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Optimizing the conditions for hydrothermal liquefaction of barley straw for bio-crude oil production using response surface methodology

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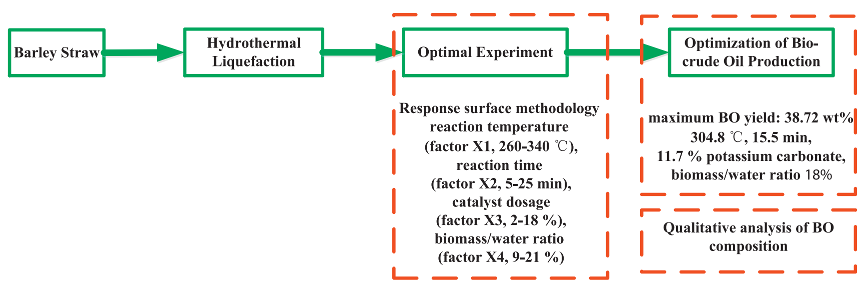
HIGHLIGHTS

- Response surface methodology was utilized for optimization of HTL of barley straw.
- Temperature, catalyst dosage and biomass/water ratio had significant influence.
- A maximum BO yield of 38.72 wt% was obtained at optimum operating conditions.
- The experimental data are in good agreement with predicted values.
- Qualitative analysis of the BO product composition

GRAPHICAL ABSTRACT



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ABSTRACT

The present paper examines the conversion of barley straw to bio-crude oil (BO) via hydrothermal liquefaction. Response surface methodology based on central composite design was utilized to optimize the conditions of four independent variables including reaction temperature (factor X_1, 260–340 °C), reaction time (factor X_2, 5–25 min), catalyst dosage (factor X_3, 2–18%) and biomass/water ratio (factor X_4, 9–21%) for BO yield. It was found that reaction temperature, catalyst dosage and biomass/water ratio had more remarkable influence than reaction time on BO yield by analysis of variance. The predicted BO yield by the second order polynomial model was in good agreement with experimental results. A maximum BO yield of 38.72 wt% was obtained at 304.8 °C, 15.5 min, 11.7% potassium carbonate as catalyst and 18% biomass (based on water). GC/MS analysis revealed that the major BO components were phenols and their derivatives, acids, aromatic hydrocarbon, ketones, N-contained compounds and alcohols, which makes it a promising material in the applications of either bio-fuel or as a phenol substitute in bio-phenolic resins.

1. Introduction

Nowadays, issues related to energy security, climate change mitigation, and sustainable development enhanced the overall utilization of renewable energy, which is the world's fast-growing energy source. Among them, bioenergy is the largest renewable energy source worldwide, the total supply of which accounted for 10.3% of the global energy

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supply in 2014 (Kummamuru, 2017). Barley straw, an agricultural residue, represents one of the largest lignocellulosic biomass in Denmark. In 2016, almost 2.17 million tons of barley straw was produced. Unfortunately, 34.12% was left on the field and has not been utilized yet. Only 22.56% was converted to energy through combustion and power generation etc., 29.74% was used as fodder (Denmark, 2014). Therefore, there is an urgency to find suitable solutions to convert remaining straw. One of the effective methods for crops straw utilization is biofuel production through fast pyrolysis (Das and Sarmah, 2015; Hsieh et al., 2015; Xu et al., 2017) and hydrothermal liquefaction (HTL) (Gollakota et al., 2018; Midgett et al., 2012; Younas et al., 2017), which is anticipated to provide 27% of global transportation fuels by 2050. Most importantly, it is estimated that for OECD countries 2.1 Gton of carbon dioxide in the atmosphere can be reduced every year according to such use of biofuels (IEA, 2012).

HTL has gained significant interest in recent years, and has been demonstrated to be competitive with thermochemical routes such as pyrolysis for converting biomass into biofuels due to feedstock flexibility, high energy and resource efficiency of the process and high output product quality (Patel et al., 2016; Suárez-Iglesias et al., 2017). Feedstock flexibility and process efficiency are important factors for the sustainable operation of new biofuel technologies. HTL converts diversified biomass in hot compressed liquid (water/organic solvent) into four different products: bio-crude oil (BO) with higher heating values up to 38 MJ/kg (Toor et al., 2011), aqueous phase containing multiple organic compounds which can be reused in this process (Déniel et al., 2016; Hu et al., 2017; Zhu et al., 2015) or utilized for cultivation of microalgae afterwards (Hu et al., 2017), solid residues used for heating or as soil amendment (Yu et al., 2017), as well as gaseous products mainly including CO_2 and H_2. In particular, BO a promising alternative energy source with high energy density, has the potential to be used as a liquid fuel in boilers, engines and turbines or chemical feedstocks (Xiu and Shahbazi, 2012). Therefore, HTL of barley straw with emphasis on BO production was conducted in this study.

