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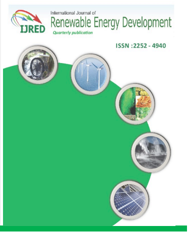

Research Article

Bio-oil Synthesis from Cassava Pulp via Hydrothermal Liquefaction: Effects of Catalysts and Operating Conditions

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ABSTRACT. The influence of catalysts and operating conditions on the conversion and yield of bio-crude oil from CP via the hydrothermal liquefaction technique (HTL) were studied. HTL is commonly used to convert CP to bio-crude oil (BCO). Three independent factors—reaction temperatures (250–350 °C), reaction times (30–90 min), and CP concentrations (5–20 wt.%)—were investigated. Proximate analysis showed that CP comprises 84.61% volatile matter and 13.59% fixed carbon. The ultimate analysis demonstrated that CP has carbon and oxygen levels of 44.86% and 46.91%, respectively. Thermogravimetric analysis showed that CP begins to decompose at temperatures between 250–350 °C. The results show that KOH is the most suitable catalyst because it provides the highest BCO yield when compared to other catalysts under the same operating conditions. We found that the ideal operating conditions for maximizing BCO performance are 250 °C, pressure of 17.0 MPa, 90 min, 5 wt.%. Under these conditions, Fourier transforms infrared analysis showed that the most abundant chemical bonds found in BCO were CH_3-O, CH_3-C, and CH_3. The findings of the CHNS analysis showed that BCO has an H/C ratio of 2.25, similar to that of petroleum and bio-diesel. Results from a gas chromatograph-mass spectrometer indicate that a fatty acid group is the main component of BCO. ©2020. CBIORE-IJRED. All rights reserved

Keywords: Cassava pulp, Hydrothermal liquefaction,Bio—crude oil, Bio-oil synthesis, Response surface methodology

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1. Introduction

The depletion of petroleum has driven the search for renewable sources and proper conversion methods. The thermochemical conversion (TCC) process is used to convert solid biomass into liquid and gaseous products. Furthermore, it has been widely researched (Suzuki *et al.* 1988). The leading TCC technologies include direct combustion, pyrolysis, gasification, hydrothermal liquefaction, and hydrothermal gasification. Gasification is used to convert solid biomass into a synthesis gas comprising hydrogen, carbon dioxide, carbon monoxide, and methane (Basu 2010), whereas liquid bio-oil is the main product of both pyrolysis and hydrothermal liquefaction. The main limitation of pyrolysis, which is appropriate for high-oxygen-content products (Mohan, Pittman, and Steele 2006), is that the feedstock must be dried before the process is initiated (Brown 2011); the drying process requires extra energy and time, leading to low process efficiency. Furthermore, the typical pyrolysis temperature, which is generally in the range of 350–700 °C, is considered to be very high (Babu 2008).

Hydrothermal liquefaction (HTL), a TCC process that converts solid biomass into bio-crude oil (BCO) by dissolving organic compounds in a subcritical solvent, has advantages over the other TCC processes and has been widely investigated for crude BCO synthesis (Tungal and Shende 2014). HTL does not require a drying process to remove water from the feedstock (Yang *et al.* 2014), and the HTL process uses pressurized water as a solvent. This process is, therefore, environmentally friendly (Christensen *et al.* 2014). Recently, an increasing amount of literature has been published on HTL with various types of feedstock. Several high-water-content feedstocks have been investigated and converted to BCO via HTL (Jiang and Savage 2017).

Cassava is a drought-resistant crop capable of being grown in areas with unpredictable rainfall patterns that usually lead to the ineffective cultivation of several other plants. Worldwide, cassava production has recently reached 278 million tons. The top three largest cassava-growing regions in the world are Nigeria, the world's largest producer of cassava with a production of approximately 59.4 million tons; Thailand, with approximately 31.7 million tons; and the Congo, with approximately 30 million tons (FAOSTAT Statistical Database 2019). Approximately 33% of the original weight of cassava can be extracted as starch, and the processed dry weight of the

