

Synthesis of activated carbon using bagasse and recycled carbon fibers

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Abstract Text

Activated carbon was prepared using bagasse and carbon fiber (RCF) recycled from carbon fiber reinforced polymer (CFRP). The RCF surface has a sufficient amount of functional groups and can be used as a catalyst for the hydrolysis of bagasse cellulose. An RCF–bagasse composite was fabricated by ultrasonic irradiation. During cellulose hydrolysis, carbon from the bagasse was activated using sulfuric acid, which impregnated the cellulose pores. When bagasse was subjected to high temperatures, the impregnated pores decomposed, resulting in micropores. The addition of RCF increased the specific surface area of activated carbon by up to 20% when heat treatment was performed at a temperature higher than the carbonization temperature of bagasse.

Keywords: Recycled Carbon Fiber, Bagasse, Recycling

1 Introduction

Over the past few decades, functionalization of materials has become highly advanced, allowing the synthesis of many new materials that have enriched our lives. However, the widespread use of modern materials has also created problems related to the disposal of used materials. In this study, we propose a strategy for effectively using bagasse, the sugarcane pomace that is currently a waste material, and carbon fiber reinforced polymer (CFRP), which is expected to become a major waste material in the near future [1].

Sugarcane is mainly grown in tropical and subtropical regions of the world, and its global annual production is 1907.02 million metric tons. After the extraction of sugar from sugarcane, a large amount of bagasse comprising stems and leaves remains. Although it can be used to extract bioethanol [2], the majority of the bagasse is discarded. If this waste bagasse is left untreated for a long period, it can dry out and become a fire hazard [3].

Bagasse is a lignocellulosic biomass composed of natural polymers of cellulose, hemicellulose, and lignin [4]. In acid saccharification, an acid such as sulfuric acid or hydrochloric acid is used as a catalyst to hydrolyze the sugars in lignocellulose [5]. In this study, the residue (sulfuric-acid lignin [6]) generated by acid saccharification was used as a precursor for producing activated carbon. To form micropores in plant-based raw materials, it is necessary to decompose cellulose by acid saccharification. If the hydrolysis reaction of cellulose can be performed efficiently, activated carbon with a high specific surface area can be obtained. A previous study reported the

efficiency of the hydrolysis reaction of cellulose in nitric acid solution and converted cellulose to glucose using salicylic acid as a catalyst [7]. The hydrolysis rate of cellulose increased when activated carbon having both carboxyl and phenolic hydroxyl groups was used as a catalyst [8]. These studies show that such hydroxyl groups can be used as catalysts for the hydrolysis reaction of cellulose. The surface of carbon fibers recycled from CFRP (RCF) has oxygen-containing functional groups. In the manufacturing process, surface oxidation treatment is performed by introducing oxygen-containing functional groups such as hydroxyl, carboxyl, and ketone groups to the carbon fiber surface [9, 10]. These functional groups form chemical bonds with the epoxy resin matrix to increase the adhesion between the carbon fiber and the resin. To utilize RCF, we also used these oxygen-containing functional groups as a catalyst for the hydrolysis of cellulose in bagasse to synthesize activated carbon.

CFRP recycling methods [11] have been used for treating waste bagasse. However, because thermosetting resins, mainly epoxy resin, are used as the matrix polymer in CFRP, it is difficult to remold new CFRP products from waste CFRP materials. Therefore, only the carbon fibers are recycled from waste CFRP, which are generally reused as filler [12]. Many thermal and chemical decomposition methods have been developed to decompose and remove only the resin from the CFRP at high temperature [13]. The resulting RCF are typically only 2–10 mm long [14]. Even if the RCF has the same mechanical properties as new fibers, they cannot be used to produce fabrics and prepregs because of their short length. However, if RCF with a length of 25–50 mm could be obtained, they would be suitable for producing nonwoven fabric. If the fiber length is ≤ 10 mm, the RCF can be used as a reinforcing material for injection molding with polypropylene or polyamide [15, 16]. To use carbon fiber as a reinforcing material, it should be longer than the critical fiber length (700 μm) [17]. Because the fibers tend to become shorter with repeated recycling, their potential reusability decreases over time.

