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Optimization of hydrothermal liquefaction of palm kernel shell and consideration of supercritical carbon dioxide mediation effect

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ABSTRACT

The production of bio-oil from palm kernel shell (PKS) via subcritical and supercritical hydrothermal liquefaction was investigated. In order to maximize the bio-oil yield, design of experiment and optimization was performed using Response Surface Methodology (RSM) with central composite rotatable design (CCRD). Four factors which included temperature (330–390 °C), pressure (25–35 MPa), reaction time (60–120 min) and biomass-to-water ratio (0.20-0.50 wt/wt) were investigated. The regression model developed gave accurate predictions and fitted well with the experimental results, with coefficient of determination R^2 of 0.9109. Based on the model, the optimum liquefaction condition was predicted to be at temperature of 390 °C, pressure of 25 MPa, reaction time of 60 min and biomass-to-water ratio of 0.20 with a prediction yield of 15.48 wt%. This condition was validated by experimental runs which produced an average of 14.44 wt% bio-oil yield. Then, the mediation effect of supercritical CO_2 on bio-oil yield was studied. Hydrothermal liquefaction of PKS was performed at the optimum condition in the presence of supercritical CO_2. The effect of supercritical CO_2 was found to be insignificant at higher liquefaction temperature of 390 °C but it was significant at lower liquefaction temperature of 300 °C, producing bio-oil yield of 11.35 wt%. GC/MS analysis showed that phenolic compounds constituted the major portion of the bio-oils, while ketones, aromatic compounds and carboxylic acid were also detected.

1. Introduction

Recently, increased attention has been given to the valorization of alternative renewable energy sources in response to the gradual depletion of fossil fuels and the mitigation of environmental pollution. Among various renewable energy sources, biomass utilization has garnered great interest of research studies due to the abundance of multiple types of biomass worldwide, which provides many prospects for conversion to biofuels (for heat and power generation) and value-added chemicals, thus lessening our heavy dependence on crude-based resources [1]. The utilization of lignocellulosic biomass as feedstocks in the production of second generation biofuels and biochemicals is favorable compared to other types of biomass as they do not compete with food production and they are the most abundant biomass available [2,3].

In particular, pyrolysis and liquefaction are the two major thermochemical treatments that produce bio-oil (or biocrude) from biomass in a single step [4]. Compared to pyrolysis, liquefaction has been pointed out to be a promising technology for bio-oil production as this process does not require pre-drying of biomass feedstocks and it operates at a relatively lower temperature (about 250–400 °C), hence energy conserving and cost effective [5]. Hydrothermal liquefaction (HTL) is especially preferred in the conversion of biomass to bio-oil as water is not only used as a medium in which the reaction occurs, but it also serves as a reactant, solvent and catalyst for the process [6]. Besides, water is a green and environmentally benign solvent, non-toxic, nonflammable, cheap and more importantly, it is naturally present in biomass [7]. At subcritical and supercritical conditions, water possesses superior properties to aid dissolution and degradation of biomass, such

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Table 1
Characteristics of PKS.

Structural content	
Hemicellulose (%)	24.1
Cellulose (%)	24.6
Lignin (%)	45.4
Ultimate analysis (dry basis)	
C (%)	50.31
H (%)	6.05
N (%)	0.46
S (%)	0.00
O* (%)	43.18
Proximate analysis (dry basis)	
Volatile matter (%)	80.71
Fixed carbon (%)	14.68
Ash content* (%)	4.61
Higher heating value (MJ/kg)	18.5

*calculated by difference.

as low dielectric constant (ε = 5–20) [8], weak hydrogen bond (η = 0.05–0.40) [9], high diffusivity (of the order of 10^{-3} cm^2/s) [10] and reactivity [11].

Supercritical carbon dioxide is another green solvent that is commonly used in many industrial processes due to its low critical parameters (31.1 °C, 73.8 bar), low cost, non-toxicity, easy separation and recovery [12]. The mediation effect of carbon dioxide in subcritical and supercritical water processes has been explored by several researchers. Addition of supercritical carbon dioxide into subcritical and supercritical water promotes in situ formation and dissociation of carbonic acid from the reaction of water and carbon dioxide at elevated temperature and pressure, which served as a natural catalyst in hydrothermal processes [13]. Hence the use of harmful mineral acids (such as hydrochloric acid and sulfuric acid) as catalyst can be avoided. Ruenngam et al. performed the hydrothermal hydrolysis of hesperidin aided with supercritical CO_2 which served as a catalyst for hydrothermal degradation process [14]. Effect of supercritical carbon dioxide on the rate of liquefaction of cellulose is also reported by Brunner [11]. Gosselink et al. studied the depolymerization of lignin in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals [15]. Singh et al. investigated the product distribution of bio-oils resulted from hydrothermal liquefaction of rice straw in the presence of supercritical carbon dioxide [16].