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roots is typically discarded as solid waste, known as cassava pulp (CP) (Chavalparit and Ongwandee 2009). Dry CP comprises approximately 20–30% starch and 60–70% moisture on a wet weight basis. It also contains small amounts of fiber, protein, and cyanide (Pandey *et al.* 2000). Typically, raw CP has a moisture content of approximately 80% (Charmongkolpradit and Luampon 2017) and contains 32.57% cellulose, 11.64% hemicellulose, 4.35% lignin, and 2.88% ash (Samnuknit, Boontawan, and Boontawan 2017). In Thailand, CP is considered as a waste byproduct from the starch industry and is widely used as animal feed (Srisaikham, Isobe, and Suksombat 2018) and biogas feedstock (Panichnumsin *et al.* 2006). The study on the anaerobic co-digestion of cyanide-containing CP with pig manure. The digester startup, with a loading of 0.5–1 kgVS/m^{3}d, was performed in 60 days. The results showed an average volatile solid removal and a methane yield of 82 and 0.30 m^3/kgVS, respectively; the performance of the digester was stable between 2 and 6 kg VS/m^{3}d (Glanpracha and Annachhatre 2016). Some studies on the utilization of CP as pyrolysis feedstock have also been conducted (Pattiya 2011). Furthermore, a few studies on CP gasification have been performed, and a heating value of 4.5–8.0 MJ/Nm^3 has been obtained (Sornkade, Atong, and Sricharoenchaikul 2015). Thus, a substantially long time (60 days) is required to convert CP to methane via anaerobic digression; in addition, a substantial amount of energy is required to dry CP prior to the gasification or pyrolysis processes. Consequently, for HTL, it is advantageous to use the raw CP directly without expending energy to dry it.

A recent review has shown that HTL has been widely employed using different feedstocks to determine the corresponding conversion feasibilities and oil yields. The BCO composition and yield strongly depend on the type of feedstock and process conditions. A number of earlier studies have concentrated on using locally available materials (Pedersen *et al.* 2015), and some have focused on using aquatic biomass (Chen *et al.* 2012; Minowa *et al.* 1995). According to Minowa et al., the conversion of biomass to bio-oil is dependent on several factors, such as the type of feedstock, reaction temperature, reaction time, feedstock concentration, catalyst type, and type of solvent. Furthermore, HTL experiments have involved the use of both homogenous (Anastasakis and Ross 2011; Biller and Ross 2011; Inoue *et al.* 1994) and heterogeneous catalysts (Matsui *et al.* 1997; Duan and Savage 2011) to increase the bio-oil yield and improve the properties of the yield. In several experiments, Na_2CO_3 was used as a homogeneous catalyst owing to its prior use in the lignocellulosic biomass HTL to improve bio-oil production (Duan and Savage 2011; Shakya *et al.* 2015). Response surface methodology (RSM) has been widely used to reduce the number of experiments when determining the feasibility of the use of a local material as biomass and to optimize the chemical process (Latchubugata *et al.* 2018; Sulaiman *et al.* 2018; Hakalin *et al.* 2018), especially in bio-oil synthesis (Barbanera *et al.* 2018).

To the best of our knowledge, there has been no report in the available literature on the catalytic hydrothermal liquefaction of CP. Therefore, in this study, the effects of different types of catalysts, including the effects of potassium hydroxide (KOH), sodium hydroxide (NaOH), and sulfuric acid (H_2S0_4) on the liquefaction of CP are investigated. The focus of this study was the conversion of CP, which is widely available as a feasible feedstock in Thailand, to BCO via HTL. RSM was used to optimize the experimental conditions, including the reaction temperature, reaction time, and biomass concentration, using a suitable catalyst selected based on experiments. The compositions of the resultant BCO and wastewater from the process were also analyzed. This research will provide essential insights into the HTL of CP. Furthermore, the results of this research provide a basis for future works in this field.

2. Materials and Methods

2.1 Material

The CP used in this study was obtained from a starch factory named Eiam E-sarn Tropica Starch Industry Co., Ltd. in Ubon Ratchathani Province, Thailand. The fresh CP needs to be dried prior to the experiments to investigate the effect of CP concentration. The drying process was performed at 105 °C for 48 h. Then, the dried CP was powdered in a rotary mill with a screen size of 0.25 mm (60 mesh). Deionized water was obtained from Summit Crop., Thailand. KOH, NaOH, and H_2SO_4 were purchased from Chemipan Co., Ltd (Bangkok, Thailand).

