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ON THE COVER: On the left is a synchrotron-based three-dimensional microtomography image of cotton hull before pyrolysis (top) and after pyrolysis (bottom). This is the first application of this technique to image such materials, which are relevant for biofuel production and agricultural applications. On the right is a two-dimensional cross-section of the previous three-dimensional reconstruction. See Keith Jones, Girish Ramakrishnan, Minori Uchimiya, and Alexander Orlov, p 1628.

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Treatment of Waste Gases by Humic Acid

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ABSTRACT: Humic acid (HA) is a natural adsorbent and has special physical and chemical characteristics that form the foundation for disposal of pollutants from a combustor flue gas. HA, which occurs widely in soil, water, and low-rank coals, has already been proposed as a candidate that can be used as a sorbent for air pollution control. A flue gas desulfurization and denitrification (FGDD) process employing HA seems like a promising approach. It is a better choice using HA−Na as a desulfurization additive to improve wet limestone scrubbers or other FGDD processes. This paper reviews the recent development of waste gas treatment by HA with special reference to HA for removal of SO_2, NO_x, CO_2, H_2S, and heavy metals.

1. INTRODUCTION

Humic substances (HS) originate from the decay of animals, plants, and other biological activities of microorganisms in the environment, which are widely distributed in water, soil, and low-rank coals. As natural polyelectrolytes, the presence of HS is crucial to preserve the production and quality of soil, remove inorganic pollutants, improve industrial agents, and treat some diseases. Therefore, HS act as a important role in the fields of agriculture, environment, industry, human health, and medicine.[1]

The prominent characteristics of HS have caught the attention of more investigators. Research progress in the exploitation of their physicochemical characteristics and structure has been achieved in the recent decades, and HS have been applied to many practical applications under the guidance of that new knowledge.[2] HS are referred to as a black or brown, amorphous, complex heterogeneous mixture of organic substances with similar properties. HS are composed of C, H, O, N, and S atoms; however, the structure is complicated. Some functional groups including −COOH, −OH, and −O− are contained, which endows HS with a heterogeneous mixture. Depending on their source, extraction, and analysis method, the typical molecular mass of HS is from a few hundred to several thousands, and the size range is from 1 nm to several hundred nanometers.[3−5]

The chemical and physical properties of HS have been studied by many researchers. On the basis of employing new analysis techniques (e.g., XPS, NMR, SEM, TEM, ESR), the physicochemical characteristics of HS have been revealed, such as chelation, compexation, adsorption, and ion-exchange capacity.[6,7] It is worth noting that the chemical structure of HS is close to the source of the origin. The latest research indicates that HS are formed from relatively small molecules, which have similar characteristics, and are held together via supramolecular interactions.[8]

HS can be further subdivided depending on their solubility in acids and bases. The groupings are termed humic acid (HA), fulvic acid (FA), and humin.

(1) Humic acid (the part of HS that is soluble in dilute alkali but insoluble in acidic solution); this characteristic gives a theoretical basis for precipitation and separation of HA fertilizer after desulfurization and denitrification.
(2) Fulvic acid (the part of HS soluble in all pH conditions).
(3) Humin (the part of HS insolube in alkali or acid).

HA can also be divided into "natural HA" and "artificial HA". Natural HA is further classified as soil HA, water HA, and coal HA. Artificial HA includes fermentation HA (FHA), chemical synthesis HA, and oxidized regenerated HA. Although the total amount of soil HA and water HA is very large, the percentage is very low. The main material of HA in industry is low-grade coal, such as peat, lignite, and weathered coal.

The total amount of HA runs up to one trillion tons. HA, partly bonded with potassium, calcium, and sodium, into potassium humate (HA−K), calcium humate (HA−Ca), and sodium humate (HA−Na) by their oxygen functional groups respectively, is the major component of low-rank coals (e.g., peat and lignite).[9−11] HA and HA−Na possess potential application in industry because of their thermostability, and no obvious destruction takes place even after exposing them under 250 °C for 60 min.[12]

HA can be extracted from low quality coal with either sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3), and we can also get HA by the fermentation of waste biomass.[13] To sum up, as a kind of natural adsorbent, HA has a wide range of origins, lower price, and special physical and chemical characteristics, which gives it the potential to control SO_2, NO_x, H_2S, CO_2, and heavy metals in exhaust gas.

2. PHYSICAL AND CHEMICAL BASIS OF HA IN WASTE GAS TREATMENT

2.1. Structural Characterization. Generally, the structural characterization of HA includes elemental analysis, measurement of oxygen-containing functional groups, measurement of molecular weight or distribution of molecular weight, and some other important features such as C/H, E_4/E_6, etc. HA is

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