

Adsorptive removal of odour substances and NO and catalytic esterification using empty fruit bunch derived biochar

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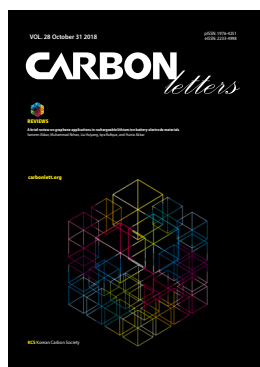
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Abstract

Empty fruit bunch (EFB) char was used to remove NO_x and odorous substances. The physicochemical properties of the EFB chars were altered by steam or KOH treatments. The Brunauer-Emmett-Teller surface area and porosity were measured to determine the properties of the modified EFB chars. The deNO_x and adsorption test for hydrogen sulphide and acetaldehyde were performed to determine the feasibility of the modified EFB chars. The KOH-treated EFB (KEFB) char revealed higher deNO_x efficiency than with commercial activated carbon. The Cu-impregnated EFB char also had high deNO_x efficiency at temperatures higher than 150°C. The KEFB char showed the highest hydrogen sulphide and acetaldehyde adsorption ability, followed by the steam-treated EFB char and untreated EFB char. Moreover, the product prepared by sulfonation of EFB char showed excellent performance for esterification of palm fatty acid distillate for biodiesel production.

Key words: char, adsorption, activation, catalyst, pyrolysis

1. Introduction

Pyrolysis is known to be an efficient method for biomass conversion [1-7]. Among the products of pyrolysis, biochar is a material with great potential for use as adsorbent and catalyst for the removal of contaminants in air and water matrices [8-17]. The catalytic and adsorbent properties of biochar differ according to its surface area, pore properties and mineral content.

Selective catalytic reduction (SCR) is considered a representative deNO_x method and various catalysts have been used for SCR [18-26]. Recently, the use of biochar as catalyst support for the SCR process was suggested. Cha et al. [27] used biomass char produced from the pyrolysis of rice straw and sewage sludge as a supporting material for Mn impregnation and reported that Mn-impregnated char had high deNO_x efficiency.

Jo et al. [28] activated biochar using KOH solution and found that the activated char showed higher deNO_x efficiency due to the improved surface properties and surface area caused by the chemical treatment. Kong et al. [29] impregnated three types of metal oxides (V₂O₅, MnO and CuO) on KOH-treated char and assessed their ability for NO removal using ammonia (NH₃) at 160°C.

Odour substances emitted from food waste consist mainly of hydrogen sulphide (H₂S), NH₃, organic acids and aldehydes [30]. They are also classified as harmful air pollutants owing to their offensive odour and negative effects on the environment and human health.

A range of methods, including such as absorption, adsorption, biological treatment and ozone oxidation, have been applied to the removal of these odorous substances [30]. In particular, the adsorption method is used more widely than other methods because of its simplicity, low operating cost and high efficiency.

Recently, biochar-catalyst prepared from saccharides and biomass by incomplete carbonization followed by sulfonation, has attracted much attention from researchers

because of its low preparation cost and high catalytic activity [31-40]. Wang et al. [38] and Dehkhoda et al. [40] used hardwood biochar as support in the synthesis of solid acid catalysts, and the product exhibited high catalytic activity for the esterification reaction.

In this study, the feasibility of biochar as an alternative material to activated carbon for the removal of NO_x and odour substances was evaluated. Biochar was obtained from pyrolysis of empty fruit bunch (EFB) and was activated by treatment with steam or KOH. The efficiencies of the steam-treated EFB (SEFB) and KOH-treated EFB (KEFB) chars as catalysts for deNO_x were tested, as well as for adsorbents of hydrogen sulphide (H₂S) and aldehyde (CH₃CHO). In an attempt to improve the biochar properties, Cu was also added to the treated biochar and its catalytic and adsorbent activities were compared with those of the other treated biochars.