In this study, we present a recycling method for carbon fibers shorter than the critical fiber length, with the aim of producing activated carbon with a high specific surface area and well-developed micropores using bagasse as a raw material with the RCF. The activation process involved the formation of nanoscale micropores inside the raw material, which increases its internal specific surface area and can impart adsorption capacity to the carbon material. Such materials have a wide range of applications in catalysis and clean energy production and storage [18-20].

2 Experimental

2.1 Materials

Sulfuric acid was used as a catalyst for the hydrolysis of cellulose in bagasse. The bagasse used as the precursor of the activated carbon was obtained from Okinawa-Kokuto Corporation (Okinawa, Japan). The bagasse contained small fibers with a length < 10 mm and width of 1–3 mm, and large fibers with a length ≥ 50 mm and width ≥ 10 mm (**Fig. 1a**). The bagasse was pulverized using a household juicer (Vitamix) with a rotation speed of $\sim 6,000$ rpm. After pulverization for 10 min, uniform fibers of length ≤ 10 mm and width of 1–2 mm were obtained (**Fig. 1b**).

The fiber length of the RCF used in this study was less than the critical fiber length (700 μm). CFRP fabricated using the hand lay-up molding method using carbon fibers (T700S, Toray) and epoxy resin (JER, Mitsubishi Chemical) was pulverized using a cutter mill (IKA, MF10 basic) [12]. The crushed material that passed through a 100-mesh wire net to remove the coarse materials, such as resin, was designated as RCF. The fiber length distribution of the RCF was calculated using a digital microscope (KH-8700, HiROX Co., Ltd.) (**Fig. 2**).

The resin on the RCF surface was observed using a field-emission scanning electron microscope (FE-SEM, SM-7500F, JEOL) as shown in **Fig. S1**. The weight loss of the CFRP and RCF was measured using a thermal gravimetry/differential thermal analysis system (TG/DTA; STA7200, Hitachi High-Tech Science Co., Ltd.) by heating the samples to 700 $^{\circ}\text{C}$ under a flow of nitrogen

gas (**Fig. S2**). Based on these results, the total weight loss was determined and the amount of resin that could be removed by the cutter mill was calculated (41%).

2.2 Synthesis and characterization

When using RCF as a catalyst, good contact between the RCF and bagasse is important. In a 100-mL screw tube, bagasse, RCF, and water were ultrasonically treated for 15 min using an ultrasonic cleaner (US-5KS, SND Co., Ltd.) to thoroughly combine the bagasse and RCF.

We investigated two processes (process A and process B) for the synthesis of activated carbon. In process A, sulfuric acid with a concentration of 10 wt% (10 mL) was added to the bagasse (1.0 g) and then held at 150 °C for 24 h using a hot plate (RCH-100, EYELA) to hydrolyze the cellulose [21]. Then, the bagasse was heated to its carbonization/activation temperature, T , for 1 h using an electric tubular furnace (diameter of 41.5 mm, length of 800 mm, Irie Shokai Co., Ltd) under nitrogen gas with a flow rate of 200 mL/min. In process B, heating was also performed up to T for 1 h, but the bagasse was not previously treated held at 150 °C. **In both cases, the exhaust gas was collected in the bottles with water at the outlet of the reactor.** Finally, to obtain the activated carbon in both processes, the material was cooled to room temperature, ground using a mortar, washed in water to remove the sulfuric acid, and then dried to remove the water. These processed are summarized in **Fig. 3**. In addition, to investigate the effect of sulfuric-acid treatment on the bagasse without RCF, 98% sulfuric acid treatment was performed at 150 °C for 24 h to produce a control sample.