In Malaysia, oil palm (*Elaeis guianensis*) wastes are lignocellulosic biomass that are produced in tremendous amounts (~86.9 Mt/year as in 2010) as a result of large scale plantations [17]. These wastes have been used as feedstocks for generation of fuels in the form of solid, liquid and gas [18–21]. In this study, the optimization of bio-oil production from palm kernel shell (PKS) is investigated systematically using response surface methodology (RSM). The use of RSM reduces the number of experiments required to generate statistically validated results [22]. RSM has been widely applied on the optimization studies of various industrial and complex processes [20]. A few studies on the optimization of reaction parameters of liquefaction of biomass to bio-oil using RSM have been reported. Mazaheri et al. optimized five parameters (temperature, residence time, particle size, specimen loading and catalyst loading) in the catalytic liquefaction of oil palm fruit press fiber using subcritical water [23]. Gan and Yuan performed optimization study on the hydrothermal liquefaction of corncob involving four factors [2]. Guo et al. [24] and Liu et al. [25] optimized three reaction parameters for microwave-assisted liquefaction of macroalgae, *Sargassum polycystum C. Agardh* and *Ulva prolifera*, respectively.

Table 2
Central composite rotatable design matrix and actual response of bio-oil yield.

Run	Coded Variables				Bio-oil yield (wt%)
	Temperature (°C) X_1	Pressure (MPa) X_2	Reaction time (min) X_3	Biomass:water ratio (wt/wt) X_4	
1	(−1) 330	(+1) 35	(+1) 120	(+1) 0.50	3.89
2	(−1) 330	(−1) 25	(+1) 120	(+1) 0.50	3.55
3	(−1) 330	(+1) 35	(+1) 120	(−1) 0.20	6.12
4	(0) 360	(0) 30	(0) 90	(+α) 0.65	5.45
5	(0) 360	(-α) 20	(0) 90	(0) 0.35	11.44
6	(0) 360	(0) 30	(+α) 150	(0) 0.35	7.66
7	(0) 360	(+α) 40	(0) 90	(0) 0.35	5.89
8	(+1) 390	(−1) 25	(+1) 120	(−1) 0.20	13.10
9	(−1) 330	(+1) 35	(−1) 60	(+1) 0.50	3.59
10	(0) 360	(0) 30	(0) 90	(0) 0.35	7.83
11	(0) 360	(0) 30	(0) 90	(0) 0.35	7.25
12	(−1) 330	(−1) 25	(−1) 60	(+1) 0.50	3.44
13	(+1) 390	(−1) 25	(−1) 60	(−1) 0.20	15.55
14	(+1) 390	(+1) 35	(+1) 120	(+1) 0.50	8.48
15	(-α) 300	(0) 30	(0) 90	(0) 0.35	3.00
16	(+α) 420	(0) 30	(0) 90	(0) 0.35	12.76
17	(0) 360	(0) 30	(0) 90	(0) 0.35	9.88
18	(−1) 330	(+1) 35	(−1) 60	(−1) 0.20	6.33
19	(+1) 390	(+1) 35	(−1) 60	(+1) 0.50	10.05
20	(+1) 390	(+1) 35	(+1) 120	(−1) 0.20	14.73
21	(0) 360	(0) 30	(-α) 30	(0) 0.35	7.00
22	(0) 360	(0) 30	(0) 90	(0) 0.35	7.97
23	(0) 360	(0) 30	(0) 90	(0) 0.35	7.80
24	(−1) 330	(−1) 25	(−1) 60	(−1) 0.20	6.48
25	(0) 360	(0) 30	(0) 90	(-α) 0.05	13.74
26	(+1) 390	(+1) 35	(−1) 60	(−1) 0.20	15.85
27	(+1) 390	(−1) 25	(−1) 60	(+1) 0.50	14.06
28	(0) 360	(0) 30	(0) 90	(0) 0.35	7.05
29	(+1) 390	(−1) 25	(+1) 120	(+1) 0.50	13.45
30	(−1) 330	(−1) 25	(+1) 120	(−1) 0.20	6.59

The primary objectives of the present study are to optimize the parameters for hydrothermal liquefaction of PKS for bio-oil production and to study the interactions of the process variables using RSM with central composite rotatable design (CCRD). Then, mediation effect of supercritical CO_2 in the hydrothermal liquefaction of PKS for bio-oil production was investigated and reported.

2. Materials and methods

2.1. Feedstock pre-treatment and characterization

Raw palm kernel shells (PKS) supplied by FELCRA Nasaruddin Oil Palm Mill, Bota, Perak, Malaysia were first washed with water thoroughly to remove sand particles and impurities. They were then dried in the oven at 80 °C for 48 h, grinded with a FRITSCH Cutting Mill and sieved to a particle size of < 710 μm before being used as feedstock in all the experiments.

The feedstock was characterized for their structural contents, higher heating value (HHV), ultimate and proximate analysis. PKS was sent to Forest Research Institute Malaysia (FRIM) for analysis on the structural contents which consist of hemicelluloses, cellulose and lignin. Ultimate analysis was performed using a LECO 932 CHNS Analyzer while proximate analysis was performed following procedures and method reported in the literature [26]. HHV was estimated based on the result of proximate analysis and correlation reported in the literature [26]. The characteristics of PKS are shown in Table 1.