

DSC study of curing in smokeless briquetting

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Abstract

Briquettes potentially suited for smokeless fuel were successfully prepared from mixtures of previously pyrolyzed coal and biomass, and mixed with sugar cane molasses as binder. Briquettes were cured at 200°C in air for different times, and the physical performance of the cured briquettes were studied using the water and impact resistance tests (WRI and IRI). Since curing was an exothermic process, the residual heat of reaction evolved was considered to be an indication of the degree of curing. In this work, the degree of curing as a function of time was monitored quantitatively, measuring the residual heat of reaction at each condition studied by differential scanning calorimetry (DSC), and compared with the physical characterization. The results implied that the technique did not give a fast alternative to WRI and IRI tests, but was very useful in describing the mechanism by which the molasses behaved as binders. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lignite and subbituminous coals can be converted from a somewhat limited material to compact briquettes with better utilization of its properties, such as handling, storage and a higher calorific value [1]. The main problem of the coal from Teruel basins, as it is known, is the high sulphur content. However coal can be briquetted with biomass, reducing in this way the sulphur content, while keeping a similar calorific value. Briquettes potentially suited for smokeless fuel are successfully prepared from mixtures of previously pyrolyzed coal and biomass, and mixed with sugar cane molasses. In this way, the low grade lignite dust can be converted into compact and stable fuel of a

higher quality which can be used for domestic and industrial purposes. Special attention has been paid to the amount of sulphur and its distribution in products (carbonized, gases and ash). This study is a part of a broader study focused on the optimization of mechanical properties and sulphur distribution in the coal–biomass briquettes [2].

The present work is concerned with a study of the mechanism by which molasses behave as a binder over the carbonized material, using a different approach. Since curing is an exothermic process, the heat evolved can be detected quantitatively by differential scanning calorimetry (DSC). The degree of curing can be monitored by measuring the residual heat of reaction at each condition studied. DSC has been used for a long time to study the degree of curing and vitrification of polymers [3,4]. The cure kinetics can be also studied using various non-isothermal DSC scans,

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which allow the calculations of the activation energy [5,6]. DSC has been used as well to interpret the interlocking phenomena, by which the network of certain polymeric materials is formed involving incomplete curing [7]. Crosslinking and degree of cure of thermosetting materials can be described by the quantification of exothermic peaks by DSC [8]. The technique developed for polymers seemed to be suitable for the study of molasses curing in smokeless briquettes.

A better understanding of the physics and chemistry of briquetting could lead to better binder performance, taking into account the cost-effectiveness and the range of coals which could be briquetted successfully [9]. One most important characteristics of all types of agglomerates is their strength. All values obtained by methods designed to characterize the mechanical properties, are empirical and theoretical predictions because the strength component that causes agglomerate to fail it is not well known. The relationship between physical performance of briquettes and degree of cure obtained by DSC is described in this work.

2. Experimental

The material used was prepared by co-pyrolysis at 600°C of Maria coal (Teruel basins) and olive stone in order to reduce the sulphur content and increase the high calorific value of the material. Pyrolysis was carried out in a swept-out fixed bed (200 mm length \times 20 mm i.d.) under Argon heated at a rate of 10°C/min. Molasses obtained as a by-product of sugar cane production were used as binder. A mixture of 75% char and 25% molasses were briquetted in a press at 125 MPa. CaCO₃ is added to char in an atomic ratio of Ca/S = 1 as adsorbent for sulphur oxides produced in the combustion. Green briquettes were cured at 2°C/min until 200°C in air atmosphere and the curing time varied from 1 min to 4 h.

The briquette strength was studied from the impact resistance test. Each briquette is repeatedly dropped from 2 m height until it fractures. The number of pieces the briquette breaks into is recorded. These data are then used to calculate what is called the impact resistance index (IRI). For laboratory work, an IRI value of 50 was adopted as the lowest accep-

table impact resistance for fuel briquettes being developed for industrial or domestic applications [10]. All the briquettes studied passed this test, successfully (i.e., briquettes did not break after 10 drops), but another parameter can be obtained from the test, the percentage of mass lost in the ten drops.

