CATALYTIC COMBUSTION OF GRAPE SKIN WASTES IN A CONICAL SPOUTED BED COMBUSTOR

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Abstract - In this paper, catalytic combustion of grape skins and scrapes has been performed in a conical spouted bed combustor. Combustion has been carried out with inlet air temperature of 550 ºC using Pd/Al_2O_3 catalyst in the spouted bed regime. Combustion efficiency has been calculated from the concentration of CO_2, CO (% volume), monitorized by Testo 350 gas analyzer, in the exhaust gases.

Index Terms - Biomass waste, catalytic combustion; conical spouted beds; grape skin waste

I. INTRODUCTION

Wine sector generates a large amount of organic wastes, suitable for energy valorization, such as pomace constituted by skins and scrape obtained after the extraction of the grape juice [1]; lees; and vinasse precipitates generated in the clarification process of the fermentation and maturation of wine [2], and vinasse depleted of the wine obtained from the sludge washing waters and sewage sludge suitable for energy valorization. Vineyard (Vitis vinifera) is one of the most important fruit crops of the world, with a worldwide extension of 7.5 million Ha of cultivated lands a global grape production of almost 76 million tons and wine production of 241 million of hl in 2016 [3].

Thermal treatment of renewable fuels allows to increase the added value of these wastes by energy valorization. The challenge of thermal treatment is provide a sustainable technology with high efficiency. Incomplete combustion of biomass combustion might result in the emission of environmental pollutants such as CO, CH4, polycyclic aromatic hydrocarbons (PAHs), and volatile and semi-volatile organic compounds (VOCs). Noble-metals based catalysts such as Pt and Pd have been proven to have high activities for removal of VOCs from exhaust gases at low temperature [4].
The mechanism of catalytic oxidation of CO over Pd/Al2O3 can be expressed by reactions (1)-(3). CO and the O2 are chemisorbed giving the substrate-catalyst complexes by the Langmuir-Hinshelwood mechanism. However, CO is adsorbed more strongly than oxygen.
CO (g) + M □===□ CO-M (1)
O_2 (g) + 2M □===□ 2 O-M(2)
CO-M + O-M ===□ CO_2 (g) + 2M (3)

where M is the sorption position on the surface of the catalyst. The overall reaction for the oxidation of CH_4 is expressed by eq. (4). Although some authors proposed that CH_4 oxidation happens via the Eley-Rideal mechanism, with not all reactive adsorbed on the catalyst surface [5], other authors reported that CH4 oxidation occurs by means the Langmuir–Hinshelwood mechanism [6] in which O_2 is adsorbed quickly and irreversibly on the Pd catalyst, whereas CH_4 is adsorbed slower [7-8]. However, other authors reported that CH_4 oxidation takes place via the Mars and van Krevelen redox mechanism, where the catalyst oxidizes CH_4 while the oxidation state of the catalyst is maintained by O_2 [9-11].
$CH_4 + 2O_2$ ----□ $CO_2 + 2H_2O$(4)

Spouted bed is a clean technology suitable for gas-solid contact of coarse solids, of irregular texture or sticky, of a wide particle size distribution [12], due to the vigorous cyclic movement of the particles breaks agglomerates in the spout allowing efficient gas-solid contact, avoids problems inherent to fluidized beds, such as segregation [13], and defluidization and provides high degree of turbulence in the bed. This technology presents a technological innovation. It has low energy consumption, has easier and more economic construction and operation than other systems used for thermal valorization of wastes (such as moving beds, rotary kilns, or fluidized beds). Moreover, combustion in spouted beds can be performed without inert material. This technology has been satisfactorily applied for catalytic beds [14-15] and because of the high mass and energy transfer it has been performed successfully for thermal treatment of biomass wastes by drying [16-18] and by combustion [16, 19-21].

II. EXPERIMENTAL

The thermal treatment has been conducted in a experimental unit, Fig. 1, which comprises a conical combustor, a blower, two high efficiency cyclones, an electrical preheater and thermocouples. The conical combustor, Fig. 1, is made of AISI-310S stainless steel, it has an angle of 36º, base diameter of 0.03 m and inlet gas diameter to inlet dryer diameter ratio, D_o/Di, 1/2, 2/3 and 1, and it is externally insulated to reduce heat loss. Biomass used has been wastes of grape skins and scrapes obtained during the pressing of the grape to

obtain grape juice, Fig. 2 with a density of 1050 kg/m^3, a mean Sauter diameter, ranging from 3 to 7 mm and a moisture content of 125 wt% (dry basis) measured by Mettler Toledo HB43-S Halogen hygrometer.