The specific surface areas of the samples were obtained from nitrogen adsorption and desorption isotherms at 77 K using a specific surface area/pore distribution analyzer (BELSORP-mini II, MicrotracBEL Corp.) based on BET theory [22]. As a pretreatment before measurement, a vacuum heating pretreatment device (BELSORP-vac II, MicrotracBEL Corp.) was used for deaeration of the sample at 573 K under vacuum (less than 10 Pa) for 3 h to remove the adsorbed water molecules from the micropores. The specific surface area of the synthesized activated carbon, S_b , was calculated from eq. (1):

$$S_b = \frac{S - x_{RCF} S_{RCF}}{1 - x_{RCF}} \quad (1)$$

where x_{RCF} is the weight ratio of RCF and activated carbon with RCF; and S and S_{RCF} (**Table S1**) are the specific surface areas of the activated carbon with RCF and only RCF after the carbonization/activation treatment, respectively. Here, x_{RCF} was calculated on the basis of the mass balance using the measured masses of the RCF and bagasse shown in **Tables S2** and **S3**, **where the yield of the activated carbon was calculated to be 31.7 ~ 54.8%.**

3 Results and Discussion

3.1 Effect of acid treatment on the specific surface area of activated carbon

The effect of sulfuric acid treatment on the bagasse at $x_{RCF} = 0$ was investigated by solid-state ^{13}C NMR (AS300, BRUKER) (**Fig. 4**). The peaks at a chemical shift of 60–110 ppm weakened after acid treatment (**Fig. 4b**), implying that the cellulose decomposed and was removed through hydrolysis when 98% sulfuric acid treatment was performed at 150 °C for 24 h. Therefore, sulfuric acid behaved as a catalyst for the hydrolysis reaction of the bagasse. During process A at $T = 500$ °C, 98 wt.% sulfuric acid treatment resulted in an S_b of 414.5 m²/g, while the use of 10 wt.% sulfuric acid resulted in a higher S_b of 601.9 m²/g. With the higher acid concentration, the hydrolysis reaction proceeded more easily, resulting in an increase in the pore size of the bagasse and a lower S_b . Therefore, the 10 wt.% sulfuric acid treatment is considered more suitable and was used for synthesizing activated carbon with a high specific surface area.

Finally, processes A and B were compared (**Fig. 5**) using the nitrogen adsorption/desorption isotherms (**Fig. S3**). At any T , S_b obtained by process A was larger than that achieved by process B. The sulfuric acid treatment at 150 °C for 24 h contributed to the development of micropores (smaller than 2 nm) by removing cellulose from the pores in the bagasse. However, when the bagasse was treated with only sulfuric acid, the final specific surface area was 0.759 m²/g and the pores derived from cellulose did not become micropores. Thus, it is clear that the micropores develop when the carbonization and activation were performed after sulfuric acid treatment. Therefore, process A with 10 wt% sulfuric acid treatment was used to synthesize activated carbon. The adsorption isotherms of activated carbons produced at 300–500 °C show that they all contained micropores. Hardly any hysteresis was observed in the isotherm of activated carbons prepared at 500 °C, whereas hysteresis was observed in those synthesized at 300 °C. In addition, the lower treatment temperature resulted in a larger mesopore volume than higher temperatures. As T increases, S_b first increases, then becomes constant, and finally decreases above a certain temperature [23]. This is consistent with the S_b of the sample with $x_{\text{RCF}} = 0$ increasing with increasing T (**Fig. S4**).

3.2 Effect of RCF on specific surface area of activated carbon

To investigate the role of RCF as a catalyst for the hydrolysis reaction, the amount of the functional groups present on the RCF surface was quantitatively evaluated using the Boehm titration method [24–26]. The total amount of oxygen-containing functional groups on the RCF (920.1 mmol/g) was considered sufficient for use as a catalyst for the hydrolysis of cellulose, where the cellulose forms oligomers and glucose [27]. The carboxyl, hydroxyl, and lactone functional groups contributed 656.7 μmol/g (~71%), 186.7 μmol/g (~20%), and 76.7 μmol/g (~8%), respectively, to the total.

Fig. 6 shows an SEM image of the RCF and bagasse composite prepared using ultrasonication, where the RCFs were embedded in the bagasse. This composite bagasse was used to synthesize activated carbon by process A (**Fig. S5**).

