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Study of the reactivities of chars from sulfur rich Spanish coals

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Abstract

Large coal reserves in Spain are an important source of energy. Their mediterranean coals are characterized by a high sulfur content. Thus, the combustion of these coals can cause serious environmental effects due to the release of SO_x. Coal gasification with advanced technologies has the potential to provide a clean fuel that produces electric power while minimizing the emission of air pollutants. The measurement of char reactivity associated with coals is essential when the gasifier design and fuel efficiency has to be optimized in the industrial process. In this paper we use a procedure (particle size ca. 500 μm, sample mass 15.5 mg, CO_2 and air reactant gases, near isothermal conditions) to determinate the reactivity of chars from Utrillas subbituminous coal, Calaf and Mequinenza lignites by thermogravimetry at 900 °C. The procedure also provides proximate analysis information which allows to establish the suitability of these coals for the gasification process and affords a quick comparison between different coal types. This paper presents the results of the reactivities of chars from three coals from Spain and describes the main properties of these coals which influence the gasification process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry; Char; Mediterranean coal; Reactivity; Sulfur rich

1. Introduction

The key for a successful design of gasifier is to understand the properties and thermal behavior of fuel as fed to the gasifier. The properties of fuel which influence the gasification process are reactivity, calorific value, moisture, volatile matter, ash content and composition.

In this paper, we calculate the reactivity obtained by thermogravimetry and describe other properties to assess the suitable coals for the gasification process. The aim of coal gasification is to convert coal into a combustible gas, suitable for use as a fuel. The simplest way to obtain a combustible gas from coal is to carbonize the coal, that is, to heat it in the absence of air.

Understanding the reactivity of chars is essential for the efficient design of gasifier and fuel efficiency in industrial processes [1,2]. Char in this paper refers to the devolatilized product of coal at 900 °C. Reactivity is defined as the rate at which coal reacts in an oxidizing atmosphere, subsequent to devolatilization and determines the rate of reduction of carbon dioxide to carbon monoxide in the gasifier. Rank of coal exerts a major influence on char reactivity, with low rank chars being typically more reactive than those prepared from high rank coals [3]. However, coal type, mineral matter, char preparation method, pore struc-

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ture and reactant gas also exercise different effects [4–6].

A comparison of quantitative results of the reactivity of chars from mediterranean sulfur rich Spanish coals by thermogravimetry has been determined. On the other hand, the most gasification processes are designed to produce electricity at low cost and high efficiency from low rank coals with low and moderate calorific values [7,8]. The most of biomass fuels have heating values in the range of 10–16 MJ/kg, whereas liquid fuels posses higher heating values [7].

In addition, the proximate analysis of coal is a fundamental and internationally recognized aspect of coal characterization involving the determination of four parameters, i.e. moisture, volatiles, fixed carbon and ash (derived from the inorganic mineral contents). Ash content and composition have impact on smooth running of a gasifier. Melting and accumulation of ashes in the reactor causes slagging and clinker formation. No slagging occurs with fuel if the ash content is below 5% [8,9]. Volatile matter and inherently bound water in the fuel are produced in the pyrolysis zone at the temperatures from 100 to 150 °C forming a vapor consisting of water, tar, oils and gases.

Charcoal contains a lower percentage of volatile matter (3–30%) compared to other materials such as crop residue: 63–80%, wood: 72–78%, peat: 70% and coal: up to 40–45%, which produces more tar and consequently causes problems to the internal combustion engines [8,9].

Higher ranking coals means less contained water, more carbon and consequently higher economic value, however ash content and volatile matter (principally hydrocarbons) are also important in order to define their quality. The determination of these parameters by thermogravimetry (TG) [10] gives an example of the variable atmosphere thermal analysis technique.

The samples selected for this study are the following: (a) Utrillas subbituminous coal are taken from the Maestrazgo basin, located in the Iberian Range linking zone with the southernmost sector of the Catalan coastal range, deposited during middle Albian (Lower Cretaceous, ca. 105 Ma) [11]; (b) Calaf lignite belongs to La Segarra Lacustrine System (Eastern Ebre basin) and was deposited during early Oligocene (ca. 35 Ma) [12] in a lacustrine basin; (c) Mequinenza lignite bearing sequence is included in Los Monegros Lacustrine System (SE Ebre basin) and was deposited during late Oligocene (ca. 30 Ma). Evaporitic facies were developed mainly in the marginal lacustrine zones while carbonate and lignite deposits were dominant in inner lacustrine areas [12]. Mequinenza coal has generated substantial interest because of its high sulfur content [13]. According to Dulong formula [14] Utrillas, Calaf and Mequinenza coals have moderate calorific values calculated on moisture and ash free basis: 25, 18 and 23 MJ/kg, respectively.

2. Equipment and method

The equipment used in this study was a CAHN thermobalance TG-151. The specifications of the equipment are: balance capacity: 100 g; sensitivity: 10μg; maximum temperature ($P = 1$ bar): 1100 °C; maximum heating rate: 25 K/min; crucible: quartz (CAHN).