2.2 Apparatus and experimental procedure

The HTL experiments were conducted in **a** 100 mL non-stirred batch Ni-alloy reactor with an internal diameter of 25 mm **(**Model**:** CY-100x, Zhengzhou CY Scientific Instrument Co**.**, Ltd**)**. A 3.0 kW electric heater was equipped with an automatic temperature controller to heat the reactor**.** The operating pressure was monitored by the in-built-in pressure sensor, which was also used for monitoring the overpressure release**.** The arrangement of the HTL reactor and its associated instrumentation is shown in Figure 1**.**

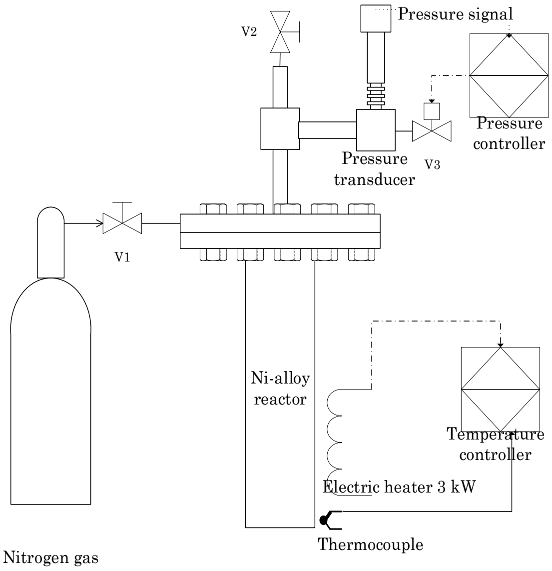

Fig. 1 Schematic of the experimental set up for the production of BCO from CP

First, the dried CP powder was weighed and mixed with the solvent (deionized water) and the catalyst (if needed) at the desired concentration. Next, nitrogen gas was used to purge the reactor for 5 min. and set the initial pressure to 1.0 MPa. Then, the reactor was heated; the heating rate for all experiments was set at 10 °C/min. Thus, the pressure during the reaction was autogenous in the range between 6.0–20 MPa.

After reaching the desired reaction time, the reactor was cooled down rapidly to ambient temperature by quenching it in water, after which the gaseous products were vented freely without any further analysis. Furthermore, dichloromethane (DCM) was then employed to extract bio-oil from solid residue and deposited on the reactor wall. The liquid and solid products were removed from the reactor and separated by filtration. Subsequently, the reactor was washed with 100 mL DCM to rinse out any reaction products that might be stuck on the inside of the reactor; this washing procedure was repeated three times for each tested condition. The aqueous product was separated from the DCM solution using a separatory funnel. Finally, the solid residue from the filtration was dehydrated at 105 °C for 48 h. DCM was removed from the BCO using a rotary evaporator, and all products were weighed to calculate the yield. The separation procedure is shown in Figure 2. The yield was calculated according to Equation 1.

$$\text{Yield}_{\text{oil}} = \left(\frac{W_{\text{oil}}}{W_{\text{B}}}\right) \times 100 \qquad (1)$$

Where

- $\text{Yield}_{\text{oil}}$ is the BCO yield (%)
- W_{B} is the weight of the biomass feedstock (g)
- W_{oil} is the weight of BCO (g).

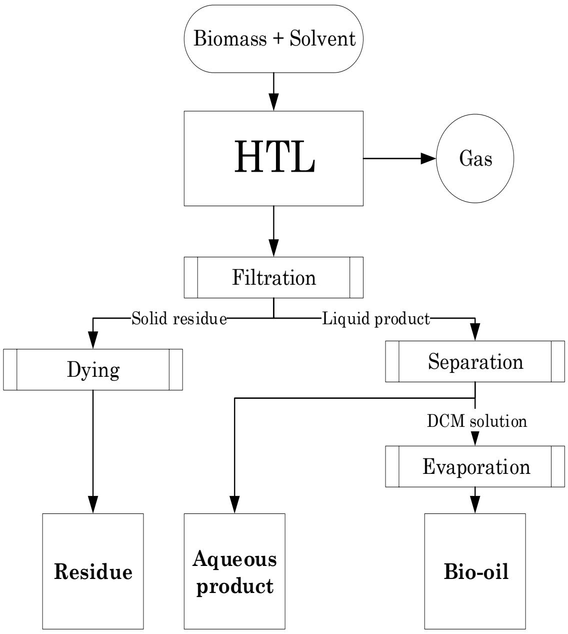

Fig. 2 BCO and solid residue separation procedure diagram

2.3 Feedstock and product analysis

Elementary analysis of the raw material was performed using a CHNS/O analyzer model 2400. In contrast, the proximate analysis of the raw material was performed using the ASTM standard (ASTMD 3173 and ASTMD 3175) methods. Thermogravimetric (TGA) analysis was carried out using the Rigaku Thermo Plus 2 TG-DTA TG8120 model. CP analysis was conducted at a 10 C°/min. heating stage. The analysis was undertaken in a temperature range of 28 °C to 800 °C in the presence of a nitrogen atmosphere. The nitrogen purge gas flow rate was 20 mL/min. Furthermore, 3.70 mg samples of CP were used for the analysis.