2. Experimental

2.1. SEFB and KEFB biochar

First, EFB was subjected to pyrolysis at 500°C to obtain biochar. For the steam treatment (SEFB), the biochar was heated to 700°C at 5°C/min and then maintained at 700°C for 1 h under a mixture of steam (1.62 mL h⁻¹) and nitrogen gas (50 mL min⁻¹). For the KOH treatment of EFB char, a mixture of KOH and biochar (1:1) was dissolved in distilled water and then dried in an oven at 105°C. After sufficient drying, the KEFB char was heated to 700°C at 5°C/min and was maintained at that temperature for 1 h under nitrogen gas (50 mL min⁻¹). To remove the K⁺ ions remaining after the KOH treatment, the biochar was neutralized with 5.0 M HCl and then washed with distilled water. After this, it was dried thoroughly in an oven at 105°C. For the copper treatment, 5, 10, or 20 wt% of Cu was used to impregnate 5 g portions of KEFB char to produce three variants of Cu-KEFB. After the incipient wetness impregnation, the Cu-impregnated KEFB (Cu-KEFB) biochar was dried at 110°C under air and heated at 350°C for 3 h under nitrogen gas.

2.2. Sulfonated EFB (Sul-EFB) biochar

For the sulphur treatment, EFB biochar was ground to powder and a 15 g sample was sulfonated using 50 mL concentrated sulphuric acid (95–98%). The sample was soaked for 1 h in a 500 mL flask, with temperature controlled at 90°C in an oil bath. After cooling to ambient temperature, the mixture was stirred in distilled water and filtered. Washing with hot distilled water followed by filtration was repeated to eliminate the residual sulphate ions. After the final filtration, the sample was placed in an air drier for 24 h at 80°C.

2.3. Characterization

The N₂ adsorption-desorption method (Sorptomatic instrument, Thermo Ins) was applied to analyse the surface area, pore size and volume of the biochar according to a procedure reported elsewhere [41,42]. Elemental analysis and total acid

density were also performed using the back-titration method to determine the compositional and surface properties (carboxylic, phenolic and sulfonic groups) of the sulfonated EFB char.

2.4. NO_x, H₂S and aldehyde removal efficiency of SEFB and KEFB biochars

A NO_x removal test was performed using a SUS tube reactor. For this, 3 mg of experimental biochar was loaded inside the SUS tube with quartz wool at both ends of the biochar. Constant concentrations of NO and NH₃ gases (1000 ppm) were supplied to the reactor at temperatures ranging from 50 to 300°C together along with a mixture of oxygen (10 %) and nitrogen gas (90 %). The total flow rate of the gas was 100 mL min⁻¹ and the calculated space velocity (WHSV) was 20,000 mL/g_{cat}·h. The overall efficiency of each biochar for NO_x removal was calculated using Eq. 1. The inlet and outlet concentration of NO was measured using a NO_x analyser (42i-HL, Thermo Fisher Scientific) connected online.

$$100 \times \frac{C_{NO}^i - C_{NO}^o}{C_{NO}^i}$$

The efficiencies of the EFB biochars for removal of H₂S and aldehyde were tested in a Tedlar bag. For this, 10 ppm of H₂S and aldehyde were placed in a 10 L Tedlar bag together with 0.1 g of EFB biochar. The concentration of H₂S or aldehyde remaining after 5, 10, 30 and 60 min of adsorption was analysed using a gas-detecting tube (Gestec).

2.5. Esterification performance of fatty acids over Sul-EFB biochar

Catalytic esterification of free fatty acids over each biochar was also evaluated in this study. For this, a mixture of palm fatty acid distillate (PFAD; supplied by SK Chemical Co., Ltd., Korea) and methanol (MeOH; MeOH to PFAD molar ratio, 15:1) was stirred together with Sul-EFB biochar (5 wt% of initial oil) at 75°C for 24 h on a hot plate using a magnetic stirrer (250 rpm). After reaction, the final biodiesel oil was obtained using vacuum filtration to eliminate the residual biochar and to evaporate the MeOH. The EN 14103 method was applied to quantify the fatty acids methyl esters (FAMES) in the final biodiesel sample after esterification using biochar. For this, a gas chromatography-flame ionization detector (GC-FID; Agilent Technology) with a capillary column (SP-2380, Supelco: 30 m length, 0.25 mm inner diameter, 0.2 µm film thickness) was used together with nonadecanoic acid methyl ester as an internal standard. The GC-FID measurements were repeated three times.