According to Shaw et al. [4], amounts of 15.5 ± 0.01 mg for each sample were weighted into a quartz crucible and placed within the thermobalance. The thermobalance was flushed with nitrogen for 5 min, and the sample was heated in nitrogen (0.2 l/min) to 110 °C at 25 K min^{-1}.

The sample was held at 110 °C for 5 min and then heated to 900 °C (at 25 K/min) where it was held for further 10 min to ensure that all volatiles were driven off and a constant weight attained. The char was then kept at 900 °C and the atmosphere changed to dry air or carbon dioxide (0.2 l/min). Weight changes were monitored as a function of time.

The temperature plateau at 110 °C allows the moisture content of the coal to be calculated as the weight loss [15]. The volatile matter is calculated from the change in weight between the moisture calculation point and that at which the reactant gas is introduced. Ash is determined by re-weighing the crucible after completion of the reaction. This procedure allows both proximate analysis and reactivity data to be obtained from the same test (Fig. 1).

A run was made for all the procedures with an empty crucible which was then subtracted from each sample run. This removes the effects of buoyancy in the system that occurs due to the change of density in the furnace atmosphere.

The maximum rate of fixed carbon loss along with the maximum rates of moisture and volatile loss may

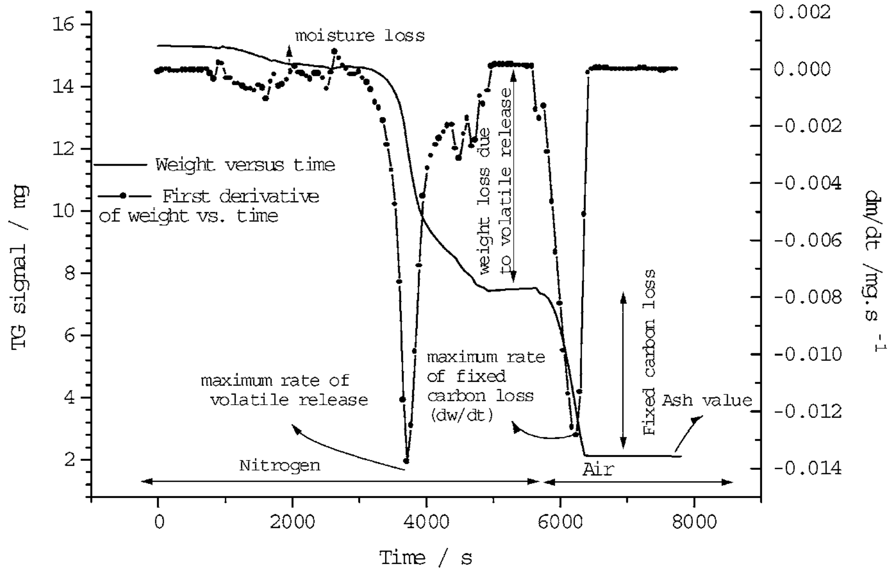

Fig. 1. Characteristics of thermogravimetric reactivity analysis of Mequinenza lignite in dry air at 900 °C.

Table 1
Proximate analyses of Utrillas, Calaf and Mequinenza coals

Coal sample	Moisture (%)	Volatile (%)	Fixed carbon (%)	Ash (%)	Volatile (%) DAF	Fixed carbon (%) DAF
Utrillas	4.6	38.2	41.4	15.9	48.0	52.0
Calaf	13.1	41.0	30.3	15.6	57.5	42.5
Mequinenza	4.6	46.5	35.1	13.8	57.0	43.0

be calculated from the first derivative of experimentally derived weight trace. Reactivity can then be calculated according to the formula $R = -W_0^{-1}$ $(\mathrm{d}w/\mathrm{d}t)$ [4,16,17] where R is the maximum reactivity, W_0 the initial weight of the char on a dry ash-free (DAF) basis and $\mathrm{d}w/\mathrm{d}t$ the maximum rate of fixed carbon loss. R expressed in h^{-1}.

3. Results and discussion

Proximate data for the Utrillas, Calaf and Mequinenza coals are shown in Table 1. Table 2 shows the percentages of C, H and S on dry and ash free basis for all three mediterranean coals selected for this study. Reactivity results in dry air and carbon dioxide are given in Table 3.

