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# Preparation of steam activated carbon from black liquor by flue gas precipitation and its performance in hydrogen sulfide removal: Experimental and simulation works

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## ABSTRACT

Activated carbon was prepared from black liquor by steam activation. The BET specific surface area, pore volume and average pore diameter of resultant carbon activated at 900 °C can reach 1010 m<sup>2</sup>/g, 0.65 m<sup>3</sup>/g and 3 nm respectively. The relative humidity contributes to the adsorption of H<sub>2</sub>S on carbon, while the increased adsorption temperature and inlet concentration show an unfavorable condition for adsorption. Kinetic model yield a satisfactory result in parameters estimation and prediction for breakthrough time with different inlet H<sub>2</sub>S concentrations. The surface diffusion is significant to the effective diffusivity during mass transfer under experimental condition. The dynamic experimental results indicate a good performance in H<sub>2</sub>S removal.

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## 1. Introduction

BL (black liquor) is the one of the main by-products produced from the biomass pulping process. It usually represents up to 15% w/w of total amount, which is composed of lignin, low molecular weight organics, and the rest being chemicals from the digesting process [1]. One of the most challenging technical hurdles during straw paper pulping is to cost-effectively separate lignin from BL in order to fulfill energy cascade utilization and material recycling [2]. The flue gas (CO<sub>2</sub>) is found to be effective to separate lignin from BL during acidification [3]. However, this process needs to be intensified during acidification, when it was compared with conventional mineral acid acidification [4]. In our recent work, the combined process, which employed flue gas precipitation together with continuous hydrothermal treatment, was found to effectively intensify the separation step. This process shows a significant reduction of the demands of evaporation and downstream wastewater treatment. It shows a promising separation approach comparing to the conventional approach of multi-stage evaporation and subsequent alkali recovery [5]. Among

the mature processes for utilization of the precipitated lignin, preparation of the Ac (Activated carbon) is one of the most feasible and economical approaches due to the easiness of directly employing the existing infrastructure of production of Ac [6]. In this paper, one of our focuses is on the preparation of Ac from BL by steam activation.

Hydrogen sulfide is one of the common malodorous compounds that can be found in natural gas and emission from industrial plants [7]. The efficient removal of H<sub>2</sub>S has been a strategic issue in relation to many industrial processes such as GTL (Gas to Liquid) process, IGCC (integrated gasification combined cycle) processes and PEMFCs (proton exchange membrane fuel cells) devices. In the FTS (Fischer-Tropsch Synthesis), the sulfur poisoning of the catalysts, especially the Cobalt based catalyst, has been a difficult problem to solve [8]. The deactivation of the catalyst occurred only a few days or even a few hours in the presence of H<sub>2</sub>S with a concentration of a few ppm [9]. In the IGCC process, it is necessary to reduce the emission of the sulfur impurities and to avoid corrosion of the process facilities, especially at supercritical phase in presence of moisture [10]. The acceptable H<sub>2</sub>S concentration for gas turbines in the IGCC process is about 1 ppm [11]. In PEMFCs, it is essential to reduce the H<sub>2</sub>S concentration down to as little as 0.1 ppm to protect the noble metal catalysts used in the electrode materials [12–13]. Among various sulfur removal techniques, the physisorption using Ac at ambient temperature and pressure is found to be economical and cost-effective for

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<sup>1</sup> Author has same contribution to this work in part of kinetic modeling and material characterization.

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## Nomenclature

$c$	concentration of adsorbent in the gas phase (mmol/g);
$c_p$	average concentration in the pores of the adsorbent (mmol/g);
$c_b$	breakthrough concentration (ppm);
$c_0$	initial concentration (ppm);
$D_e$	effective diffusivity (m/s);
$D_k$	Knudsen diffusivity (m/s);
$D_m$	molecular diffusivity (m/s);
$D_p$	pore diffusivity (m/s);
$D_s$	surface diffusivity (m/s);
$D_z$	axial diffusivity (m/s);
$\Delta H$	isosteric enthalpy (kJ/mol);
$k_{\text{overall}}$	overall mass transfer coefficient ( $\text{s}^{-1}$ );
$K_L$	Langmuir constant (L/mg);
$l$	length of bed (m);
$m_s$	mass of adsorbent (kg);
$M$	gas molecular weights;
$n_s$	average adsorbent loading (mmol/g);
$N_m^*$	adsorption saturation capacity (mmol/g);
$P$	pressure (kPa);
$Q$	volume flow rate ( $\text{m}^3/\text{s}$ );
$q$	concentration of adsorbent in the adsorbed phase (kg/mol);
$q_s$	the average concentration of adsorbent in the adsorbed phase reaching equilibrium (kg/mol);
$R$	pressure gases constant (0.00831 KJ/mol K);
$r_p$	radius of adsorbent (m);
$S$	mass balance source term (mol/s);
$t$	time (s);
$t_b$	breakthrough time (min);
$T$	temperature (K);
$u$	superficial fluid velocity (m/s);
$v_A$	molecular volume of A ( $\text{m}^3$ );
$v_B$	molecular volume of B ( $\text{m}^3$ );
<b>Greek characters</b>	
$\alpha$	specific surface area per unit bed volume ( $\text{m}^{-1}$ );
$\varepsilon_b$	porosity of the bed;
$\rho_s$	adsorbent density ( $\text{kg}/\text{m}^3$ );
$\tau$	tortuosity factor;
$\mu$	viscosity of the fluid (Pa/s);

medium and small scale sulfur removal units such as residential fuel cell system [14].

