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Dolomite effect on steam co-gasification of olive pomace, coal and petcoke: TGA-MS analysis, reactivity and synergistic effect

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ABSTRACT

The dolomite effect on the co-gasification process for binary and ternary blends of coal, petcoke and olive pomace was studied by thermogravimetric analysis (TGA) coupled with mass spectrometry (MS). Additionally, gas emissions, the synergistic effect and the residue morphology obtained were also evaluated. Ternary blends showed lower weight loss and higher reactivity than binary ones during gasification. Weight loss in the binary and ternary blends containing dolomite was lower than in the parent ones. Regarding gas emissions, the highest H_2/CO ratio and the lowest sulphur and nitrogen compound emissions were obtained for the binary blend of petcoke and olive pomace containing dolomite. On the other hand, the highest synergistic effect was observed in the binary blend containing dolomite. To sum up, the best results were obtained when dolomite was in the blend in which the higher H_2/CO ratio, synergistic effect and reactivity and lower pollutant emissions were observed. Finally, the residue obtained from the co-gasification process could be used as an adsorbent for removing pollutant gases.

1. Introduction

Despite the rise in population worldwide, standards of living have improved in recent decades. This has led to a higher demand for energy. To date, almost 80% of the demand for energy has been satisfied by fossil fuels, which are non-renewable and whose combustion contributes to the emission of greenhouse gases (GHG). For this reason, the European Union has set two goals for 2030: to increase the use of renewable energies until they make up 27% of total energy consumption and to reduce CO_2 emissions by 40% in comparison with 1990 levels [1,2]. Although, energy resources such as solar, wind, geothermal and nuclear energy are an alternative to generate heat and power, they cannot produce gaseous, liquid or solid fuels. In this context, biomass has been deemed one of the few viable options there are for replacing fossil fuels. Among all types of biomass, agro-industrial wastes are obtained in large quantities from the industrial processing of fruit. In Spain, olive pomace is a suitable option as the olive oil industry is one of the most important industrial subsectors in the country. Olive oil production in Spain represents 45% of total worldwide production, and generates a large amount of seasonal waste [3].

Nowadays, the most common technique of obtaining clean syngas is by steam reforming of natural gas. Nevertheless, natural gas can also be used directly as an alternative fuel [4]. In this respect, steam gasification of biomass for the production of clean syngas should be an interesting alternative from an environmental and financial point of view. This can be defined as the thermal degradation of biomass at a high temperature, which leads to intermediate products such as bio-oil and end products such as syngas, among others. However, industrial gasification of biomass is limited due to both its lower calorific value and energy density, and its higher tar yield, unstable supply and the heterogeneity of biomass as a raw material.

In this sense, co-gasification of coal and biomass can improve the performance of biomass gasification, thereby reducing its seasonal shortage [5]. However, petroleum coke or petcoke (PC) is a refinery by-product whose production has increased in recent years due to the increasing demand for petroleum [6]. PC consists in polycyclic aromatic hydrocarbons with high carbon content. It has a high calorific value and availability, low ash and hydrogen contents and a low price. However, one of its main drawbacks is its high sulphur content. Moreover, the high volatile matter present in biomass and the high fixed carbon content in petcoke makes their co-gasification attractive in terms of high-quality syngas production. In this regard, co-gasification of coal, petcoke and olive pomace is one of the alternatives to solve problems associated with gasifying each of them separately. Furthermore, studying the synergetic effects in co-gasification is essential to the development of co-gasification technology [7–10].

On the other hand, catalysts are often used in thermochemical conversion processes such as pyrolysis or gasification processes in order

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to improve the quality of gas products which are given off, which promotes tar and hydrocarbon reactions [11]. In industrial or bench scale processes, catalysts can be added to the gasifier or to a secondary reactor to treat the products generated [12]. Using catalysts can increase the operational costs of the process, so a detailed search for a suitable catalyst should be carried out. In this respect, there are synthetic catalysts that provide excellent results, but as the cost of using them is high and the operating conditions needed for them to perform optimally are restricted, using them on an industrial scale is not recommended. Natural catalysts can lead to good catalytic performance and, also, they are usually less expensive and more environmentally-friendly than synthetic ones [13]. Among these, dolomite is one of the most used catalysts because it is an inexpensive, natural and abundant mineral [14]. Moreover, dolomite promotes hydrocarbon reforming reactions during gasification, decreasing tar production and the concentration of gaseous hydrocarbons in the gas phase [15–17].

Some recent studies have been focused on the co-gasification process with different raw materials. Wei et al. (2017) studied the effects the blended ratio had and combining the gasification temperature and the blended ratio in co-gasification reactivity of petroleum coke, char and rice straw by means of TGA [18]. Ren et al. (2017) analysed how reactivity and synergetic effects influenced co-gasification of petcoke and coal [10]. A comparison between binary and ternary blends of olive pomace, coal and petcoke. was recently reported by our research team [19].

On the other hand, the effect dolomite has on the gasification process has also been studied. Chunguang et al. (2017) selected dolomite bed material for biomass gasification [20]. Conesa et al. (2015) studied the gasification and pyrolysis process with dolomite [21]. Biomass steam gasification over NiO/ Dolomite in hydrogen rich gas production was recently reported [17]. Chiodo et al. (2017) analysed syngas production by catalytic steam gasification of citrus residues using dolomite as a catalyst [22]. In all these studies there were better results when dolomite was present.