BCO was the main focus of this study. Consequently, product characterizations were made only for BCO. A CHNS analyzer, Fourier transform infrared (FTIR) spectrometer, and gas chromatograph-mass spectrometer was utilized to perform several chemical analyzes. Elementary (CHNS) analysis was performed using CHNS-628, obtained from LECO Corporation, and the carbon, hydrogen, nitrogen, and sulfur contents in the BCO samples were determined. FTIR spectroscopy was performed using a Nicolet 6700 FT-IR Spectrometer supplied by Thermo Scientific. Samples were scanned in the range of 450–4000 cm^{-1} with a resolution of 8 cm^{-1}. The BCO composition was determined using gas chromatography-mass spectroscopy (GC–MS) (a Clarus 680 (GC) directly connected to a Clarus SQ 8 C (MS) was used; both were obtained from Perkin Elmer). The injection port and detector were operated at 250 °C with the GC oven heated to a temperature of 45 °C for 10 min. and then to 250 °C at 3 °C/min.

2.4 Experimental setup

Three different catalysts, KOH, NaOH, and H_2SO_4, were used to investigate their influence on the BCO yield. The experiments were carried out using the hydrothermal process described above with a reaction temperature of 350 °C, a reaction time of 60 min, a CP concentration of 10 wt.%, and a catalyst concentration of 1 wt.%. Furthermore, to simulate the experiment, we used three main factors and three levels of central composite design (Design-expert, V8.0, Stat-ease, Inc., USA). After the most suitable catalyst was determined from the first experiment and some single-factor trials, the parameters were set, as shown in Table 1. The reaction temperatures, reaction times, and CP concentrations were varied in the range of 250–350 °C, 30–90 min, and 5 wt.%–20 wt.%.

Table 1
Experimental conditions proposed by CCD for the HTL of cassava pulp

		Coded levels		
Variable	Coded Symbols	-1	0	+1
Reaction temperature (°C)	A	250	300	350
Reaction time (min.)	B	30	60	90
CP concentration (wt.%)	C	5	10	20

3. Results and discussions

3.1 Characterization of feedstock

Ultimate analysis, proximate analysis, and calorific value are generally used to describe properties of solid biomass fuels. The proximate analysis provides a primary means of evaluating the behavior of a solid biomass fuel when it is heated. The moisture content, volatile matter, ash, and fixed carbon content of the feedstock are also considered in proximate analyses. In contrast, the main aim of the ultimate analysis is to specify the elementary composition of the solid fuel material. The calorific value of the fuel is a direct calculation of the chemical energy contained in the fuel. Table 2 indicates that the hydrogen, carbon, and oxygen contents in CP were estimated to be 6.28%, 44.8%, and 46.91%, respectively. Moreover, Table 2 also illustrates that CP is a sulfur-free and low-nitrogen-content feedstock. High levels of carbon and hydrogen have a beneficial impact on High heating value (HHV), whereas high levels of oxygen decrease HHV (Abnisa and Wan Daud 2015). Table 2 indicates that the percentage of volatile matter in CP is 84.61%, whereas the fixed carbon and ash contents in CP are 13.59% and 1.80%, respectively. It is noted that a high content of volatile organic material results in high volatility and reactivity, which consequently favors the production of large quantities of liquid and gas products, whereas the presence of fixed carbon contributes to the formation of char (Jahirul *et al.* 2012). The presence of lower hydrocarbons, a high HHV, volatile matter, and low amounts of sulfur also clearly demonstrates that CP is a reliable and suitable alternative source for the production of liquid fuels.

3.2 Thermogravimetric analysis (TGA) of feedstock

TGA analysis provided an outline of the thermal behavior of the feedstock. From Figure 3, the thermal decomposition of CP started at approximately 50 °C and sharp decomposition occurred between 250 °C–350 °C. Furthermore, over 95% of the CP was decomposed when the temperature reached approximately 540 ° C. The high percentage of mass loss observed from the TGA analysis suggested that 250–350 ° C was an appropriate temperature for optimizing the conversion of CP to a liquid product.

