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Synergestic effect in the steam co-gasification of olive pomace, coal and petcoke: Thermogravimetric-mass spectrometric analysis

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ABSTRACT

A comparison of the gasification performance of olive pomace, coal, petcoke and their binary and ternary blends was carried out by means of TGA (thermogravimetric analysis) coupled with mass spectrometry (MS). The thermochemical behavior of the raw materials was a function of their composition and inorganic content. Olive pomace had a low ash content, a high volatile content and a low moisture. Moreover, olive pomace presented the highest reactivity. On the other hand, olive pomace presented the highest H_2, CO, CO_2, CH_4 and NO emissions, while the highest SO_2 release was obtained with petcoke, showing the output stream coming from the gasification of coal the highest H_2/CO ratio. The presence of olive pomace in the blends improved their reactivity, increased the H_2 release and the H_2/CO ratio, and decreased the CO yield. A synergistic effect was observed in the gasification of the binary blend of olive pomace and petcoke. On the contrary, the gasification of the binary blend of olive pomace and coal presented an antagonistic effect. In ternary blends, either ssynergistic or antagonistic effects were observed, which depended on raw materials ratios in the feed. Finally, the lower the olive pomace ratio in the blends, the higher the porosity of the remaining residue was.

1. Introduction

The development of alternative renewable energies is linked to the growing climate change concern owing to greenhouse gas emissions. In addition, population growth and their socio-economic development require large amounts of energy, converting the biomass in one of the most viable options for a sustainable future.

Among all kind of biomass, the olive pomace is a suitable candidate in countries like Spain, which produces about 45% of worldwide olive oil production [1], generating large amount of seasonal wastes. In this sense, 1 ha of olive tree can produce about 2500 kg of olives and 875 kg of olive pomace. In 2015, the Spanish annual production of dry olive pomace was about two millions tons [2].

Thermochemical conversion of biomass is considered as one of the most promising processes for biomass utilization [3]. In this sense, the steam gasification is one of the most effective, clean and efficient processes to produce hydrogen and electric power from biomass. The interest in gasification of biomass is due to the higher power generation efficiency that can be produced in Integrated Gasification Combined Cycle plants (IGCC) compared to that generated in power plants of direct combustion and steam cycles [4]. In addition, the product gas from biomass gasification can also yield methanol or fuels through the Fischer-Tropsch process [5]. However, the industrial gasification of biomass is limited due to its lower calorific value and energy density, its higher tar yield, its heterogeneity as raw material and its unstable or seasonal supply.

On the other hand, coal gasification is a traditional and well-known technology. However, gasification plants must reduce their CO_2 emission from coal gasification as result of the Kyoto protocol and Paris agreement since they are responsible of about 44% of the global CO_2 emission [6]. A potential alternative to mitigate this situation could be to co-gasify coal and biomass.

On the other hand, the petcoke (PC) production has increased in recent years due to the increasing demand of crude oil (31 kg of petcoke are produced from 1 ton of crude oil) [7]. The PC is a black carbonaceous solid consisting of polycyclic aromatic hydrocarbons with high carbon content, high calorific value, low ash content, high availability, and low hydrogen content. In addition, it is being considered apart from its low price as an attractive feedstock for gasification [8]. Nevertheless, the low reactivity leads to expensive processes that operate at higher temperatures and longer times and require the use of catalyst [9]. In this regard, the co-gasification of coal, petcoke and olive pomace appear to be as one of the alternatives to gasify coal and petcoke in a more efficient way.

The first chemical step in the gasification process is the co-pyrolysis one. The co-pyrolysis process can affect the product distribution, the

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gasification reactivity and the char morphology, among others. In this sense, some studies have been focused on the co-pyrolysis of biomass and coal and its impact on the co-gasification reactivity. According to Zhu et al. [10], the highest gasification reactivity of biomass and coal blends was showed at 750 °C due to the presence of potassium. Krerkkaiwan et al. and Ellis et al. studied the effect of the pore structure in the co-pyrolysis process [11,12].

Other studies have been focused on the co-gasification process. In this regard, Pan et al. studied the co-gasification process using coal and biomass [13]. Trommer et al. analysed the pyrolysis and steam gasification kinetics of petcoke and estimated the corresponding rate constants [14]. Fermoso et al. studied the effect of different operating variables during the combined co-gasification of coal with biomass and petcoke [15]. Jayaraman et al. studied the gasification characteristics of petcoke and mixtures of coal-petcoke using thermogravimetry and mass spectrometry analysis (TGA-MS) [16]. Wei et al. studied the effects of the gasification temperature and composition on the reactivity of petroleum coke char and biomass mixtures by means of TGA [17]. Nevertheless, fewer studies have compared the steam co-gasification process of three different raw materials as that raised this one by considering binary and ternary blends olive pomace, coal and petcoke [8,18–20].

