A novel catalyst prepared from black liquor for biodiesel conversion: An optimization study

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Abstract. This paper reports a new approach for high-value conversion of black liquor into biochar to catalyse the transesterification for biodiesel conversion using waste fry oil (WFO). The central composite design (CCD) and response surface methodology (RSM) were employed to optimize the biodiesel preparation using the catalyst prepared from the paper pulp black liquor precipitated biochar. The transesterification reaction is catalysed by oxidative functional groups (enolic) on the surface of biochar. The effect of alkaline loading in biochar, carbonization temperature, the methanol to oil ratio and the catalyst loading were systematically investigated. The optimal biodiesel conversion conditions were achieved as the following: 27wt\% (alkaline loading in biochar), 585 °C (carbonization temperature), 7 (methanol to oil ratio) and 5.5 wt\% (catalyst loading), with the biodiesel yield of 95%.

Keywords: Biochar; Black Liquor; Biodiesel; Optimization

1. Introduction
The biodiesel has been regarded as one of the complementary renewable resources for mitigating CO\textsubscript{2} emissions from fossil-derived fuels [1-6]. The biodiesel is produced by the transesterification of oils (vegetable or animal fats) with alcohol such as methanol, ethanol [7]. The process is achieved by the addition of heterogeneous acid/base catalyst through batch or continuous operations with various catalytic performance ranging from 80\% to 99\% [8,9]. The black liquor (BL) is the by-product from the pulping process and it has attracted great attention for years in both industry and academy [2, 10]. Recently, we have developed a novel approach in precipitation of BL from KOH/NH\textsubscript{4}OH paper pulping using corn straw or cotton fibre to prepare highly active biochar\textsuperscript{11,12} In order to further expand its range of application, the prepared biochar was used to catalyse the biodiesel synthesis. Therefore, in this work, we aim to perform statistical analysis and to identify the best conditions for biodiesel synthesis using the prepared biochar derived from paper pulp black liquor.

2. Experimental

2.1. Characterization of catalyst and biodiesel
Morphological analysis was performed by using a JSM-7001F+INCA X-MAX Field emission electron microscope (Joel, Japan).
The elementary analysis was conducted by X-ray Fluorescence Spectrometry (Rigaku Japan).

Gas chromatograph GC were obtained on a Shimadzu 2014 GC equipped with a flame ionized detector (FID) for conversion analysis. The operational conditions were kept at the recommended conditions for analysing liquid hydrocarbons such as olefin and paraffin.

ICP-OES analysis was performed to ensure the bulk analysis aligning with mapping analysis (Perkin Elmer, USA) [13].

2.2. Experimental design and statistical analysis
The pretreated wasted frying oil was used in this work. The biodiesel synthesis was performed at 70 °C with a duration of 4 hours. The detailed biodiesel preparation with quantitative characterization (correlation and integration for GC and 1H-NMR results), calculation of conversion can be found from previous reports in detail [7, 14].

In this work, the CCD with four critical preparation parameters affecting biodiesel preparation were investigated. The detailed experimental designs were listed in Table 1.

| Independent variable | Symbol | -β  | -α  | 0  | α  | β  |
|----------------------|--------|-----|-----|----|----|----|
| Alkaline loading/%   | X₁     | 15  | 20  | 25 | 30 | 35 |
| Temperature/°C       | X₂     | 500 | 550 | 600| 650| 700|
| MTO /-               | X₃     | 6   | 7   | 8  | 9  | 10 |
| Loading/-            | X₄     | 3   | 4   | 5  | 6  | 7  |

The polynomial quadratic expression with the correlations of the preparation parameters is shown as the following:

\[ Y_i = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i,j=1,i\neq j}^{4} b_{ij} X_i X_j \]

where \( Y_i \) refers to the calculated predictions, \( b_i \) and \( b_{ij} \) are constants obtained polynomial expressions regressions, and \( X_i, X_j \) are the investigated experimental variables. The catalyst used in this work was prepared by our recently reported approach of preparing biochar from cotton pulping black liquor via hydrothermal treatment [15]. The obtained potassium carbonate-rich biochar was further carbonized at 585 °C, which was then optimized from the CCD experiment for maximizing the biodiesel conversion, in the tubular furnace with inert \( \text{N}_2 \) as an atmosphere.