Table 2
Characteristics of CP

Characteristics	Amount
Ultimate analysis (wt.%)	
Hydrogen	6.28
Carbon	44.86
Nitrogen	0.13
Oxygen	46.91
Sulfur	0.02
Proximate analysis (wt.%)	
Volatile matter	84.61
Fixed carbon	13.59
Ash	1.80
High heating value (kJ/kg.)	17,531

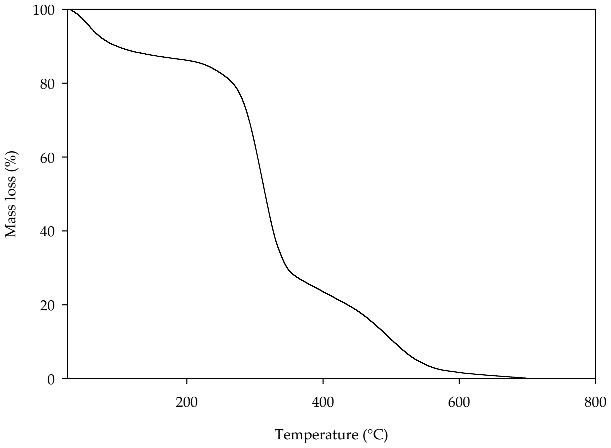

Figure 3. TGA curve for CP

3.3 Effect of catalyst on BCO yield

The yield of BCO, when different catalysts were used at 350 °C, is shown in Figure 4. The type of catalyst significantly affects the BCO yield at 350 °C. As shown in Figure 4, without a catalyst (NON), the hydrothermal process results in a BCO yield of only 7.5%. The maximum BCO yield, which was 17.2%, was achieved using KOH. Based on the results, the catalytic activity could be ranked in the following sequence: KOH > NaOH > NON > H_2SO_4. Similar results were obtained in previous studies (Barbanera et al. 2018; Karagöz *et al.* 2005). Generally, the use of an alkaline catalyst (i.e., KOH or NaOH) favors the formation of oil products but obstructs the formation of char. During subcritical water treatment, the alkaline solution was observed to function as a catalyst in the decomposition of lignocellulosic biomasses.

This catalyst also promoted restricted depolymerization reactions of hemicelluloses and cellulose molecules via the hydrolytic cleavage of the glycosidic bond, leading to the formation of organic acids. The auto-hydrolysis reactions during organic acid generation increased the degradation of cellulose and lignin.

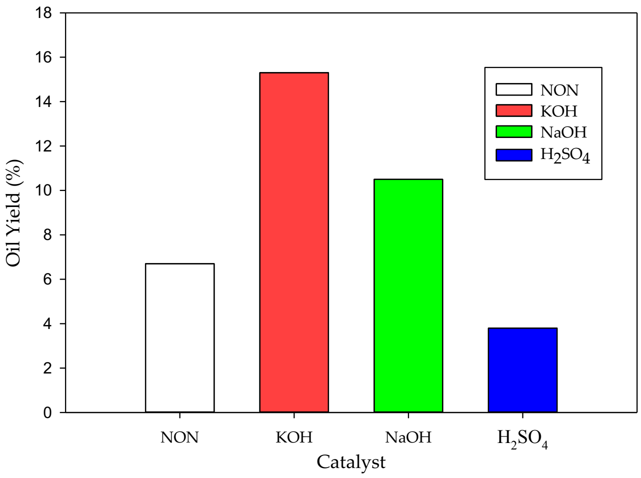

Fig. 4 BCO yield with respect to the use of various catalysts and the absence of catalysts

Table 3
Experimental results of 20 experimental runs

Run	Independent variables			Response variables	
	A: (°C)	B: (min.)	C: (wt.%)	BCO Yield (%)	
				Experimental	Predicted
1	300	60	12.5	6.73	7.41
2	350	30	5.0	10.4	14.35
3	300	90	12.5	4.00	8.20
4	300	30	12.5	8.64	5.72
5	300	60	12.5	6.77	6.85
6	300	60	20.0	9.84	4.79
7	300	60	12.5	6.72	6.85
8	300	60	12.5	6.73	6.85
9	250	60	12.5	5.20	5.70
10	300	60	12.5	6.72	6.85
11	350	60	12.5	11.81	8.24
12	300	60	12.5	6.24	6.85
13	350	30	20.0	9.52	10.82
14	250	90	20.0	9.10	6.96
15	250	90	5.0	23.6	21.93
16	350	90	5.0	6.04	4.03
17	250	30	20.0	0.60	0.95
18	350	90	20.0	5.50	7.36
19	300	60	5.0	7.36	9.79
20	250	30	5.0	9.20	7.26