Despite the works listed above, there have been few reports comparing the effect the presence of dolomite has on co-gasification for different binary and ternary blends [23]. In this work, catalytic and non-catalytic co-gasification of binary and ternary blends of coal, petcoke and olive pomace have been compared in terms of reactivity, outlet-gas emissions, H_2/CO ratios of the effluent and, synergistic effect and ash morphology was carried out.

2. Materials and methods

2.1. Materials

The raw materials used in this research were olive pomace obtained from “Aceites Garcia de la Cruz” olive oil mill, Madridejos (Toledo, Spain), coal from Puertollano mines (Ciudad Real, Spain), and petcoke from a refinery. These samples were dried in an oven for 5 h, milled and sieved to an average particle size of between 100 and 150 µm. Additionally, dolomite was used as a catalyst and was purchased from the company, Sigma-Aldrich.

The ultimate analysis and the proximate analysis were carried out according to standards UNE 15104:2011, UNE–EN ISO18123, UNE 32–004-84 and UNE 32002–95, while the metal content in the samples was determined by inductively coupled plasma spectrometry (ICP). The proximate analysis, the ultimate analysis and the metal content in the samples are listed in Table 1. Table 2 shows the composition of the blends prepared here and the name used to identify them.

2.2. Equipment and procedures

2.2.1. TGA-MS analysis

Co-gasification of the samples considered here was carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO) coupled with a mass spectrometer (Thermostar-GSD 320/quadrupole mass analyzer; PFEIFFER VACUUM). Each sample was analyzed at least three times, and the average value was recorded. The experimental error in weight loss evaluation was ± 0.5% whereas that for temperature measurement was ± 2 °C.

The co-gasification process was carried out in three different steps. Firstly, the moisture in the sample was removed at 105 °C. Then, the pyrolysis process was performed at temperatures ranging from 105 to 1000 °C and a heating rate of 40 °C/min with a constant flow of 200 Nml/min in an Ar atmosphere. Finally, the samples were subjected to a steam gasification process at 900 °C for 60 min. Steam was generated in a bubbler system. The Ar was bubbled through degassed water heated to 33 °C. Assuming that the Ar-$H_2$0 mixture was saturated, a gas stream with 5 vol% of water in Ar was obtained. The initial sample weight was fixed at 20 mg with particle sizes ranging from 100 to 150 µm. Finally, the gas produced during co-gasification was analyzed by means of a mass spectrometer (Thermostar-GSD 320/quadrupole mass analyzer; PFEIFFER VACUUM).

2.2.2. Char reactivity

Char reactivity was calculated with the following equation:

$$Ri = -1/wi{\cdot}dw/dt = (1/(1{-}xi)){\cdot}dxi/dt \quad (1)$$

where x_i and w_i represent the conversion and the weight of char at any time, respectively. Char reactivity, which depends on temperature and gas composition, describes the conversion trend throughout gasification. In this work, reactivity at 50% of char conversion (R_{50}) was considered for comparative purposes [24–28].

2.2.3. Scanning electron microscopy (SEM)

A Phenom ProX desktop scanning electron microscope (SEM) was used to evaluate the morphology of the samples.

3. Results and discussion

The co-gasification process for the coal, petcoke and olive pomace blends were initially studied in previous research [19]. Three binary blends and a ternary blend were evaluated in order to obtain the best one. Fig. 1 shows the thermogravimetric analysis and the H_2/CO ratio obtained during the co-gasification process for ternary and binary blends of coal, petcoke and olive pomace. Table 3 lists the reactivity parameter at 50% of char conversion (R_{50}) and the time required to achieve 50% char conversion (t_{50}). As regards the pyrolysis process (Fig. 1a), it can be seen that the weight loss in the binary blends containing olive pomace (samples 50B0C50P (43.42 wt%) and 50B50C0P (13.26 wt%)) was higher than that observed in sample 0B50C50P, which was directly associated with the biomass content. In this sense, the weight loss detected in the ternary blend was the highest one. Regarding the gasification process (Fig. 1a), samples 50B25C25P and 50B0C50P displayed the greatest weight loss and the highest char reactivity (Table 3).

Moreover, the synergistic effect the blends had was also studied (Fig. 1b–e). Thus, the experimental and theoretical weight losses (wt.%) were compared. Theoretical data were calculated using the following linear correlation [29]:

$$Y_{th} = Y_{coal}F_{coal} + Y_{petcoke}F_{petcoke} + Y_{biomass}F_{biomass} \quad (2)$$

where F_{coal}, $F_{petcoke}$ and $F_{biomass}$ represent the fractions of coal, petcoke and olive pomace in the blends, and Y_{coal}, $Y_{petcoke}$ and $Y_{biomass}$ are the weight losses (wt.%) obtained by means of thermogravimetric analysis during the co-gasification process.

The theoretical and experimental weight loss data in sample 0B50C50P (Fig. 1b), constituted by coal and petcoke, practically overlapped, so synergistic or antagonistic effects were discarded. For its part, the TGA curves for sample 50B0C50P (Fig. 1c) also overlapped during the pyrolysis process. Nevertheless, in the gasification process,