Study on the optimization of co-HTC conditions towards maximized fuel performance and lower sulfur contents of ROM coal/lignocellulosic biomass hydrochars

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Abstract. Run-of-mine (ROM) coal and rice straw (RS) were upgraded by co-hydrothermal processing in oxidative acid/alkaline solvents. Optimization of co-HTC parameters was performed using the Taguchi method to investigate optimal conditions for the production of hydrochars with desired fuel properties. Based on calculations of S/N ratios, hydrochar with the best combustibility can be produced using the lowest reaction temperature (180 °C) and residence time (4 h), hence minimizing energy consumption. Hydrochars produced using optimal conditions for the best EY and PA indices had very high HHV values of 29.4 and 29.0 MJkg⁻¹, respectively. In addition, ROM coal/RS hydrochars prepared using optimal conditions were characterized by lower sulfur contents (0.00 - 0.41 wt.%) and considerably low post-combustion ash contents.

1. Introduction
With the continued growth in global industrialization, there is a need for the development of eco-friendly fuels to meet the rising demand for energy. In China, energy generated from coal accounted for ~56% of the country’s electricity consumption [1]. However, due to concerns over CO₂ emissions from the combustion of coal [2], the co-firing of coal and biomass has been proposed to reduce emissions in coal-fired plants. ROM coal is coal obtained directly from the mine without processing. Thus, both ROM coal and untreated biomass are accompanied by undesirable properties which can lead to poor performance and the release of pollutants during combustion. Specifically, ROM coal is usually characterized by considerably high sulfur contents and some mineral impurities [3, 4], while biomass on the other hand is accompanied by high moisture contents and very low energy density [5]. Hence, there is a need for the upgrading of both ROM coal and biomass to meet the various specifications required for the intended use. As co-firing remained the most promising approach for the utilization of biomass in coal-fired power plants, co-hydrothermal carbonization seemed suitable for the processing of ROM coal and biomass into solid fuel with desirable properties. Co-hydrothermal processing of biomass and coal can be beneficial in increasing the energy contents of biomass and coal, while reducing undesirable impurities such as the amount of incombustible minerals, sulfur contents and oxygen containing volatile contents [6].
In the present study, ROM coal and rice straw (RS) were facilely upgraded by co-hydrothermal processing in oxidative chemical (acid/alkaline) solvents to enhance the removal of sulfur contents. Due to the complexity of factors affecting the properties of product hydrochars, optimization of co-HTC parameters was performed using the Taguchi method to investigate optimal conditions for the production of hydrochars with desired fuel properties. Four performance indicators were selected, namely fuel ratio, energy yield, proximate analysis index and the combustibility index. Signal-to-noise (S/N) ratios were evaluated from recorded characterizations data to determine optimal conditions of the co-HTC process. Characterization of the product hydrochars was performed by elemental analysis, proximate analysis and thermogravimetric analysis. The determination of optimal parameters for the co-HTC of ROM coal and rice straw can be beneficial in maximizing the desired hydrochar properties while minimizing experimental costs.

2. Experimental methods

2.1. Materials
ROM coal used in this work was obtained from a local coal mine in Shanxi Province, China. A lab scale high-speed rotary pulverizer was used to crush the coal into a particle size of about 60 mesh. Rice straw powder (~100 mesh) was purchased directly from an online store and recorded as RS. Chemical reagents such as acetic acid, potassium hydroxide, hydrogen peroxide and methanol were purchased from Sinopharm Chemical Reagent Co. Ltd. in Shanghai, China. Prior to the experiments, ROM coal and RS were blended using three different weight ratios (7:3, 5:5, 3:7).

2.2. Taguchi optimization
Optimization of process conditions was performed by application of the Taguchi L9 (3^4) orthogonal array, to systematically examine the optimal conditions for the production of hydrochar with the desired properties. Reaction temperature, residence time, blending ratio and solvent type were selected as key process parameters for the HTC experiments. A total of three reaction solvents were used in the HTC experiments, including distilled water, acid and alkaline solutions.

The Taguchi method (Genichi and Wu 1980) is one of the most sensible optimization design methods used to minimize the sets of experiments to be implemented in a comparative study, given a number of process parameters (or factors) and levels [7]. The L9 orthogonal array applied in the present work has a total of 4 factors at 3 levels. The array can effectively compress the number of experimental runs from 81 to 9 only, thereby reducing the overall experimental costs and required time.