Table 4
Analysis of variance on BCO yield

Source	SS*	df	MS**	F Value	p-value Prob > F	Remark
Model	6499.87	9	722.21	10.57	0.0005	significant
A-Temperature	1192.64	1	1192.64	17.45	0.0019	significant
B-Time	144.70	1	144.70	2.12	0.1763	
C-Concentration	6.56	1	6.56	0.096	0.7630	
AB	1048.82	1	1048.82	15.35	0.0029	significant
AC	194.05	1	194.05	2.84	0.1229	
BC	954.85	1	954.85	13.97	0.0039	significant
A^2	379.30	1	379.30	5.55	0.0402	significant
B^2	98.22	1	98.22	1.44	0.2582	
C^2	303.54	1	303.54	4.44	0.0613	significant
Residual	683.43	10	68.34			
Lack of Fit	493.70	5	98.74	2.60	0.1587	not significant
Pure Error	189.73	5	37.95			
Cor Total	7183.30	19				

R^2 = 0.9094, adj. R^2 = 0.8192, pred. R = -1.4437, adeq. precision =11.669
* SS is Sum of Square,** MS is Mean square

Alkalis also act as hydrolytic reactants for macromolecular lignin disintegration in the biomass (Barbanera et al. 2018). Therefore, owing to its higher catalytic activity, KOH was selected for use in subsequent optimization experiments.

3.4. Sample workup and analysis

Optimization was performed to determine the optimum conditions for BCO production using the Design Expert 8.0 program. Table 3 shows that the yield and conversion of each experiment are in a range of 0.6–23.6 % and 27.8–96 %, respectively.

Design Expert 8.0 software was used to analyze the results via multiple regression analysis. The results of the BCO yield are listed in Table 4. The statistical analysis showed that the suggested model of conversion was highly significant, possessing a very low P-value (p = 0.0005) and a rather high F-value (F = 10.57). A mathematical model in terms of the operating condition for BCO yield is given in quadratic regression with a base 10 logarithm in Equation 2. The transformation of the response is an important component of any analysis of the data. Transformation is required if the error (residuals) is a function of the magnitude of the response (predicted values). The base 10 logarithm transformation was chosen base on the highest R^2 value.

$$\begin{aligned}\log_{10}(\mathrm{BCO}_{\mathrm{yield}}) = &-0.417 + 5.585\mathrm{x}\,10^{-3}\mathrm{A} \\ &+ 0.049\mathrm{B} - 0.198\mathrm{C} - 1.72\ \mathrm{x}\ 10^{-4}\mathrm{AB} \\ &+ 5.068\ \mathrm{x}\ 10^{-4}\mathrm{AC} + 4.275\ \mathrm{x}\ 10^{-4}\mathrm{BC}\end{aligned} \qquad (2)$$

Where

- BCO_{yield} is BCO yield (wt.%)
- A is reaction temperature(°C)
- B is reaction time (min.)
- C is CP concentration (wt.%), respectively.

3.5 Graphical interpretation of the response surface models

Two variable response surface plot was created for illustrating the effect of the independent variables on BCO yield while the other variable was kept constant. The effect of the operating conditions on the BCO yield was plotted as a contour, as shown in Figures 5. Figure 5 depicts the response surface as a function of the reaction temperature (A) and reaction time (B) with a kept CP concentration (C) of 5 wt.%. As shown in Figure 5, with an increase in temperature, the BCO yield decreases and gradually tends toward constancy. A possible explanation for this result is that a reaction temperature higher than 250 °C causes the BCO to convert to synthesis gas owing to condensation, re-polymerization, or cracking reactions; this can be inferred from the TGA curve, which indicates that the decomposition of CP starts at a low temperature. Figure 6 shows the contour plot as a function of the reaction temperature (A) and CP concentration (C) with a kept reaction time (B) of 90 min. As presented in Figure 6, the BCO yield also decreased rapidly when the CP concentration or reaction temperature increased. These findings suggest that the amount of water used has a substantial effect on the conversion of CP to BCO. The highest BCO yield is 23.6 wt.%, when the reaction temperature, reaction time, and CP concentration are maintained at approximately 250 °C, 90 min, and 5 wt.%, respectively.