The pore characteristics were measured to evaluate the effect of the RCFs on S_b . **Fig. 7** shows the relationship between x_{RCF} and S_b of activated carbon with a yield of 20 wt% prepared by process A at T values of 500, and 700 °C. The pore-size distributions of these samples are shown in **Fig. S6**. The effect of x_{RCF} on S_b is discussed using the S_b values obtained at $T = 500$ °C, which is the temperature at which sufficient carbonization of bagasse occurred. The main constituents of bagasse are cellulose, hemicellulose, and lignin, which have thermal decomposition temperature ranges of 200–300, 240–400, and 280–900 °C, respectively [28, 29]. At $x_{\text{RCF}} = 0$, a large difference was observed in the S_b values between 300 and 500 °C, as shown in **Fig. 5**, where S_b was higher at 500 °C because of the thermal decomposition of cellulose. At T values of 500 and 700 °C, where sufficient carbonization occurs, S_b tended to increase with increasing x_{RCF} . The addition of RCF effectively increased S_b because RCF functioned as a catalyst to accelerate the hydrolysis of cellulose in bagasse.

4 Conclusions

Here, a method to synthesize activated carbon using bagasse and RCF from CFRP was developed. The RCF surface has a sufficient amount of the functional groups to function as a catalyst for the hydrolysis reaction of cellulose. The RCF and bagasse were combined by performing ultrasonic irradiation in water. Hydrolyzing the cellulose is essential to develop micropores when activated carbon was produced from bagasse using sulfuric acid as an activator. Sulfuric acid impregnates the pores and removes cellulose from the bagasse at high temperatures; these pores act as a template for the development of micropores. The addition of RCF increased the maximum specific surface area of activated carbon by 20% when heat treatment was performed at a temperature that enabled sufficient carbonization of bagasse. The RCF increased the specific surface area while producing activated carbon from bagasse. This

method could also be applied to produce activated carbon using lignocellulose as a raw material, instead of bagasse.

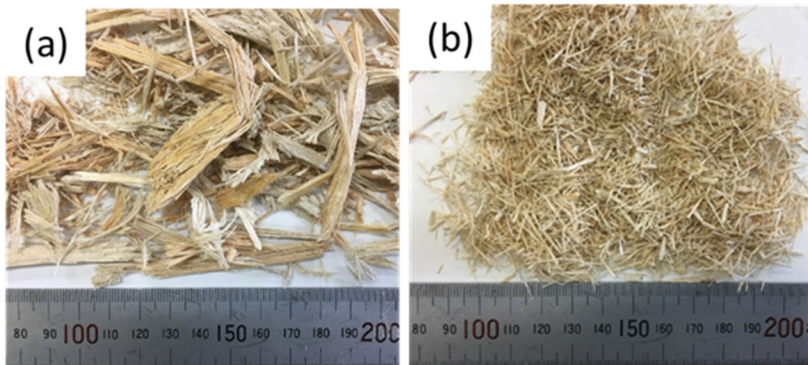


Figure 1. Bagasse (a) before and (b) after pulverization.

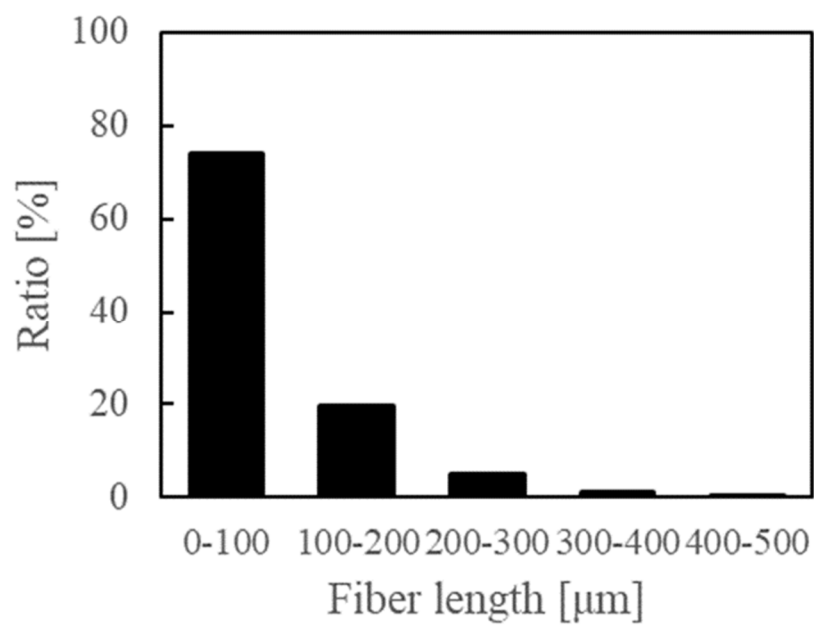


Figure 2. Size distribution of RCF recycled from CFRP.