2.3. Hydrothermal carbonization
Co-hydrothermal carbonization of ROM coal and rice straw was performed in a non-stirred 100 mL Teflon-lined stainless steel reactor. The acid solvent was prepared by mixing 50 mL of acetic acid (pH 3.0) and 10 mL of 30 % hydrogen peroxide solution, while the base solvent was prepared by adding 50 mL KOH solution (pH 10.0) to 10 mL methanol. For each experiment, 10±0.01 g of ROM coal +RS blends and 60ml of the reaction solvent were loaded into an autoclave. Following thorough mixing, the autoclave was transferred into a vacuum heating oven and heated at the specific temperature (180/220/260 °C) for a specified residence period (4/6/8 h). After heating, the autoclave was cooled to room temperature, and the solid product was filtered, washed in distilled water, and finally dried at 105 °C for 24 h. The dried hydrochars were denoted as HC-X (with X representing the order of HTC experiments), and stored in a desiccator for further characterizations.

2.4. Hydrochar characterization
Characterization of ROM coal/RS hydrochars was performed by elemental analysis (Perkin Elmer 2400 Series II, Germany), proximate analysis (ASTM) and thermogravimetric analysis (STA 2500 Regulus, Germany). Higher heating values of the ROM coal, RS and the product hydrochars were evaluated using the results of elemental analysis as shown in Eq. (1).
HHV(MJ/kg) = 0.3491C + 1.1783H + 0.1005S − 0.1034O − 0.0151N − 0.0211Ash \hspace{1cm} (1)

where C, H, O and N represent the weight percentages of carbon, hydrogen, oxygen and nitrogen in the sample. The energy yield (EY) was calculated using Eq. (2).

\[
EY(\%) = HY \times \frac{HHV_{hc}}{HHV_{fs}} \hspace{1cm} (2)
\]

where HY refers to the weight ratio of the product hydrochar to the initial ROM coal+RS feedstock, HHV_{hc} and HHV_{fs} represent the high heating values of the product hydrochar and the feedstock used, respectively. Fuel ratio and the PA index were calculated using Eq. (3) and Eq.(4) below:

\[
FR = \frac{FC}{VM} \hspace{1cm} (3)
\]

\[
PA = \frac{FC \times VM}{M \times Ash} \hspace{1cm} (4)
\]

where FC, VM and M represent weight percentages of fixed carbon, volatile matter and moisture, respectively. The combustion characteristic index (S) was calculated using to determine the overall fuel combustion performance. S is defined as the measure or ease of a fuel to burn in the presence of air and constant heating, and it is evaluated by integrating the combustion properties as shown in Eq. (5):

\[
S = \frac{(dW/dt)_{max} \times (dW/dt)_{mean}}{T_i \times T_f} \hspace{1cm} (5)
\]

where \(T_i\) and \(T_f\) are the ignition and burnout temperatures, respectively, and \((dW/dt)_{max}\) and \((dW/dt)_{mean}\) refer to the maximum and mean values of the derivative thermogravimetric (DTG) curve, respectively.

Sulfur removal (SR) efficiency was determined using the sulfur contents of raw feedstocks and the product hydrochars as follows:

\[
SR Efficiency (\%) = \frac{(S_{fs}-S_{hc})}{S_{fs}} \times 100 \hspace{1cm} (6)
\]

where \(S_{fs}\) and \(S_{hc}\) represent the weight percentage of sulfur contents in the initial feedstocks and the corresponding hydrochars, respectively. \(S_{fs}\) is calculated based on the proportions of ROM coal and RS in the sample.