In addition, another report states that cellulose and hemicellulose could be converted to BCO at moderately low temperatures (260–300 °C) (Minowa, Zhen, and Ogi 1997). This result matches the observations made in earlier studies (Karagöz *et al.* 2006).

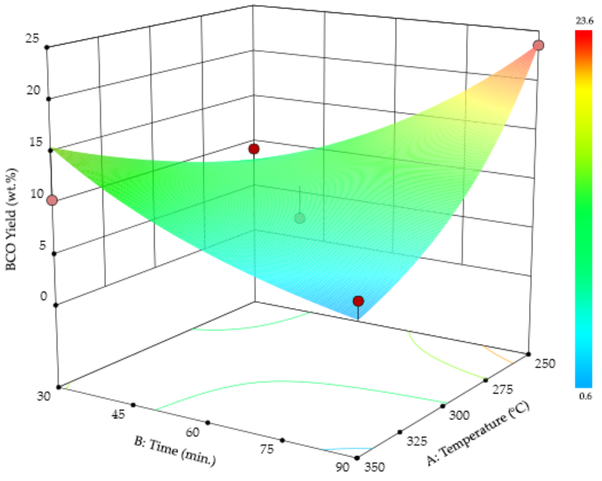

Fig. 5 Response surface plot of BCO yield as a function of reaction temperature and reaction time

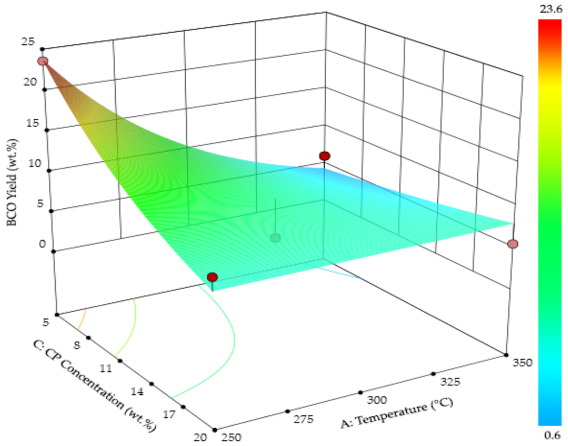

Fig. 6 Response surface plot of BCO yield as a function of reaction temperature and CP concentration

3.6 Optimization of CP HTL

In order to optimize the reaction condition, the partial derivatives of the regression model were equalized to zero, according to A, B, and C, respectively. The result was computed as follows: A=250 °C, B=90 min., and C=5 wt.%. Under this condition, the BCO yield was predicted to be 23.74%. Experimental work on this condition was conducted on the basis of the maximum experimental yield. Throughout this study, the maximum BCO yield at 250 °C, 90 min., and 5 wt.%, of 23.6%, is obtained.

3.7 Characterization of BCO

3.7.1. Fourier transform infrared (FTIR) spectroscopy analysis

The results of the BCO FTIR analysis were consistent with that of GC-characterization. The results of the FTIR analysis showed that the obtained oil had similar chemical bond (function group) characteristics, in which six main peaks were clearly defined during the study. Based on this observation, this section only discusses FTIR analysis on the liquid product obtained at optimum conditions of 250 °C reaction temperature, 90 min reaction time, and 5 wt.% CP concentration. As shown in Figure 7, the FTIR analysis showed that CH_3-O, CH_3-C, and CH_3 were the most extensive chemical bonds detected in the BCO produced from CP. The functional group of CH_2-S was generally detected at the peak of approximately 648 cm^{-1}, which indicated the presence of the methylene group. Additional Methyl group was detected at wave number 1,039 cm^{-1} for CH_3-C and between 1,348–1,400 cm^{-1} for CH_3. The methylene group(-CH_2) was also detected at the wavenumber 1,578 cm^{-1}. The functional group that relates to methyl were also detected at high wavenumber; CH_3-C, and CH_3-O-C were detected at 2,294 cm^{-1} and 3,346 cm^{-1}, respectively.

