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Analysis of coal wettability by inverse gas chromatography and its guidance for coal flotation

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ARTICLE INFO	A B S T R A C T		
A R T I C L E I N F O Keywords: Coal flotation Surface energy Hydrophilicity index IGC	In coal flotation, the hydrophobicity of fine coal is a crucial factor that affects coal flotation recovery and performance. How to accurately characterize the surface hydrophobicity of coal becomes a research hot spot in coal science. This paper used a novel characterization technology, namely inverse gas chromatography (IGC) to characterize the wettability and hydrophobicity of fine coal particles by analyzing their surface energy. Five coals with different coal ranks were used as coal samples in this investigation, and the flotation results of five coal samples were obtained under the same flotation conditions. Throughout this paper, a good correlation between flotation recovery and surface energy was found and the hydrophilicity index of coal was calculated using the ratio of the specific component of surface energy to the total surface energy. A higher hydrophilicity index of coal leads to a lower flotation recovery. The flotation recovery is not governed by the coal rank but is determined by the surface energy of coal particles, i.e. the hydrophilicity index and the work of adhesion. The IGC is demonstrated to be a potential method for predicting the flotation recovery of fine coal in the coal preparation industry.		

1. Introduction

Coal flotation is a sort of separation technology involving a threephase interface reaction between gas, liquid and solid [1,2]. To recover coal particles successfully, the effective collision, attachment of coal particle with the bubbles are necessary. In general, a better wettability of particle leads to a worse hydrophobicity and a lower flotation recovery [3,4]. The surface physicochemical properties, such as functional groups, lattice defects, chargeability have significant effects on the wettability of minerals and coal [5–7]. The surface energy distribution can reflect the physical and chemical property [8]. Therefore, the surface energy reflects the potential properties of the coal surface and is a very valuable parameter to indicate the wettability and hydrophobicity of coal.

The surface energy of a certain material is defined as the extra amount of energy on the surface relative to the inside. The surface structure and chemical composition are different from its internal counterparts [9]. Compared with the internal molecules, there exists extra energy on the surface, which is regarded as the surface energy. The surface energy γ_t insists of the dispersion component (or non-polar component) γ^d and the polar component γ^{sp} , where γ^{sp} contains a Lewis acid component γ^+ and a Lewis basic component γ^- [10]. The

roughness of the solid surface and the non-polar functional groups determine the dispersive component, and the polar component is affected by the type and amount of polar functional groups on the solid surface [11]. Solid surface energy is closely related to its wettability and surface hydrophobicity. This is because that wetting is an interfacial phenomenon, referring to process where the gas is replaced by the water. When the liquid spread on the solid surface, the system energy would decrease to achieve a lower energy and stable state. If the surface energy of a certain material is high, it may be wetted more easily, since tons of energy will release during that process, otherwise it turns to be more hydrophobic. There is a strong co-relationship between the wettability and its surface energy. Therefore, the surface energy parameters become an important criterion to indicate the hydrophilicity of solid surface.

It has been reported that the surface energy is usually calculated using the contact angle method. However, the test accuracy of the contact angle method is usually limited because of the solid surface heterogenous. The contact angle method requires pellet or block samples. Sometimes the direct compression process is necessary to ensure that the power material into the pellet one, which can lead to the heterogeneity. The heterogeneity here includes the roughness, the various pores structures and permeation caused by the crack. Contrary

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to the contact angle method, the inverse gas chromatography (IGC) is a dynamic method for the analysis of surface energy. It is a particularly suitable technique that allows a fast and accurate determination of the surface energy, the dispersive component and the interaction with a polar probe [12,13]. Using the IGC to determine the surface energy has been applied to the characterization of solid surfaces in the past decade [14].

Mohammadi-Jam et al. [15] selected three size ranges of quartz particles to measure their surface energy and flotation recovery, and finally the surface energy shows the consistency with the flotation results. Rudolph and Hartmann [16] introduced ΔG_{pwb} to evaluate the hydrophobicity of the mineral surface and pointed out that the amphiphilic collector reduced the high specific surface free energy of small fractions of the mineral surface. Nowak and Pacek [17] used the IGC to measure the surface energy of catalyst particles at elevated temperatures. Ho et al. [18] out-lined the relation between the fine particles loading and heterogeneity of the surface by using the IGC to obtain the surface energy index.