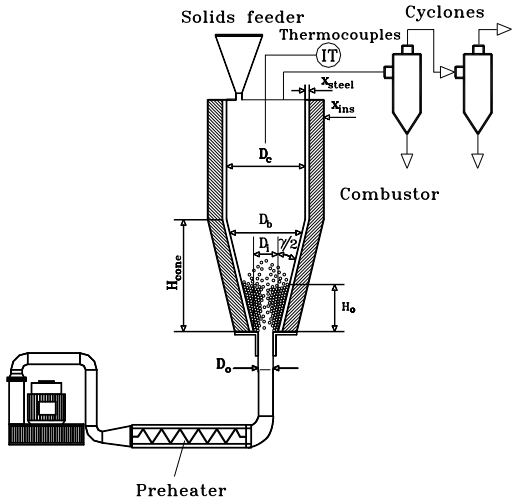


Fig. 1. Schematics of the experimental plant and of the conical spouted bed combustor with an outline of solid particles movement in the spouted bed regime.



Figure 2. Particles of grape skins and scrapes.

III. RESULTS

In order to perform the combustion in a conical spouted bed reactor, the operating regimes for beds consisting of grape skins for thermal exploitation have been determined in a pilot plant provided with the conical spouted bed contactor. The stable regimes have been delimited from the evolution of pressure drop with air velocity, Figure 3, measured by increasing gas velocity from zero over the spouted bed regime. Then gas flow is slowly reduced until the spout collapses at minimum spouting velocity. Maximum pressure drop obtained by decreasing the gas velocity is much lower than that measured by increasing it, showing a pronounced hysteresis. As the gas velocity is increased, the bed passes from the state of fixed bed, to the stable regime of spouted bed, corresponding to the maximum pressure drop. Spouted bed regime in beds of grape skins in conical spouted bed reactor is determined when standard deviation of pressure drop fluctuations is lower than 10 Pa [22].

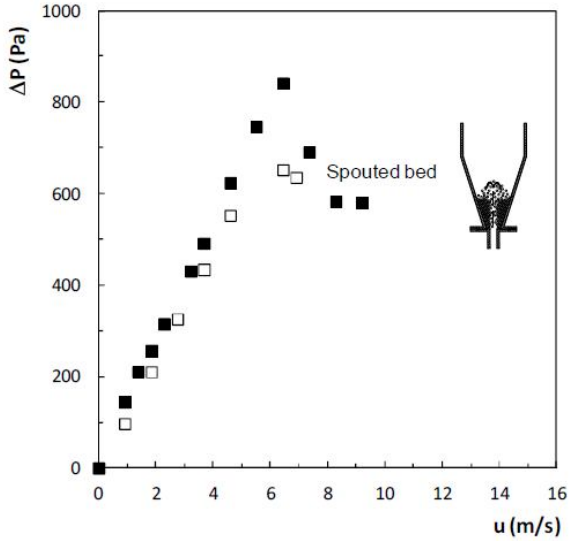


Fig. 3. Particle Evolution of pressure drop with air velocity for beds of grape skins. □= 36º, D_o= 0.04 m and particle states in the different regimes.

The experimental values of minimum air velocity corresponding to attain the spouted bed regime for beds made of grape skin wastes are depicted in Figure 5 against stagnant bed height, H_o. An outline of solid particles in the fixed bed and in the spouted bed regime is plotted in Fig. 4 too. As shown, at each stagnant bed height, as air velocity increased from zero, the bed passes from the fixed bed to the spouted bed regime at the minimum spouting velocity. All studied systems are stable and spouted bed regime is reached in all of them. As observed, an increase in the stagnant bed height and the inlet air temperature lead to higher minimum spouting velocities.

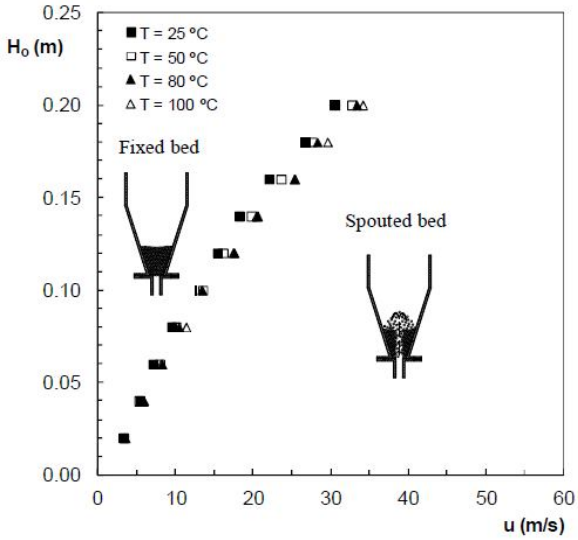


Fig. 4. Operating map of stagnant bed height versus the gas velocity. Experimental system: □= 36º D_o= 0.03 m. (a) grape skins wastes of d_S= 4.47 mm.

