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A Novel Biomass Supported Na_2CO_3 System for Flue Gas Desulfurization

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Abstract: The breakthrough and stoichiometric SO_2 adsorption efficiencies of a biomass supported Na_2CO_3 system (80 wt %Na_2CO_3/straw) have reached 48.9 % and 80.6 % respectively at a desulfurization temperature of 80°C.

Keywords: Straw, adsorption efficiency, SO_2.

Studies on recyclable solid sorbents[1-6] in dry desulfurization processes have been the subject of much recent attention. For example, in the NOXSO and Powder-Particle Fluidized Bed (PPFB) processes[1-3], Na_2CO_3/γ-Al_2O_3 has been employed as a regenerative sorbent for SO_2 in order to realize the subsequent transformation of SO_2 at operating high temperatures. However, the outlook for actual application of the processes in currently operating power stations is not promising due mainly to the complex processes involved high cost of the sorbents and high energy consumption. Therefore, a cheap, easily obtainable and disposable sorbent seems to be a solution for the development of a highly efficient, industrially acceptable desulfurization system. Utilization of biomaterials or abandoned biomaterials (BIOM), of which the major component is cellulose $(C_6H_{10}O_5)_n$, is a creative new approach to the problem[7]. The BIOM includes straw, rice husks and stalks, dried branches and leaves, waste papers and similar materials.

The wheat straw employed as the BIOM in this work was composed of 40.50 % C, 5.58 % H and 45.26 % O based on elemental analysis (Elementar Vario EL, Germany). The typical preparation procedure for an 80 wt % Na_2CO_3/straw mixture was shown in literature[7]. The reference sorbent Na_2CO_3/γ-Al_2O_3 was prepared according to the literature[2].

The SO_2 removal experiment was carried out under atmosphere pressure at 70~300°C, using a fixed-bed quartz reactor, in which the sorbent (0.33 g) was supported on a quartz frit of medium porosity. The flow rate was 40 mL/min. The simulated flue gas contained 1960 ppm SO_2 with N_2 as the balance gas. An FT-IR spectrometer

(Vector 22, Bruker) with an on-line cell was used to monitor the SO_2 concentrations

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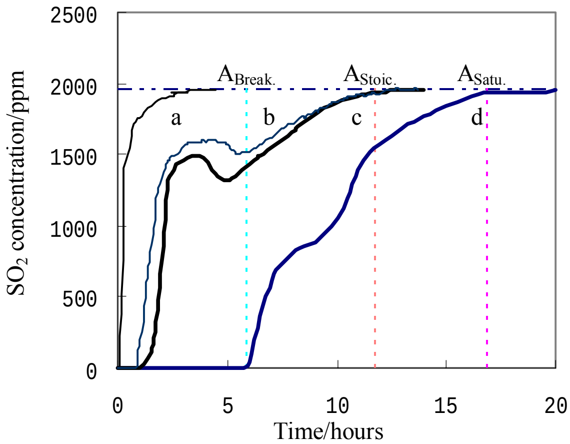
before and after the reactor. The adsorption efficiency η (breakthrough/stoichiometric[8,9]/saturation) of the sorbent is given by $\eta = f_s / f_c \times 100$ %, where f_c is the amount in mols of Na_2CO_3 in the sorbent and f_s is the amount in mols of

SO_2 adsorbed by the sorbent. The Na/S ratio is given by $r = 2 f_c / f_s$, and is theoretically equal to 2.

Figure 1 Desulfurization curves of sorbents at a temperature of 80°C



(a) Na_2CO_3, (b) 80 wt % Na_2CO_3/γ-Al_2O_3, (c) 20 wt % Na_2CO_3 /γ-Al_2O_3, (d) 80 wt % Na_2CO_3/straw. The adsorption efficiencies (A) for curve d have shown in the **Figure**, in which, $A_{Break.}$ = Breakthrough efficiency, $A_{Stoic.}$ = Stoichiometric efficiency, $A_{Satu.}$= Saturation efficiency.

Table 1 Result of several sorbents on removal of SO_2 at temperature 80°C

	Breakthrough			Saturation		Stoichiometric	
	Efficiency mol %	Time hours	Na/S	Efficiency mol %	Na/S	Efficiency (mol %)	Na/S
a	0	0	-	8.6	23.2	8.6	23.2
b	7.6	0.90	26.6	24.2	8.26	24.0	8.34
c	37.2	1.10	5.38	92.1	2.17	74.9	2.67
d	48.9	5.80	4.09	85.1	2.35	80.6	2.48

Figure 1 and **Table 1** show a comparison of Na_2CO_3/straw, Na_2CO_3/γ-Al_2O_3 and pure Na_2CO_3 for removal of SO_2 at a temperature of 80°C. The breakthrough and stoichiometric adsorption efficiencies of 80 wt % Na_2CO_3/straw are 48.9 % and 80.6 %, whilst that of 80 wt % Na_2CO_3/γ-Al_2O_3 are 7.6 % and 24.0 %, respectively. The activity of the 80 wt % Na_2CO_3/straw is also significantly higher than 20 wt % Na_2CO_3/γ-Al_2O_3, which is a typical sorbent employed in PPFB processes[2]. As shown in **Table 1**, the breakthrough adsorption efficiency of 80 wt % Na_2CO_3/straw is 11.7 percent higher than the 20 wt % Na_2CO_3/γ-Al_2O_3, whilst the stoichiometric efficiency is 5.7 percent higher. In addition, with respect to saturation of the sorbents, the efficiency of 80 wt % Na_2CO_3/straw is significantly higher than that of the 80 wt % Na_2CO_3/γ-Al_2O_3, and is almost equal to 20 wt % Na_2CO_3/γ-Al_2O_3. It is noteworthy that the higher saturation efficiency of 20 wt % Na_2CO_3/γ-Al_2O_3 compared with that of 80 wt %