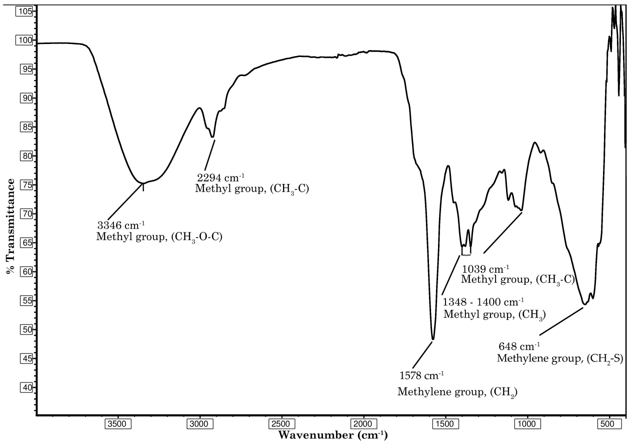

Fig. 7 FTIR spectra for BCO sample obtained from 250 °C, 90 min, and 5 wt.% condition

Table 5
Characteristics of BCO

Element	Value (wt.%)
Carbon	30.38
Hydrogen	5.68
Nitrogen	0.32
Sulfur	0.042

3.7.2 CHN/S analysis

The results of the elemental analysis of BCO obtained through the optimum condition of hydrothermal liquefaction are listed in Table 5. CP consists of large amounts of hydrocarbons, which are potential raw materials for the synthesis of high-quality liquid products (C and H). The elementary analysis showed the BCO has a high carbon and hydrogen contents of 30.38% and 5.61%, by weight, respectively. Calculations indicate that CP has an H/C ratio of 1.67, and when it is converted to BCO, it has an H/C ratio of 2.25. When compared with the H/C ratio rang in Van Krevelen diagram (Van Krevelen 1950), we found that the H/C ratio of BCO is near the bio-diesel and petroleum region. Furthermore, the analysis results show that BCO is a low-sulfur content (less than 0.05%) fuel.

3.7.3. GC/MS analysis

In this experiment, the GC/MS analysis was performed to determine the nature and type of substances present in the oil produced under optimum conditions. Detected compounds were defined by searching the MS library database, and the results are summarized in Table 6. There were a large number of compounds; the BCO produced by HTL using KOH as the catalyst was analyzed to determine the composition. Table 6 indicates that the under-studied condition produced a combined total of 24 types. The main compounds are methyl cis-9-octadecenoate, hexadecanoic acid methyl ester, and octadecanoic acid. As these compounds constitute more than 95% of the BCO fraction, a fatty acid is the main component of the BCO. The fatty acid methyl ester is formed via the formal condensation of the oleic acid carboxy group with methanol. A similar result was also reported by Loubna (Loubna *et al.* 2016).

Table 6
GC-MS result of BCO from CP

No.	Compound	Peak area (%)	RT* (min)
1	Cyclopentanone	1.09	3.178
2	Acetic acid, butyl ester	0.33	3.654
3	2-Cyclopenten-1-one	0.42	4.229
4	Cyclopentanone, 3-methyl	0.76	4.339
5	Cyclopentanone, 3-methyl	0.48	4.599
6	Acetic acid, 3-methylbutyl ester	3.68	5.604
7	3-methyl-1,2-cyclopentanedione	1.97	6.855
8	2-Cyclopenten-1-one, 2,3-dimethyl-	0.57	1.44
9	2-Cyclopenten-1-one, 2,3-dimethyl-	0.52	1.29
10	Furan, 2-acetyl-5-methyl-	1.00	2.52
11	Phenol, 4-ethyl-	1.71	4.30
12	Oxalic acid, allyl butyl ester	0.40	1.00
13	Phenol, 4-ethyl-2-methoxy-	0.99	2.49
14	2,5-Dihydroxypropiophenone	0.20	0.49
15	Decane, 2,5,9-trimethyl-	0.57	1.43
16	Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters	0.90	2.27
17	hexadecane	0.56	1.41
18	octanotic acid, 2-methyl	0.39	0.99
19	decane, 2,9-dimethyl	0.35	0.88
20	methyl undercanate	0.71	1.77
21	buten-2-ol	0.22	0.54
22	Hexadecanoic acid, methyl ester	34.23	85.86
23	Methyl cis-9-octadecenoate	39.87	100.00
24	Octadecanoic acid, methyl ester	8.07	20.25

4. Conclusions

In this study, the hydrothermal liquefaction technique successfully converted CP to BCO. The experiment was conducted in a nitrogen atmosphere autoclave batch reactor. The experimental result has shown that KOH was identified as the most suitable catalyst, which provided the highest BCO yield under the same operating condition as that of other catalysts. The operating condition of 250°C, the pressure of 17.0 MPa, 90 min., and 5 wt.% were identified to be the most desirable and appropriate to optimize the BCO yield. This condition gave the maximum BCO yield of 23.74 %.

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