3. Results and Discussion

3.1. Biochar properties

As shown in Table 1, the original EFB biochar had essentially no pore structure and lower surface area than that of the activated biochar reported in previous studies [8,43]. The unmeasurable surface area and pore volume of the untreated EFB char was increased by applying steam and KOH treatments.

Table 1. Specific surface areas and total pore volumes of EFB biochars

Biochar	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
EFB	ND	ND
SEFB	328	0.10
KEFB	700	0.24
5%-Cu/KEFB	699	0.30
10%-Cu/KEFB	624	0.27
20%-Cu/KEFB	606	0.26

ND, not detected.

Although the Brunauer-Emmett-Teller (BET) surface area and pore volume of untreated EFB char were very low, they were increased by the steam and KOH treatments. This is because the steam treatment caused diffusion of heated steam into the biochar where it expanded openings [44] and the KOH treatment cleaned pores blocked by tar particles [45,46]. KEFB had a larger BET surface area (698 m² g⁻¹) and pore volume (0.24 cm³ g⁻¹) than those of SEFB (328 m² g⁻¹, 0.10 cm³ g⁻¹). This suggests that chemical treatment using KOH is more effective for the development of biochar pores than is physical treatment using steam. Although the 5% Cu-EFB biochar had surface area similar to that of KEFB, its surface area decreased with increasing Cu content (up to 20%) due to the formation of large Cu particles in the pores [47].

As shown in Table 2, the surface area and pore volume of Sul-EFB was 2.10 m² g⁻¹ and 0.006 cm³ g⁻¹, respectively. This indicates that the sulfonation treatment of EFB biochar can make structural changes by causing the collapse and degradation of carbon. The collapse and degradation of biochar carbon indicated that activation/oxidation of biochar occurred during sulfonation [43]. The total acid density of Sul-EFB, as measured by the titration method, was 24.72 mmol g⁻¹. This suggests high accessibility of sulphuric acid into the carbon bulk of the EFB biochar and the successful formation of covalent bonds between the carbon surface of the EFB biochar and sulfonic acid. The high S-content of Sul-EFB (2.05 % in Table 3), also indicates the cross-linking of sulfonic acid groups to the carbon layer.

Table 2. Specific surface area, total pore volume and total acidity of Sul-EFB biochar

Biochar	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Total acidity (mmol g ⁻¹)
Sul-EFB	2.10	0.006	24.72

Table 3. Elemental analysis of EFB and Sul-EFB biochar

Sample	C	N	O	S
EFB	67.45	0.72	9.05	-
Sul-EFB	49.27	0.87	34.53	2.05

3.2. Biochar activity

3.2.1. NO_x removal by KEFB biochars

Fig. 1 shows the efficiency of the EFB biochars prepared in this study, for the removal of NO_x. Although the untreated EFB biochar exhibited NO_x removal efficiency lower than 30% at all temperatures, KEFB exhibited much higher NO_x removal efficiency than those of untreated EFB biochar and of commercial activated carbon. In particular, the NO_x removal efficiency of KEFB was greater than 90% at 50°C. The high efficiency of KEFB on NO_x removal at low temperature can be explained by the high physical NO_x adsorption efficiency of KEFB [27,48]. The high NO_x removal efficiency of the KEFB biochar decreased when Cu-KEFB was used at 50°C (Fig. 2). The NO_x removal efficiency of Cu-KEFB became higher than that of KEFB at temperatures higher than 150°C. The high NO_x removal efficiencies of Cu-KEFB at high temperatures can be explained by the effective catalytic reaction promoted by the Cu on KEFB.

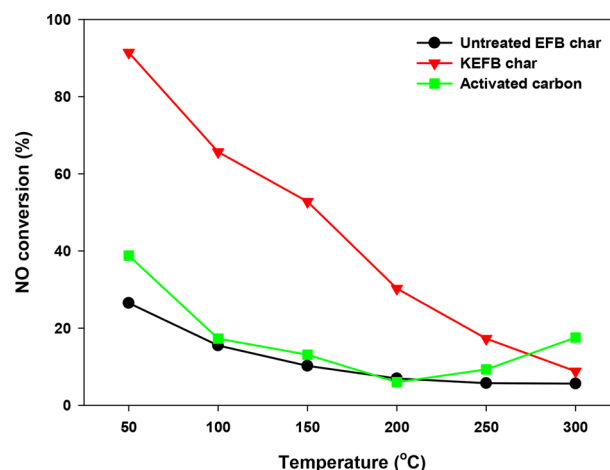


Fig. 1. NO removal-efficiencies of two EFB biochars and commercial activated carbon.

