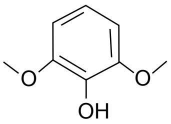


Figure 7. Fourier transform infra-red (FTIR) spectra of: (a) water-soluble bio-oil product and (b) acetone-soluble bio-oil product.

TABLE 7. GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY (GC-MS) ANALYSIS OF BIO-OIL FROM HYDROLYSIS OF PALM SHELL

Peak No.	Retention Time (min)	Relative composition by percentage area (%)	Compound name	Structure	MS-quality (%)
1	1.891	84.72	Phenol		94
2	2.352	6.72	2-methoxyphenol		97
3	3.687	8.56	2,6-dimethoxyphenol		97

vibration, indicating the occurrence of ethers. Besides that, the peak at 1110 cm^{-1} identifies the presence of alcohols.

The GC-MS analysis of bio-oil was carried out on the freshly extracted undried water-soluble bio-oil using Agilent 7890A GC system and Agilent 5975C inert Triple Axis Detector MSD. Agilent HP-5MS column (30 m x 0.250 mm x 0.25 μm) was heated up to an injection inlet temperature of 300°C. NIST08 library software was utilised. From *Table 7*, it was found that the products are phenolic components, which are formed from hydrolysis of organic bonds found in lignin structure. The absence of non-aromatic components implies that bio-oil is not the hydrolysis product of cellulose or hemicellulose. Hence, future study to optimise bio-oil yield should focus on liquefaction of lignin in the presence of catalyst.

CONCLUSION

Palm shell was significantly converted into bio-oil by catalytic hydrolysis process in HCW. It is suggested that HCW accelerates the de-polymerisation of palm shell biomass by hydrolysis process, which occurs when hydronium ions from auto-ionisation of water act as a catalyst. Yield percentage of bio-oil was predicted accurately by mathematical model as it matched well to the experimental consequences for all of the response variables studied. The NaOH solution concentration is the most effective factor for liquid product. The optimum condition was found to be at 1.5 M NaOH concentration, 10 min and 230°C, producing 74.6% of yield product. The heating values determined for acetone and water-soluble products at optimum conditions were 22.4 MJ kg^{-1} and 14.3 MJ kg^{-1} respectively. GC-MS results suggest that the bio-oil contains only phenolic components.

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