A simple immersion-in-water test on a single briquette was adopted to evaluate the resistance against disintegration and absorption of water. A weighed briquette was immersed in cold water and checked for any tendency to disintegrate by applying finger pressure at 10 min intervals. If the briquette survives 30 min immersion, it was withdrawn, wiped to remove surface moisture and re-weighed. The water resistance index was defined as 100% water absorbed, a value of 95% was accepted as a target value [10].

Calorimetric measurements were performed using a DSC 2960 TA Instruments. The calorimeter was previously calibrated with a sapphire standard. The sample weights were 10 mg. After isothermal curing, the samples were quenched to room temperature, introduced into the DSC, equilibrated at 25°C and then scanned at a heating rate of 20°C/min from 25 to 450°C.

3. Results

Fig. 1 shows the weight loss and DSC curves of the cured briquettes at 200°C for different times. Under the conditions used for this experiment, the curing reaction began at about 300°C and was observed as a large exothermic peak in the temperature range up to

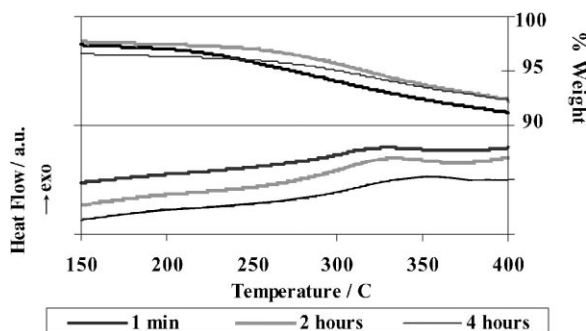


Fig. 1. DSC scans of briquettes cured at 200°C for 1 min, 2 and 4 h: variation of heat flow and weight with temperature along scan (heating ramp of 20°C/min).

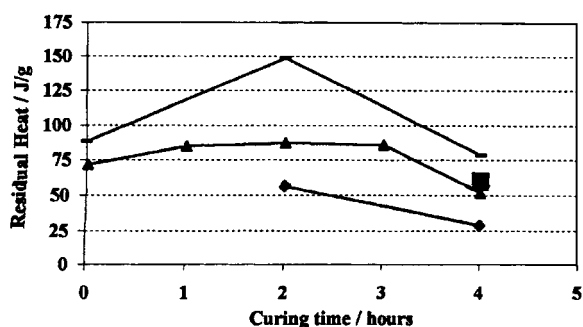


Fig. 2. Effect of curing time at 200°C over the residual heat flow in J/g for briquettes: (▲) 75% char–25% molasses, (■) briquette without CaCO₃, (◆) 75% recarbonized char–25% molasses, (-) molasses.

350°C. Provided the area under the peak gave a measurement of the amount of reaction remaining in the sample, it was clear that complete curing was not reached even after 4 h at 200°C.

The total heat of reaction was determined by integration of each curve corrected for mass loss, the results are shown in Fig. 2. Results show that the same degree of curing reached in 1 h, as measured by the remaining heat of reaction, was reached after 3 h; it was necessary to cure briquettes for 4 h to observe a decrease in peak area. No information could be obtained from peak shape, provided peak heights (proportional to maximum reaction rate) were very similar.

On the other hand, DSC peak exotherms (Fig. 3) shift to higher temperature as curing time increased,

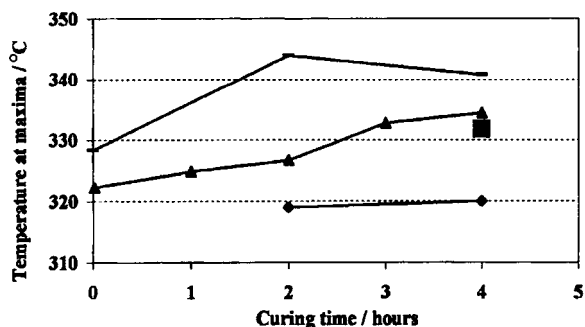


Fig. 3. Effect of curing time at 200°C over the temperature at peak maxima for briquettes: (▲) 75% char–25% molasses, (■) briquette without CaCO₃, (◆) 75% recarbonized char–25% molasses, (-) molasses.

which indicated that although peak areas were similar, higher curing times involved a different mechanism of crosslinking, since the reaction occurred at higher temperatures. This behaviour showed the double activity of molasses as binder; matrix type and chemical type. Molasses, basically disaccharides with a certain proportion of mono- and polysaccharides, can polymerize under temperature treatment, behaving as a ‘glue’ or matrix for the char particles. On the other hand, these functionalities could find electrophilic sites onto char surface and establish chemical bridges.