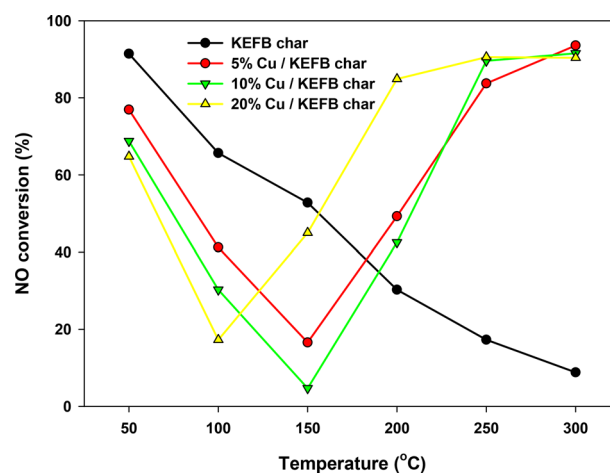


Fig. 2. Effects of different Cu amounts in KEFB biochars on NO removal.

3.2.2. Adsorption of odour emitting substances

Tables 4 and 5 show the efficiencies of the adsorption of H₂S and acetaldehyde by the EFB biochars and a commercial activated carbon, respectively. Although the H₂S and acetaldehyde adsorption efficiencies of the untreated EFB biochar were low, those of SEFB and KEFB were higher than untreated EFB and activated carbon after 10 min adsorption time. In particular, KEFB showed higher aldehyde removal efficiency than did SEFB. This can be explained by the higher BET surface area of KEFB (Table 1), which provides greater adsorption capacity.

3.2.3. Esterification of PFAD over Sul-EFB

The effect of Sul-EFB on the esterification of PFAD is shown in Table 6. The contents (vol%) of FAMES in the product diesel oil obtained from esterification of PFAD over Sul-EFB was increased to 95.08 vol% by increasing reaction time to 15 h. This indicates that the successful esterification of PFAD could be enhanced by the catalytic effect of Sul-EFB.

Table 4. Hydrogen sulphide concentration (ppm) in the Tedlar bag after adsorption by EFB biochars and activated carbon

Time (min)	EFB char	SEFB char	KEFB char	Activated carbon
0	10	10	10	10
5	8	6	4	4
10	8	4	2	3
30	7	1	1	3
60	7	1	ND	3

Table 5. Aldehyde concentration (ppm) in the Tedlar bag after adsorption by EFB biochars and activated carbon

Time (min)	EFB char	SEFB char	KEFB char	Activated carbon
0	10	10	10	10
5	9	4	ND	7
10	9	4	ND	6
30	8	2	ND	6
60	8	2	ND	6

Table 6. FAME content (vol%) from esterification catalysed by Sul-EFB

Time (h)	Catalyst-SO ₃ H
1	19.24
3	43.24
6	52.78
9	72.50
12	84.47
15	95.08

4. Conclusions

Biochar treated with steam (SEFB) and KOH (KEFB) was used as either a catalyst or adsorbent for NO_x, H₂S and aldehyde removal. KEFB had higher NO_x removal efficiency than did untreated EFB biochar and activated carbon, particularly at low temperatures. This high NO_x removal efficiency of KEFB at low temperatures was decreased by Cu impregnation. On the other hand, the NO_x removal efficiency of Cu-KEFB was higher than that of the KEFB at temperatures higher than 150°C due to the catalytic activity of Cu. The H₂S and aldehyde adsorption efficiencies of the EFB biochar were also increased by the steam and KOH treatments. Both SEFB and KEFB revealed higher H₂S and aldehyde removal efficiencies than with untreated EFB biochar and activated carbon. In particular, KEFB showed much higher aldehyde removal efficiency than the other EFB biochars and activated carbon owing to its large surface area. Moreover, Sul-EFB, which was prepared by sulfonation of EFB biochar, showed excellent performance for esterification of PFAD for biodiesel production.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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