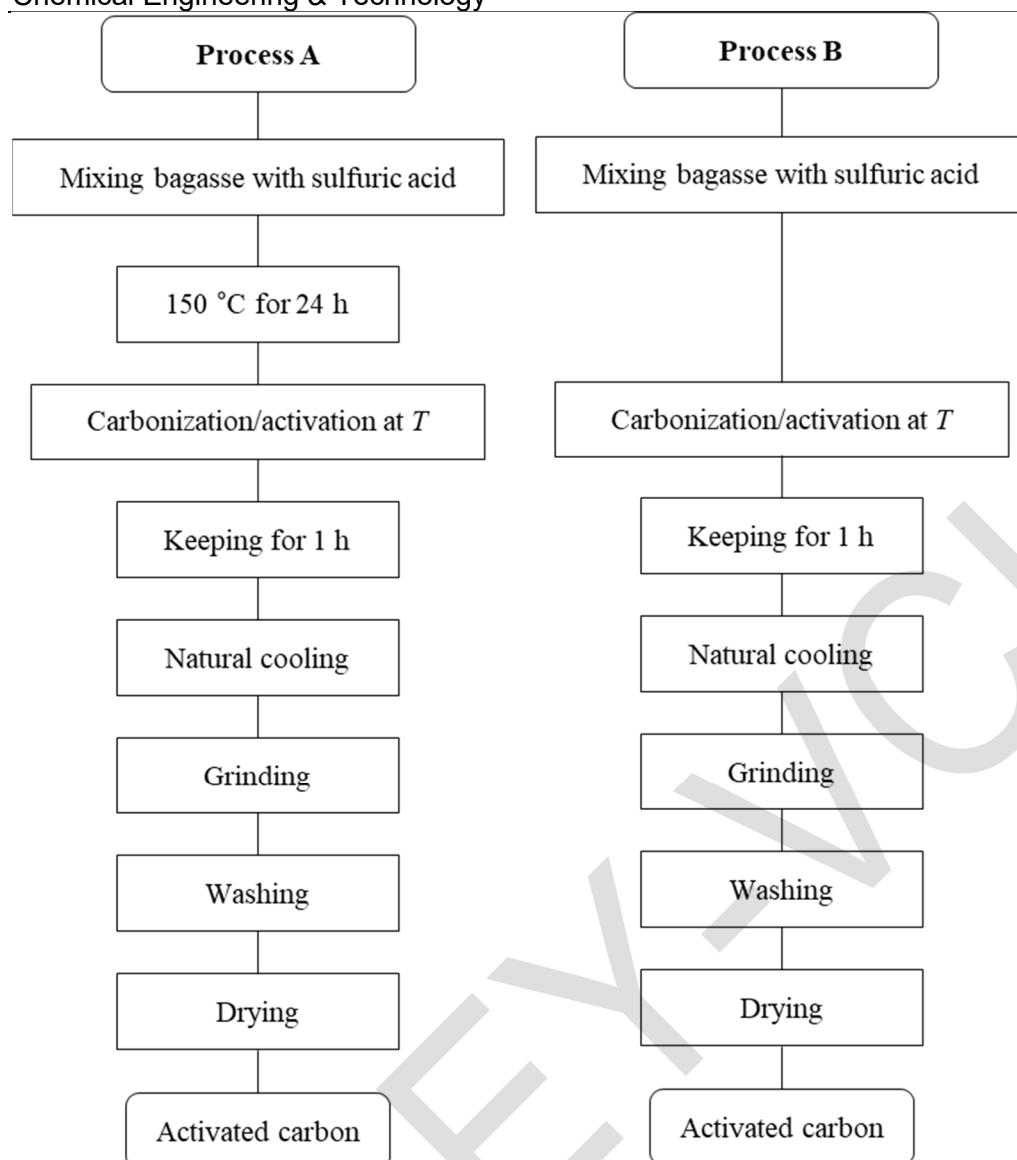


Figure 3. Flow charts of process A and process B.