In order to study the mechanism of formation of linkages between the molasses and char, briquettes of different mixtures were prepared. First of all, the possibility of CaCO₃ added to briquettes acting as basic sites to establish a linkage was studied. One briquette without the addition of CaCO₃ was prepared and cured for 4 h. The remaining heat of reaction of this briquette was only slightly higher than that obtained for the pellet with the same composition of briquettes, and the difference in peak maximum was negligible as well (see Figs. 2 and 3, points marked as ■), so the effect of CaCO₃ on the mechanism of curing was rejected.

Another possibility for study is the role of oxygenated groups on the char surface behaving as nucleophilic sites for electrophilic saccharide groups from molasses. Although chars come from pyrolysis at 600°C, it is known that this type of materials will release CO and CO₂ up to 1000°C, confirmed by temperature programmed desorption coupled with gas chromatography [11]. The char was recarbonized in the furnace at 1000°C for 10 min under an inert atmosphere. The DSC results of the briquettes made with the recarbonized char, cured for 2 and 4 h, are shown as well in Fig. 2. The remaining heat of reaction for each curing time is clearly lower than those from parent briquettes. This would seem to imply that the chances of functionalities of molasses to interact with char have decreased. Taking into account how peak maxima appear at lower temperatures (Fig. 3), the conclusions would be that the polymerisation occurs at temperature lower than the chemical crosslinking.

To study the behaviour of molasses on their own, they were heated at 2°C/min and then cured for different times. The areas under the peaks (Fig. 2) of DSC runs do not show the same trend as for briquettes, but a rather random behaviour. Visual

Table 1
Remaining heat or reaction in briquettes and molasses as a function of curing time, compared to weigh loss at impact resistance test and water resistance index (WRI)

Curing time	Briquettes			Molasses (J/g)
	J/g	IRI(%w.l.)	WRI	
Green	34.5	0.43	— ^a	— ^b
1 h	81.3		92.63	
2 h	80.6	0.06	93.87	148.7
3 h	80.8		93.81	
4 h	59.2	1.1	90.79	78.5

^a Water color indicated that part of molasses solubilized, so tests were useless.

^b Drying weight loss overlapped heat flow signal.

observation of samples confirmed that molasses cake as thin dry bubbles all over the platinum pans. Provided that curing consists of an interaction of a binder onto the electronic compatible sites of a substrate, heating the molasses involves a fast polymerization and crosslinking not comparable to curing.

So, in the case of the green briquette, where the molasses are into the inner porous surface of char by the action of pressure, it should present a high exothermic peak under DSC treatment which would mean the complete degree of reaction, or total curing. Unexpectedly, the results were the opposite. Green briquette showed a flat peak of heat of curing, with low area as show in Table 1. The briquette was prepared and the DSC experiment runs were repeated twice to confirm this result (second run, 39.03 J/g at 325.7°C). In this way it was clear that molasses only behave as real binder when dried slowly once imbibed into the char.

Apart form mechanistic studies, the interest of this experiment is to study the possibility of the DSC characterization of residual heat of curing to correlate with mechanical properties of briquettes. In Table 1, DSC peak areas are compared to the weight loss at the impact resistance index (IRI) and to the water resistance index.

As mentioned above, all briquettes passes the IRI test (IRI > 1000) and the water test (resistance to finger pressure after 20 min under water). But taking into account the results shown in Table 1, it is clear that 2–3 h curing time gave the least mass loss at impact and water tests. As it can be seen in Table 1, there is no relationship of curing degree and physical behaviour of briquettes. These results imply that this technique cannot give a fast alternative to IRI and WRI tests. Nevertheless, as seen above, it can be very useful in describing the mechanism by which the molasses behave as binders.

Acknowledgements

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