In this work, Ac was produced from flue gas precipitated lignin by means of steam activation with large specific surface area, to the best of our knowledge, has been rarely published before. In addition, modeling of dynamic adsorption of  $\text{H}_2\text{S}$  on resultant carbon was investigated in order to provide a straight forward approach for design of adsorption column, and this is another objective of this work. The effect of activation temperatures upon the specific surface area of the resultant carbons, the characterization of the carbon with the largest BET specific surface area, the effect of operational parameters such as initial  $\text{H}_2\text{S}$  concentration, adsorption temperatures, relative humidity upon breakthrough curves, were closely investigated.

## 2. Experimental section

### 2.1. Preparation of Ac

BL together with simulated flue gas with 10% (v/v)  $\text{CO}_2/\text{N}_2$  was continuously fed into reactor at 100 °C and 5 atm for 10 mins. The

**Table 1**

Elemental composition of BL, a refers to calculation by difference.

Element	Content (wt. %)
C	46
H	5
N	0.6
S	0.005
Cl	0.01
$\text{O}^a$	48.2

precipitate was then obtained by filtration. Table 1 shows elemental analysis of the obtained precipitate. In order to confirm whether the oxygen elements are also the major element in the BL matrix, we also compared the experimental heating value of BL with back calculated heating value of BL employing the major CHNS elements from Table 1, the results agree well with elemental analysis. From Table 1, the carbon content is relatively higher than other elements indicating its good property for being used as carbonaceous precursor. The solid obtained from filtration was then activated by steam (with flow rate of 0.5 SLPM) at different temperatures with duration of 120 mins. The detailed experimental setup for precipitation and activation could be found in our previous works [5]. The black liquor lignin obtained from  $\text{CO}_2$  precipitation was denoted as BL, the carbons produced from further steam activation at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C were denoted BL-500, BL-600, BL-700, BL-800, BL-900, and BL-1000 respectively.

### 2.2. Equilibrium and kinetic adsorption of $\text{H}_2\text{S}$

The isotherm of  $\text{H}_2\text{S}$  was measured by gravimetric methods using B.E.T apparatus with the spring balance at 298 K, 308 K and 318 K respectively.

The kinetic adsorption was performed in Fig. 1. The dimension of the adsorption bed is the 12.7 mm ID and 200 mm in length immersed in a thermostatic bath. The simulated  $\text{H}_2\text{S}$  gas was passed through the reactor for  $\text{H}_2\text{S}$  removal. The cylinder gas of  $\text{H}_2\text{S}$  (8000 ppm) and 5.0 Nitrogen (were supplied by Scott Gas Company) were used for simulated gas feed. The humidity was controlled by choosing the saturation temperature, which gave the desired water vapor pressure and carrier gas  $\text{N}_2$  passed through the bubbler in a specific flow rate. The  $\text{H}_2\text{S}$  concentration was varied from 200 to 800 ppm in the adsorption system. The  $\text{H}_2\text{S}$  stream constitutes were analyzed by the Gas Chromatograph (HP 6890) equipped with a PFPD (Pulsed Flame Photometric Detector). The internal reference and Quality Control (QC) were conducted to ensure acceptable experimental uncertainties. Ac sample was pelletized and seized with average diameter of 1 mm for column adsorption test. The total flow ranged from 0.2 to 1 SLPM (Standard Liter per Minutes), the packing length of the bed is 100 mm. Before each kinetic experiment, the reactor was heated up at 200 °C with high purity nitrogen as inert atmosphere to remove the moisture of the Ac.

The adsorption capacity was calculated by integrating the area above the breakthrough curve for a given inlet  $\text{H}_2\text{S}$  concentration, mass of adsorbents and flow rate as the followings [15]:

$$q_m = \frac{MC_0Q}{1000m_s} \int_0^{t_b} \left(1 - \frac{C_b}{C_0}\right) dt \quad (1-1)$$

### 2.3. Characterization of Ac

The specific surface area and porosities of the activated carbon samples were determined by nitrogen gas adsorption at 77 K at a saturation pressure of 106.65 kPa using a Micromeritics ASAP 2020 Automated Gas Sorption System. The Ac sample was degassed ( $10^{-6}$  Torr) overnight at 350 °C. The BET surface area was assessed

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