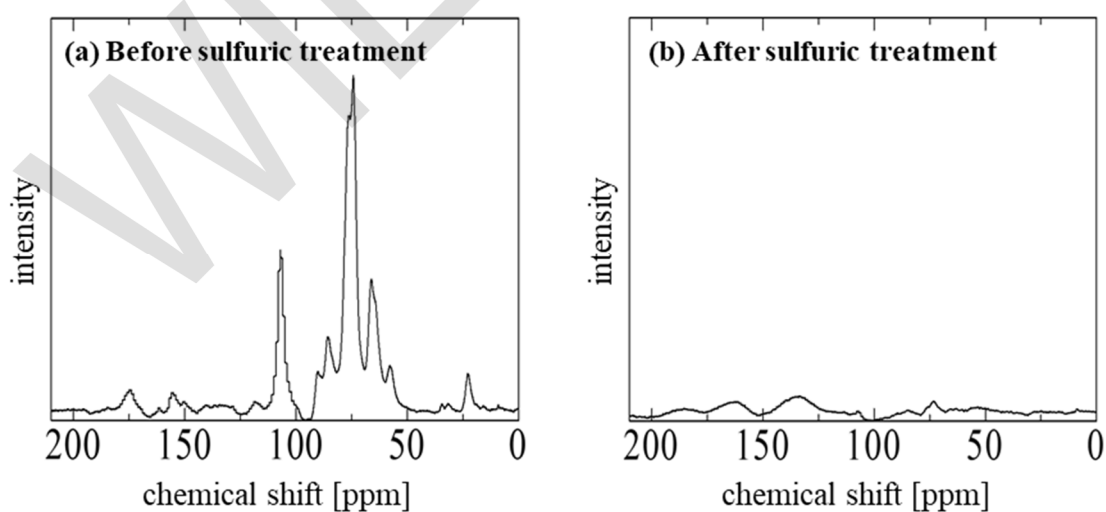


Figure 4. Comparison of ¹³C NMR peaks of the bagasse before and after 98% sulfuric acid treatment. The peaks at 110-160 and 60-110 ppm indicated lignin and hemicellulose cellulose, respectively.

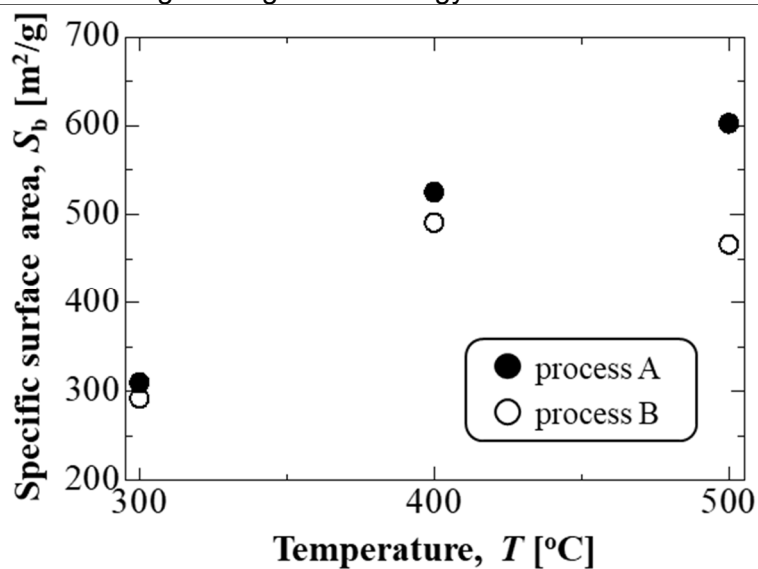


Figure 5. Specific surface areas as a function of temperature of activated carbon obtained using process A or B.