3. Results and Discussions

3.1. Fuel characteristics of hydrochars in L9 array

Physicochemical characteristics of untreated ROM coal and rice straw are shown in Table 1. According to the results, ROM coal/rice straw hydrochars prepared in the optimization experiments (HC-1 to HC-9) showed improved fuel performance based on the selected indicators. In Table 2, the FR values of ROM coal+RS hydrochars in the first temperature level (HC-1 to 3) were between 0.62 – 1.21, while those of HC-4 to HC-6 ranged between 1.13 – 1.70, and those of HC-7 to HC-9 were between 1.43 – 2.06, indicating that increasing the HTC temperature led to the reduction of volatiles. Thus, based on the FR index it was expected for the optimal conditions to include the highest temperature (260°C). Similarly, the PA indices of hydrochars increased with temperature, with the HC-8 sample having the largest value of 116.2, and HC-3 showing the lowest value of 31.1. The PA index integrates all parameters of proximate analysis, with FC and VM in the numerator, and moisture and ash in the denominator.

| Feedstock | Proximate analysis (wt%) | Elemental analysis (wt%) |
|-----------|--------------------------|-------------------------|
|           | M  | VM | FC | Ash | FR | C  | H  | O  | N  | S  | HHV |
| ROM Coal  | 2.51 | 29.7 | 47.5 | 20.3 | 1.6 | 63.8 | 3.94 | 11.8 | 0.97 | 2.16 | 25.4 |
Table 2. Fuel performances and S/N values of the produced ROM coal/rice straw hydrochars.

| Sample | Performance indicators | S/N values |
|--------|-------------------------|------------|
|        | FR | PA | EY (%) | S (×10⁻¹²) | S/N_FR | S/N_PA | S/N_EY | S/N_S |
| HC-1   | 1.21 | 51.8 | 62.6 | 8.13 | 1.68 | 34.28 | 36.70 | -221.80 |
| HC-2   | 1.16 | 63.6 | 69.0 | 6.04 | 1.27 | 36.07 | 37.67 | -224.38 |
| HC-3   | 0.62 | 31.1 | 59.9 | 7.68 | -4.16 | 29.86 | 36.00 | -222.29 |
| HC-4   | 1.13 | 76.9 | 61.1 | 5.62 | 1.07 | 37.72 | 36.27 | -225.01 |
| HC-5   | 1.23 | 87.6 | 63.0 | 5.43 | 1.82 | 38.85 | 37.17 | -225.30 |
| HC-6   | 1.70 | 44.6 | 74.3 | 6.57 | 4.59 | 32.98 | 38.12 | -223.65 |
| HC-7   | 1.43 | 74.9 | 55.1 | 5.76 | 3.10 | 37.49 | 35.98 | -224.80 |
| HC-8   | 2.06 | 116.2 | 81.2 | 4.29 | 6.29 | 41.30 | 39.12 | -227.35 |
| HC-9   | 1.80 | 57.4 | 67.3 | 4.73 | 4.96 | 35.18 | 37.47 | -226.51 |
| Average | 1.37 | 67.1 | 65.9 | 6.03 | 2.29 | 35.97 | 37.17 | -224.57 |

Energy yield was calculated to evaluate the energy recovery efficiency of hydrochars. HC-8 and HC-9 had high energy yields of 81.2 % and 67.3 %, respectively, owing to the larger heating values. Therefore, based on these findings, as part of the optimal conditions of producing hydrochars with a high energy recovery efficiency, the reaction temperature of 260 °C would be appropriate. Calculated values of the S index indicated that hydrochars in the first level of temperature (HC-1 to 3) had the best combustibility, with HC-1 having an S index of 8.13×10⁻¹², highly owing to the larger content of volatiles. Thus, it was obvious that the optimal temperature for producing hydrochar with the best S index was 180 °C. Based on the selected performance indicators, signal-to-noise (S/N) ratios were evaluated according to Eq. (7):

\[
S/N = -10\log [1/y^2] \tag{7}
\]

where y represents the value of the considered performance indicator. A higher value of S/N indicated desirable performance. Hence, the S/N values presented on Table 2 supported the results discussed above. Further analysis of the S/N ratios of each variable was conducted to evaluate the optimal conditions based on the selected performance indicators. As it can be seen in Table 3, optimal conditions based on the FR and EY indices were similar.