Production of BO from barley straw using HTL technology has been investigated in our previous studies (Zhu et al., 2015; Zhu et al., 2015; Zhu et al., 2014) where the single-factor experiments were conducted, and product yield and properties were studied as well. It showed that the maximum BO yield of 34.9 wt% was achieved at 300 °C, 10 wt% K_2CO_3 as catalyst, biomass to water ratio of 15% under a fixed retention time of 15 min. In addition, low temperature (<320 °C) and with the addition of K_2CO_3 favor BO yield. Indeed, reaction time and biomass/water ratio influence the product distribution and properties as well (Toor et al., 2011). A number of independent factors were discussed, while the interactions between them were not considered. Therefore the conditions for production of BO from barley straw using HTL technology need to be further optimized.

Response surface methodology (RSM) is an optimal design method for regression model, which is a rapid technique for development, improvement and optimizing process, based on the data from experiments conducted at a set of input variables at multiple levels. It allows established the significance of each parameter and the significant interaction between parameters. Compared with other experimental design methods, it has the advantage of optimizing nonlinear systems, providing a more precise computation of the main and interaction effects through regression fitting (Diamond, 1981; Eriksson et al., 1996; Hassan et al., 2017). Thus, this method has already been used to optimize process parameters during thermal conversion of different biomass, such as algae, cotton stalk, palm kernel shell etc. (Chan et al., 2018; Li et al., 2017; Liu et al., 2013). Li et al. (Li et al., 2017) optimized three operating parameters (microwave power, reaction temperature and time) during microwave-assisted pyrolysis. Chan et al. (Chan et al., 2018) performed optimization study on HTL of palm kernel shell using RSM with central composite rotation design (CCRD) involving four factors (temperature, pressure, reaction time and biomass to water ratio). Similarly, the CCRD was also employed by Liu et al. (Liu et al., 2013) to find the optimization conditions for HTL of macroalgae by three variables (temperature, catalyst and solvent/biomass ratio). Yet, little research has been conducted to investigate the bio-crude oil production from barley straw through HTL process.

This paper moves further to a more systematic study on the effects of four experimental variables (reaction temperature, reaction time, catalyst dosage, biomass/water mass ratio) and their interactions on bio-crude oil production based on the RSM experiment. A central composite design (CCD) experimental design was employed and the response surface model was analyzed. The validity of model was confirmed by conducting numerical examples. Finally, detailed analysis of chemical properties of BO was performed, to provide a guidance for the design of utilization of barley straw and the further pilot and industrial scale practice.

Table 1
Elemental composition of raw biomass.

Biomass	Elemental content (wt% dry basis)					HHV (MJ/kg)	Ash content (wt%)	Water content (wt%)
	C	H	N	S	O[a]			
Barley straw	44.66	6.34	0.46	0.57	47.97	17.38	4.26	6.21

[a] By difference.

2. Materials and methods

2.1. Materials and characterization

The barley straw was obtained from Denmark. Before experiment, it was grounded into small particles having a size of <1.0 mm and then dried overnight at 105 °C for 24 h. The elemental composition is shown in Table 1. The elemental analysis (CHNS) of biomass was performed with a 2400 Series II CHNS/O Element analyzer (PerkinElmer, USA). The water content was determined by calculating the weight loss before and after drying at 105 °C in an oven for at least 12 h. Higher heating values (HHVs) were measured using C2000 basic Calorimeter (IKA, German).

Typically, barley straw in Demark consists of cellulose, hemicellulose and lignin with the content of 46%, 23%, and 15%, respectively (Sander, 1997).

The reagent grade acetone was used as rinsing solvent for product separation, which was purchased from Sigma-Aldrich and used as received. Potassium carbonate (K_2CO_3) was purchased from Sigma-Aldrich and used as catalyst.

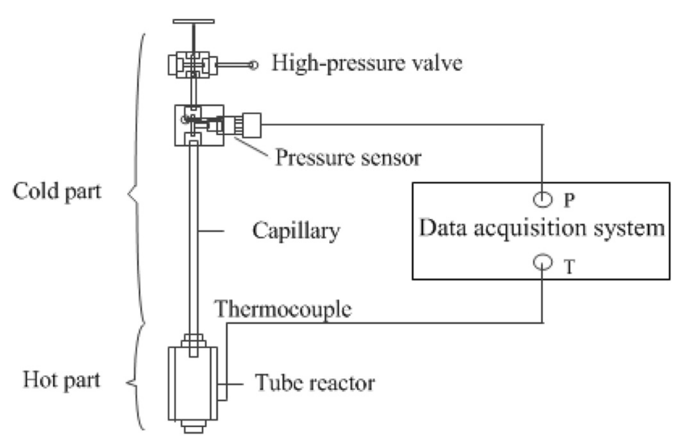

Fig. 1. Schematic diagram of micro reactor.