Na_2CO_3/straw is mainly due to the adsorption properties of the γ-Al_2O_3 support[2, 10, 11]. In brief, the data shows that the adsorption efficiency and Na/S of breakthrough and stoichiometric adsorption of the 80 wt % Na_2CO_3/straw are the best of the samples investigated. XPS analysis demonstrated that the main product in each is Na_2SO_3.

Figure 2 Effect of temperature on SO_2 removal for sorbent 80 wt %Na_2CO_3/straw.

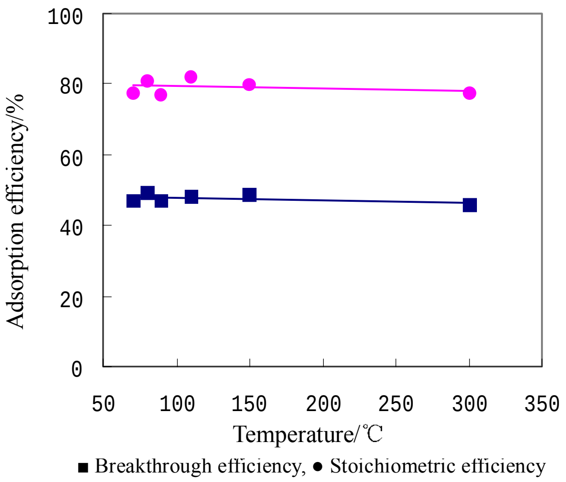


Figure 3 Curves of TGA and DTA of wheat straw.

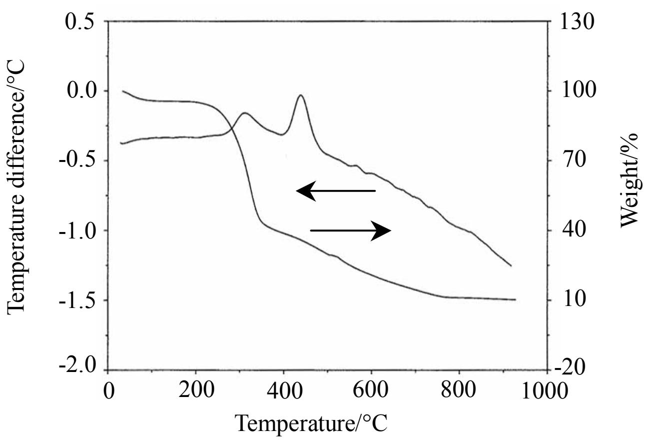


Figure 2 shows the effect of temperature on SO_2 removal for 80 wt % Na_2CO_3/straw. It can be seen that the breakthrough adsorption efficiency changes between 45.1 % and 48.9 % whilst the stoichiometric adsorption efficiency changes between 76.9 % and 82.1 % as the temperature increases from 70 to 300°C.

In order to further investigate the properties of the straw, TGA and DTA were carried out. The results are shown in **Figure 3**. The TGA weight loss curve shows that no chemical change occurs below 200°C. When the temperature rises above 200°C, the straw starts to carbonize and two stages of weight loss appear in the regions 250 ~

350°C and 350 ~ 650°C. The DTA curve shows two distinct peaks between 273 ~ 407°C and 407 ~ 510°C respectively. Both are exothermic oxidation processes, suggesting that the straw is a potential reducing agent in the temperature range 200 ~ 510°C.

It should be noted that the reduction properties of cellulose-based materials have been reported previously. Examples include reduction of NO, bivalent copper and hexavalent chromium by cellulose-based BIOM[12 - 14]. Based on previous work and this study, a more efficient and complete flue gas desulfurization (FGD) process can be proposed. The key steps in the proposed process are the enrichment of SO_2 and the subsequent reduction of SO_2 to S. The reactions are described schematically below:

$$Na_2CO_3/BIOM + SO_2 \longrightarrow Na_2SO_3/BIOM + CO_2$$

$$C_6H_{10}O_5 + 6SO_2 \longrightarrow 6S + 6CO_2 + 5H_2O$$

It can be seen from the above reactions that SO_2 is first enriched by the BIOM system and then selectively reduced to elemental S by BIOM under oxygen-free conditions. The Na_2CO_3 is capable of being recycled. In that case, suitable catalyst will be needed, and further studies are being carried out in this laboratory.

In conclusion, the sorbent Na_2CO_3 supported on straw can efficiently adsorb SO_2 at 80°C, and the desulfurization process can be operated over a large temperature range. In addition, the straw is a possible promising reducing agent for SO_2 reduction.

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