Table 3. Optimal conditions for the co-HTC of ROM coal and rice straw based on the different performance indices.

| Index | Temperature (°C) | Time (h) | Blending ratio | Solution |
|-------|------------------|----------|----------------|----------|
| FR    | 260              | 6        | 7:3            | Base     |
| PA    | 260              | 6        | 5:5            | Acid     |
| EY    | 260              | 6        | 7:3            | Base     |
| S     | 180              | 4        | 3:7            | Base     |

3.2. Validation of optimality
In order to confirm the optimality of the conditions listed in Table 3, a minimal set of co-HTC experiments was performed. Since optimal conditions for best FR and EY were similar, only one sample was prepared to represent both indicators (HC-FR&EY). As observed in Figure 1a, HC-FR&EY had the highest FC contents (61.0 wt%), followed by HC-PA (55.2 wt%), while HC-S had the lowest (34.9 wt%). All three hydrochars had considerably low moisture contents (0.86 – 2.20 wt.%), indicating the enhanced hydrophobicity of HTC derived chars. In Figure 2b, HC-FR&EY and HC-PA had very high HHV contents of 29.4 and 29.3 MJkg⁻¹, respectively. Obviously due to the lower carbonization temperature, HC-S had the lowest HHV content (21.6 MJkg⁻¹).
In Table 4, fuel performances of the best hydrochars are presented. Notably, the FR value of HC-FR&EY was 2.41, which was much higher compared to all the hydrochars prepared in the initial L9 array. The actual PA index of HC-PA was 117.5, which was also higher than the PA indices of all hydrochars prepared in the L9 array. The calculated S index value of HC-S was $41.62 \times 10^{-12}$, which was considerably higher than S indices of the initial hydrochars. In addition, the standard deviation between theoretical and experimental S/N\textsubscript{opt} values of the best hydrochars ranged between 0.09 to 6.69 %, hence confirming the optimality of the co-HTC conditions.

![Figure 1. a) Proximate analysis and b) elemental analysis of ROM/RS hydrochar samples produced using optimal conditions of the performance indicators.](image)

![Table 4. Performances and S/N ratios of ROM coal/RS hydrochars produced using optimal conditions.](image)

| Performance Indicator | HC-FR\textsuperscript{a} | HC-PA | HC-EY\textsuperscript{a} | HC-S |
|-----------------------|--------------------------|-------|--------------------------|------|
| FR                    | 2.41                     | 1.71  | 2.41                     | 0.65 |
| PA                    | 138.4                    | 117.5 | 138.4                    | 90.0 |
| EY (%)                | 76.2                     | 77.6  | 76.2                     | 63.5 |
| S ($\times 10^{12}$)  | 14.59                    | 16.89 | 14.59                    | 41.62|
| Theoretical S/N\textsubscript{opt} | 8.21                     | 41.43 | 38.42                    | -221.4|
| Experimental S/N\textsubscript{opt} | 7.66                     | 41.39 | 37.64                    | -207.6|
| Deviation (%)         | 6.69                     | 0.09  | 2.03                     | 6.23 |

\textsuperscript{a}: HC-FR and HC-EY refer to the same hydrochar sample (HC-FR&EY).

Based on the results shown in Figure 2a, ROM coal/RS hydrochars produced using optimal conditions for the best performance had very low sulfur contents (0.00 – 0.41 wt.%) compared to untreated ROM coal. HC-FR&EY and HC-PA showed remarkable sulfur removal efficiencies (>99%). In Figure 2b, it can be observed that the actual measured post-combustion ash contents were significantly

![Figure 2. a) Sulphur contents and b) post-combustion ash contents of the blended ROM coal/RS hydrochars prepared using optimal conditions.](image)
lower than the corresponding theoretical values, indicating that the co-HTC approach presented in this study can be effective in reducing residual ash contents.

4. Conclusions
In this work, optimal conditions for the co-hydrothermal carbonization of ROM coal and rice straw in oxidative chemical solvents were determined through the optimization of process parameters using the Taguchi method. The determination of optimal conditions was essential to maximize the desired hydrochar properties. The findings of our work revealed that hydrochars with the best fuel ratio and energy yield can be produced under similar co-HTC conditions, and hydrochar with the best combustibility index can be produced with the lowest co-HTC temperature and time. In addition, hydrochars prepared using the optimal conditions not only showed superior fuel properties, but also had very low sulfur contents and reduced post-combustion ash contents. Therefore, this novel study proved that ROM coal and RS can be effectively upgraded by combining co-hydrothermal carbonization with oxidative chemical solvents.

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