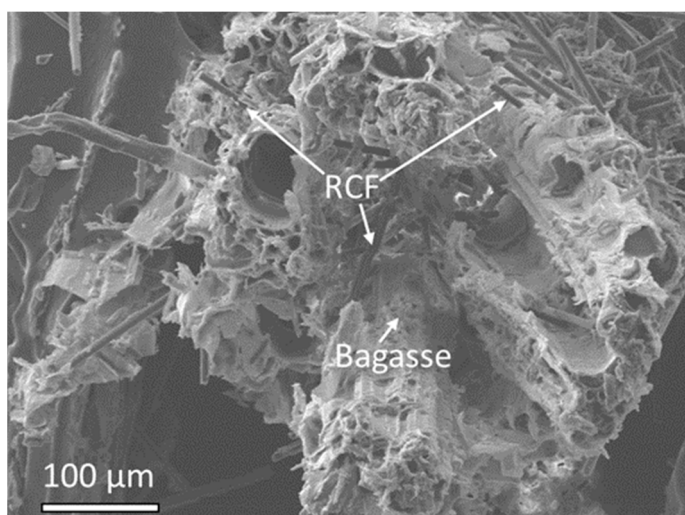


Figure 6. SEM image of the RCF and bagasse composite.

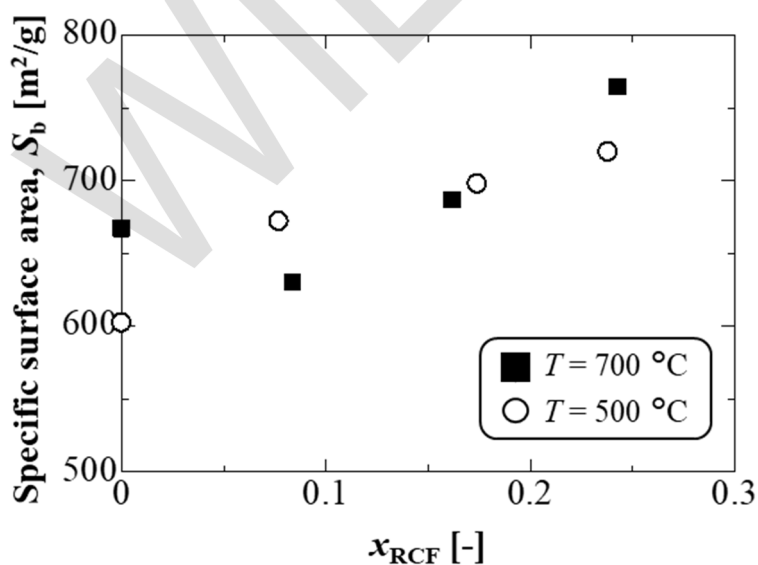


Figure 7. Effect of x_{RCF} on S_b .

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Symbols used

S	[m ² /g]	Specific surface areas of the activated carbon with RCF
S_b	[m ² /g]	Specific surface area of the synthesized activated carbon
S_{RCF}	[m ² /g]	Specific surface areas of the activated carbon with only RCF
T	[°C]	Carbonization/activation temperature
X_{RCF}	[-]	Weight ratio of RCF and activated carbon with RCF

Abbreviations

CFRP carbon fiber reinforced polymer

RCF carbon fiber recycled from CFRP

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Table and Figure captions

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Supporting Information

The SEM image of RCF with the resin is shown in **Fig. S1**. The TG-curves of CFRP and RCF are shown in **Fig. S2**. **Fig. S3** shows nitrogen adsorption/desorption isotherms of the activated carbons at each reaction temperature. **Fig. S4** shows effect of T on S_b at $x_{RCF} = 0$. **Fig. S5** shows the SEM image of the composite of bagasse and RCF after the activation. Pore size distributions of the synthesized carbon are shown in **Fig. S6**. **Tables S1** shows the specific surface area of the activated carbon from RCF at each reaction temperature. The mass data used to calculate x_{RCF} are shown in **Tables S2 and S3**.

Entry for the Table of Contents

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