The use of surface energy in pure minerals such as quartz or medicine particles has been occasionally reported. And there are a few researches focused on the IGC technology and measurement of surface energy for mineral wettability. However, until now, there is no publication regarding the application of IGC in coal flotation recovery. Because the coal is not a pure mineral, so its surface is complex and extremely homogeneous [19], it is difficult to learn whether the IGC is suitable for the identification of coal wettability as well as its flotation recovery. In this study, five coals with different coal ranks were chosen as coal samples and the flotation recovery results of these five coal samples were got. The surface energy of the five coal samples were measured using the IGC. The hydrophilicity index was then analyzed to correspond to the flotation recovery.

2. Experimental

2.1. Coal samples

In order to investigate the potential regulation between the flotation recovery and the surface energy, five coals with different coal ranks were used as coal samples. The coal rank ranges from sub-bituminous coal to anthracite coal. The ash and moisture contents of five coal samples based on air-dry basis were presented in Table 1.

For coal flotation, low ash coal particle usually has a better floatability than high ash coal. In this paper, five coal samples have similar ash contents and the effects of ash content on coal floatability can be ignored. If these coal samples have different floatabilities, it should be caused by the difference in the surface energy between different coal samples. The purpose of this paper can be well reached using these five coal samples because they have similar ash content.

2.2. IGC instrument

The IGC instrument is a powerful technology which provides the information about a wide range of important physicochemical properties such as the thermodynamic interaction parameters, the BET surface area, the work of adhesion, the acid-base properties and the surface energy [20,21]. Also, it is a valuable method for characterizing the

Table 1

Ash and moisture contents of five coal samples (on air dry basis).

Sample name	Coal rank	Ash (%)	Mad (%)
Shanbula (SBL) coal	Sub-bituminous coal	10.59	2.87
Anyang (AY) coal	Bituminous coal	11.06	1.82
Shanghaimiao (SHM) coal	Bituminous coal	12.23	1.94
Caojiatan (CJT) coal	Anthracite coal	11.35	1.26
Juji (JJ) coal	Anthracite coal	10.87	1.63

surface properties of the powders more accurately compared with contact angle and Washburn technique. Furthermore, the testing sample remains intact during the experiment, for it measures the interactions between a solid and a liquid without destroying the powder surface. The IGC Surface Energy Analyzer, SEA (Surface Measurement Systems Ltd., UK) used in this paper, is equipped with the precisely controlled injection technology. The IGC instrument is made of gas supply, mass flow controller module, solvent reservoirs, SEA injection module, sample column and FID unit. The injections of probe vapor at different surface coverages would result in a distribution of surface energy profile.

2.2.1. Basic theory for IGC technology

IGC technology is based on a pulse method which can acquire the absorption information about the probe molecules on the sample surface, and the fundamental measurement for all pulse methods is depended on the net retention volume, V_N , where volume of the carrier gas is conducted to elute a probe through the column packed with the sample. The net retention volume V_N is calculated by Eq. (1).

$$V_N = \frac{j}{m} F(t_R - t_0) \frac{T}{273.15}$$
(1)

where *F* is the flow rate at the end of column, at 1 atm and 273.15 K, *T* is the temperature of column, t_R is the retention time for the probe, *m* is the mass of experimental material, t_0 is the dead time, which is obtained from the methane injection, and *j* is the pressure gradient correction James factor [22], t_R is indicated in Fig. 1.

The dispersive part (W_a^d) and the specific part (W_a^{sp}) make up the work of adhesion (W_a) . And the total surface energy (γ_l) also consists of dispersive component (γ^d) and the specific part (γ^{sp}) , which are defined by Eqs. (2) and (3) [23].

$$W_a = W_a^d + W_a^{sp} \tag{2}$$

$$\gamma_t = \gamma^d + \gamma^{sp} \tag{3}$$

Therefore, the free energy changes of adsorption (ΔG_a) would be determined by the polar and non-polar interactions relying on the property of the chosen solvents probes as Eq. (4).

$$\Delta G_a = \Delta G_a^d + \Delta G_a^{sp} \tag{4}$$

2.2.1.1. Dispersive surface energy. The Schultz approach employs a series of n-alkanes to determine the dispersive surface energy. It would result in the only existence of dispersive forces between the non-polar solvents, such as n-alkanes and the solid surface, under the condition of non-polar probes injection. Due to the absence of polar probes, the measured specific part of the free surface energy equals to zero $(\Delta G_a^{pp} = 0)$. Thus, the dispersive component would become the unique form of free energy changes of adsorption $(\Delta G_a = \Delta G_a^d)$, so the free energy of adsorption could be drawn as Eq. (5).

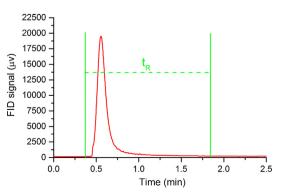


Fig. 1. The typical diagram of the n-alkenes elution process on a certain coverage to determine t_R for coal sample.

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