For better yield of the combustion, a previous drying was conducted at 105ºC. During the drying process, small solids samples (about 0.5 g) were extracted by means of a suction pump, and the solids moisture content was measured using a Mettler-Toledo HB43-S Halogen hygrometer (accuracy ± 0.01 %). The

moisture content of digested grape skins waste reduced with the time from the initial moisture content to equilibrium moisture content, and this decrease was more appreciable at high moisture content at the starting of the drying process. At the end of the drying, the variation of grape skins moisture content with the time is almost asymptotic until the equilibrium moisture content is attained. Drying time necessary to obtain equilibrium moisture content at 105 ºC is 400 minutes.

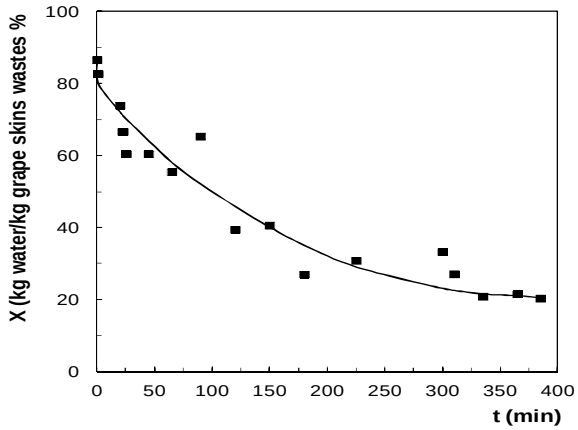


Fig. 5 Time evolution of the moisture content of a bed of grape skin wastes. Experimental system: □= 36º; D_o= 0.03 m, M= 100 g, d_S = 4.78 mm, initial moisture content 86.5 wt % (d.b.), u= 1.02 u_{ms}; T= 105 ºC.

Once the solids moisture content is reduced, catalytic combustion was carried out. The time evolution of CO_2 and CO concentration (% volume) in the flue gases obtained in the bath catalytic combustion of grape skins with the Pd/Al_2O_3 catalyst at the inlet gas temperature of 550 ºC in the spouted bed regime are depicted in Fig. 5. The CO_2, CO gases concentration increases from zero to maximum values at a time around 60 s, subsequently yields a sharp peak and finally decreases to zero. The experimental value of combustion efficiency calculated from the concentration of CO_2 and CO (% volume) gases in the exhaust stream by equation (5) is 80% [15, 21-22].

$$\eta = \frac{CO_2}{CO + CO_2} \qquad (5)$$

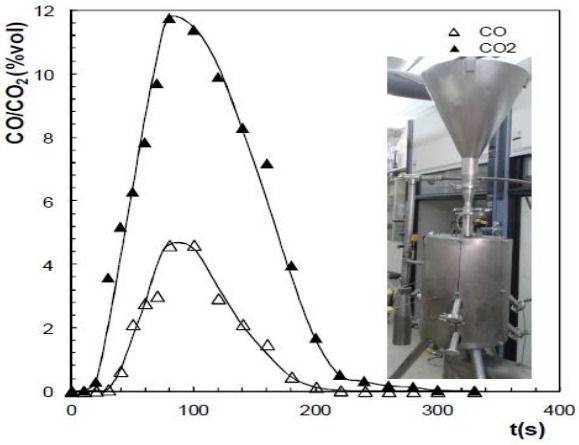


Fig. 5. Time evolution of concentration of CO_2 and CO (% volume) in the flue gases in the combustion of grape skin with Pd/Al_2O_3 catalyst at 550 ºC.

CONCLUSION

In conclusion, the suitability of a conical spouted bed plant for thermal valorization by drying-combustion of the waste of anaerobic digestion of grape skins in the spouted bed regime has been demonstrated. The range of operating regimes beds consisting of digested grape skins has been established under different experimental conditions. Spouted bed technology in conical geometry is feasible for valorization of wastes of grape skins and scrapes from wine production by catalytic combustion at temperature of 550 ºC in the spouted bed regime with combustion efficiency higher than 80%. This temperature is lower than that in conventional systems. By using the catalyst combustion yields obtained are by 5% higher than those without it at each temperature, with the same energy cost.

ACKNOWLEDGEMENTS

This work was performed with financial support from the Spanish Ministry of Economy and Competitiveness and co-funded by the European Union through ERDF funds (Projects CTQ2014-59312-P and CTQ2017-89199-P).

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