Recently, some researches focused on the reactivity and synergy in the co-gasification of coal and biomass have been reported. Thus, Hernández et al. evaluated the synergic effect in the co-gasification of biomass and coal-coke in an air gasifier [21]. Liwei Ren et al. studied the co-gasification of petcoke and coal at high temperature and evaluated the reactivity and the occurrence of synergy effects [8]. Zhang et al. reported the synergistic effect of the low-ash coal and K-rich biomass co-gasification using a TGA [22].

However, fewer studies have been reported comparing the synergistic effect in the gasification process of binary and ternary blends of olive pomace, coal and petcoke [15,19]. In this work, the gasification of three raw materials (olive pomace/coal/petcoke) and the comparison of co-gasification process of their binary and ternary blends were studied by thermogravimetric analysis (TGA) coupled with mass spectrometry (MS). A comparison of the composition of the gas evolved from the gasification of the raw materials and that coming from the co-gasification of their binary and ternary blends was performed. Moreover, the synergistic effect in the co-gasification process of binary and ternary blends was evaluated. Finally, the morphology of the remaining residue coming from the gasification of the raw materials and their blends were analysed.

2. Materials and methods

2.1. Materials

Three samples were used in this investigation. Olive pomace, coal and petcoke obtained from "Aceites Garcia de la Cruz" olive oil mill, Madridejos (Toledo, Spain), Puertollano mines, and the refinery of Puertollano (Ciudad Real, Spain), respectively. These samples were dried in an oven for 5 h, milled and sieved to an average particle size between 100 and 150 µm.

The ultimate analysis and proximate analysis was performed following the standard UNE 15104:2011, UNE–EN ISO18123, UNE 32-004-84 and UNE 32,002-95.The proximate analysis, ultimate analysis and content of metals of samples are shown in Table 1. In addition, the content of metals in the sample was determined by Inductively Coupled Plasma Spectrometry (ICP).

2.2. Equipment and procedures

2.2.1. TGA-MS analysis

The co-pyrolysis and co-gasification of samples were carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO). Each sample was analysed at least three times, and the average value was recorded. The experimental error of these measurements was calculated, obtaining an error of ± 0.5% in the weight loss and ± 2 °C in the temperature measurements. The olive pomace, coal and petcoke percentage in the sample to be gasified was modified keeping the petcoke/coal ratio in a constant value. This way, it was possible to obtain an optimal binary and ternary blend composition that allowed to establish possible synergies. The percentage used in the preparation of each blends as well as the samples denomination names are shown in Table 2.

The steam required by the co-gasification process was generated by passing the carrier gas (Ar) through the water contained in a system constituted by four bubblers connected in series immersed in a bath at controlled temperature (33 °C). This way, the saturation of the gas stream (5 vol.%) was completely achieved. Firstly, the sample was preheated at 105 °C and then kept at 105 °C for 10 min in order to remove its moisture content. Then, the sample was heated from 105 to 1000 °C at a heating rate of 40 °C/min under an Ar atmosphere with a constant flow of 200 N ml/min. The temperature was kept at 1000 °C for 10 min to ensure the completion of the pyrolysis process. Finally, the gasification step was performed under isothermal conditions (900 °C for 60 min) until the entire char was consumed. The initial sample weight was fixed at 20 mg with a particle size range of 100–150 µm.

The gas produced during the co-pyrolysis and co-gasification processes was analysed by means of mass spectrometer (Thermostar-GSD 320/quadrupole mass analyzer; PFEIFFER VACUUM). A comparison of the intensity peak areas obtained in the analysis of the different blends was performed by using a normalization procedure, thus allowing to obtain a semi-qualitative analysis of the effluent coming from the TGA device.

2.2.2. Char reactivity

Char reactivity was calculated by the following equation:

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

where x_i and w_i are the conversion and the weight of char at any time, respectively.

In this work, the reactivity at 50% of char conversion (R_{50}) was considered for comparative purposes [23–27].

2.2.3. Scanning electron microscopy (SEM)

The surface features and morphology of the samples were evaluated using a Phenom ProX desktop scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Physicochemical characterization of raw materials

The physicochemical analysis of the raw materials used in this research were carried out. Table 1 shows the ultimate analysis, proximate analysis and mineral content of coal, petcoke and olive pomace.

The main differences in the proximate analysis were found in the volatile matter (VM) and ash contents. The volatile matter content in olive pomace (80.73 wt.%) was higher than that in coal (18.83 wt.%) and petcoke (13.00 wt.%). A high volatile content can be related to the high reactivity of sample [19]. Petcoke showed the lowest VM content, which can be attributed to its low specific surface and porosity [28]. On the other hand, the coal sample presented the highest ashes content (41.10 wt.%), which is actually associated to the presence of natural inorganic substances. This content is higher than that detected for other types of coal which ranges from 7 to 20 wt.% [29]. This fact is directly related to the poor quality of the coal used in the present research. Moreover, the higher the ash content, the higher the occurrence of problems associated with fouling, corrosion and slagging are and the lower the calorific value is [30–32].