3. Discussions

3.1. Characterization of catalyst
SEM morphology and EDX results of the biochar that prepared at the optimal conditions (with the maximum biodiesel conversion) were shown in Figure 1. It is clear that the prepared biochar possessed good pore formation after carbonization treatment. According to the EDX elemental mapping characterization, the carbon, and potassium elements were found to be dominant in the biochar matrix. This result also agrees well with the bulk chemical analysis from XRF characterization shown in Table 2. The XRD and FTIR characterization of the prepared biochar obtained from the optimal condition is shown in Figure 2a and 2b, respectively.
Table 2. XRF analysis of the biochar, where LOI* refers to the loss of ignition.

| Composite/- | Percentage/ % |
|-------------|--------------|
| K$_2$O      | 25.1         |
| MgO         | 6.6          |
| SiO$_2$     | 3.1          |
| Al$_2$O$_3$ | 1.2          |
| Fe$_2$O$_3$ | 0.1          |
| LOI*        | 6%           |

Figure 1. SEM and EDX analysis of the prepared biochar under optimal condition, where a is SEM image of the sample, b1 and b2 are EDX elementary mapping of the sample for carbon (C) and potassium (K) elements.

The broad and small scattering peaks were observed for the amorphous graphite, which centred at 22° and 45° representing 010 and 020 planes of graphite [16, 17] (Figure 2a). The sharp peaks centred at 28° and 33° indicating the existences of K$_2$O in the biochar matrix [18].

The FTIR spectrum is shown in Figure 2b, where the prepared biochar remained in rich surface functional groups. The out of plane vibration spectra, which is referring to C-O vibration in the surface groups such as aromatic, and alcoholic compounds, is observed in 1604 cm$^{-1}$. The valence vibration spectra of C-H group is also observed. The fingerprint peaks representing K-O out of plane vibration at the wavenumber of 1204, 822 and 750 cm$^{-1}$ are observed [13, 19, 20]. The XRD and FTIR result also agrees well with the SEM and EDX mapping result. The biochar together with the impregnation with the basic material is expected to catalyse the transesterification reaction between WFO and methanol.
3.2. Optimization of biodiesel preparation

The RSM was used to optimize the system, the results were plot in Figure 3. The ANOVA analysis results (with only those parameters significant to the response) were shown and listed in Table 3. Of those four preparation parameters, the combination of carbonization temperature with alkaline loading and carbonization temperature with methanol to oil ratio were found to be the most significant to the response (biodiesel conversion), which also reflects from Table 3 form F value. In addition, the entire constructed model was found to be significant to the four operational parameters (with F<0.0001) [21, 22]. Among the binary operational parameters, both X1X2 and X2X3 were found to be significant, with F value reaching 0.02 and 0.003, respectively. Through experimental data regressions, the constants in the quadratic correlations are solved with the operational parameters (carbonization temperature X1, alkaline loading/% X2, methanol to oil ratio/% X3, and catalyst loading/% X4) being shown as the following.

| Table 3. ANOVA with standard errors of r² 0.94, Adjust r² 0.94, Predicted r² 0.93, adequate precision 15. |
|---------------------------------|-----|-----------------|
| **Source**                     | **DF** | **Prob>F**      |
| Model                          | 14   | <0.0001         |
| X1                             | 1    | <0.0001         |
| X2                             | 1    | 0.0231          |
| X3                             | 1    | 0.0001          |
| X1X2                           | 1    | 0.0239          |
| X2X3                           | 1    | 0.0030          |
| X1²                            | 1    | <0.0001         |
| X2²                            | 1    | <0.0001         |
| X3²                            | 1    | <0.0001         |
| Lack of fit                    | 9    | 0.0201          |
With setting for biodiesel maximum conversion as the optimization goal, the optimal conditions were achieved through RSM as the following: 27 wt% (impregnation ratio on the weight basis between $K_2CO_3$ and biochar), 585 ºC (carbonization temperature), 7 (MTO) and 5.5 wt% (loading), with the biodiesel conversion being 95%. A further validation experiment performed according to the obtained optimal conditions was conducted. The achieved biodiesel conversion is around 92%, which is around -3% uncertainties. This possible reason could be attributed to the experimental uncertainties over the entire preparation process. This yield is comparable to the literature reports of the yield range (85-98%) [23].

4. Conclusions
In this work, the catalyst prepared by hydrothermal precipitation from paper pulp black liquor biochar used for biodiesel conversion was systematically investigated. The four critical parameters, which are impregnation ratio in biochar, carbonization temperature, MTO and catalyst loading, were optimized using CCD and RSM. The optimal conditions were achieved as 27 wt% (alkaline loading in biochar), 585 ºC (carbonization temperature), 7 (MTO) and 5.5 wt% (catalyst loading), with the biodiesel conversion achieved at 95%.

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