In reference to the characterization of rank coals by proximate analysis it must be noted that lower volatile matter and a higher content of fixed carbon in Utrillas coal when compared with Mequinenza and Calaf coals, reflects its subbituminous rank [18]. The percentage of inherent moisture in Calaf coal is slightly higher than those obtained in Mequinenza and Utrillas coals, however all percentages are below 15% by

Table 2
C, H and S percentages on dry and ash free basis (DAF) of Utrillas, Calaf and Mequinenza coals

Coal sample	C (%)	H (%)	S (%)
Utrillas	73.2	5.8	5.4
Calaf	53.1	3.4	15.1
Mequinenza	60.6	5.3	13.4

Table 3

Reactivities of Utrillas, Calaf and Mequinenza coals in dry air and carbon dioxide at 900 °C where W_0 is the initial weight of the char on a dry ash-free (DAF) basis, dw/dt the maximum rate of fixed carbon loss and R the maximum reactivity

Coal Sample	W_0 (mg) DAF		dw/dt (mg s^{-1})		Reactivity DAF/h^{-1}	
	Air	CO_2	Air	CO_2	Air	CO_2
Utrillas	10.9	11.1	0.016	0.0049	5.3	1.6
Calaf	10.0	11.2	0.018	0.0055	6.4	1.8
Mequinenza	9.1	8.9	0.016	0.0047	6.1	1.9

weight which could be desirable for economical operation of the gasifier because higher moisture contents reduce the thermal efficiency and the gas quality is also poor [7].

On the other hand, these Spanish coals contains significant amounts of ash (<16%) compared to other coals such as New Zealand coals (<2%) [4] which could cause serious problems of disposal and to the internal gasifier. However, these problems become less significant if a way can be found to utilize the ash through resource recovery programs [19]. Using coal ash conserves energy by reducing the demand for typical pavement materials such as lime, cement and crushed stone, which takes energy to produce. Industry experts estimate that using 1 ton of ash avoids about 1 ton of carbon dioxide emitted from cement production [19]. Consequently, less greenhouse gases are produced that would otherwise contribute to global warming. Also, by gasifying "dirty fuels", such as liquid or solid refinery residues and coals with a high ash content, application of a combined-cycle power plant is an innovative, "clean coal" technology which aims to produce electricity more efficiently, more economically and with less environmental impact than conventional methods [20]. In the Spanish (Puertollano) integrated gasification combined-cycle (IGCC) Power Plant a mixture of local high-ash coal and petroleum coke from the nearby refinery is gasified [20]. The ability to use a broad spectrum of fuels can contribute to solve disposal problems, which makes this form of power production particularly attractive.

As it is shown in Table 3 the reactivity of Spanish coals in air is about three times higher than in carbon dioxide whereas New Zealand coals are two times higher as a maximum [4] indicating that Spanish coals could be more suitable than New Zealand coals for the gasification process. Intercomparison between different coals can be made because the combustion reaction of these Spanish coals in our device is controlled by the chemical reaction [21].

The higher rank Utrillas coal has the lowest reactivity, which is a trend consistent with the increasing reactivity with decreasing rank as it has been reported by different authors [4]. However, mineral matter can also exert influence on the reactivity. There are a number of elements which act as catalyst and influence the gasification process. Small quantities of potassium, sodium and calcium can have large influence on reactivity of the fuel [3,22]. The behavior of the basic inorganic elements (alkali, Ca, Fe) is strongly dependent on their form in the coal. Carboxyl bound alkalis, for instance, are known to volatilize and to be subsequently adsorbed by aluminosilicates derived from clays [23].

Mequinenza and Calaf coals are characterized by a high content of Fe (as pyrite) and Ca (as calcium sulfate or carbonate) detected by SEM-EDX analysis [24,25]. Many authors have reported that pyrites coalesce with clay–silica minerals to form iron–potassium aluminosilicates under combustion conditions [26]. Under reducing atmosphere, the fluxing action of iron content is even more effective: iron decomposition products favor the formation of very fusible silicates [27] depressing the melting point of ash between the temperature range 900–1400 °C.

The presence of pyrite in Utrillas and Calaf coals seem not to have an enhancement effect of the reactivity with carbon dioxide atmosphere at 900 °C because Calaf and Mequinenza coals show different percentages of pyrite (1.13 and 0.4% pyritic sulfur, respectively) and the reactivities measured in carbon dioxide are similar at 900 °C (Table 2). However the presence of iron as pyrite might increase these reactivities at higher temperature as it has been reported by different authors [3].

Calcium, a well-known catalyst for the gasification reaction, could influence the highest reactivities in Calaf and Mequinenza coals, mostly present as calcium sulfate or carbonate and detected by SEM-EDX analysis [24]. Thus, Mequinenza coal has the highest reactivity in carbon dioxide.

4. Conclusions

Char reactivities have been measured by thermogravimetry from one subbituminous coal and two lignites under dry air and carbon dioxide atmospheres, reaching the following conclusions: (a) around 900 °C the reactivity in dry air increases about three times compared to those obtained in carbon dioxide. Mequinenza and Calaf coals have the highest reactivities (ca. 6); (b) Mequinenza coal has the highest reactivity in carbon dioxide atmosphere (1.9).

While this work is in the preliminary stage, the indications are that Mequinenza and Calaf coals could be the most suitable for the gasification process and conversion of these high sulfur coals to an environmental clean fuel. Despite of its high ash content, these coals could be suitable for the integrated gasification combined-cycle (IGCC).

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