Catalysis Today 305 (2018) 13–18

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic combustion of vineyard pruning waste in a conical spouted bed combustor

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A R T I C L E I N F O

Keywords:
Biomass waste
Catalytic combustion
Conical spouted beds
Combustion
Vineyard waste

A B S T R A C T

The feasibility of a conical spouted bed combustor for the thermal catalytic exploitation of vineyard pruning waste, under different operating conditions has been analyzed. Stable-flow regimes of vine shoot beds with a Pd catalyst were determined over a wide range of combustion conditions. With the aim of improving the combustion yield, thermal exploitation of vine shoots was performed in batch mode, in a conical spouted bed combustor at temperatures ranging from 250 to 550 °C, with and without the Pd catalyst. The influence of the catalyst and inlet gas temperature on the flue gas concentration was analyzed. The experimental vine shoot combustion yield with the Pd catalyst at different inlet gas temperatures were compared with those obtained without the catalyst. The high experimental combustion efficiency calculated from the flue gases concentrations demonstrates the favorable performance of the conical spouted bed combustor for the catalytic combustion of vine shoots.

1. Introduction

Biomass is a key future renewable energy source that can replace fossil energy. Currently, biomass is the fourth largest source of energy accounting for approximately 14% of the world's primary energy consumption, in addition to offering environmental, economic, and social benefits. Directive 2009/28/CE of the European Parliament and the Council [1] establishes a mandatory target of 20% energy share from renewable sources by 2020. According to the World Energy Council projections, [2] the share of renewable energy sources will increase in 2050 to almost 20% in the Jazz scenario and almost 30% in the Symphony scenario. Biomass can be converted to useful thermal energy, electricity, and fuel for power by direct combustion, gasification, or liquidation of biomass. Exploitation of biomass as renewable energy source by the spouted beds technology may be considered an alternative that guarantees sustainable development and a clean process.

Spain has the largest extension of cultivated vineyard lands (947,000 Ha) in the world, which represented 13% of the available global land in 2013 [3]. Vineyard pruning generates over 1 ton of biomass waste per hectare [4], which is suitable for energy valorization, and is mainly composed of cellulose and lignin with a low moisture content and high C/N ratio. Although biomass waste is an excellent source of bioenergy, its application is very limited. Typically, these residues are burned on the plot, which in addition to fire hazards, causes wasteage of thermal energy. Non-catalytic combustion of vineyard residues has been studied in a 180 MJ domestic boiler, and the heavy metal emissions from vineyard residues are found to be comparable to emissions from wood chips [5]. Further, the flue gas emissions from the combustion of vineyard residues are comparable with emissions from the co-combustion of grape husks in fluidized beds with Na feldspar as an inert material [6]. As an alternative, these wastes can be mixed with soil after grinding and used as an additional source of organic or inorganic N, due to the high C/N ratio.

Spouted bed technology was explored since previous papers report the successful use of conical beds for the combustion of sawdust and agricultural wastes [7], cork [8], vineyard pruning wastes [9], fruit tree [10], and sludge wastes [11] with high combustion efficiencies, demonstrating that this technology generates high mass and energy transfer in the presence and absence of the inert material. Recent studies have reported the thermal processing of biomass in spouted beds have been reported in literature. Rasul [12] compared the combustion efficiency of wood charcoal using sand as the inert material in a conventional spouted bed with different inlet arrangements at 900 °C. The combustion of sewage sludge was studied by Barz [13] in a spouted bed cascade system at 700, 800, and 900 °C without any inert material. The influence of operating parameters on CO and CO_2 emissions during the combustion of rice husks in multiple spouted beds and in spout-fluid beds was analyzed by Albina [14]. Pimchuar et al. [15] reported preliminary results on combustibility of torrefied rice husk and other agricultural residues in a spout-fluid bed combustor. Wang et al. [16]

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https://doi.org/10.1016/j.cattod.2017.11.020
Received 7 April 2017; Received in revised form 9 November 2017; Accepted 10 November 2017
Available online 11 November 2017

performed combustion of the semi-coke obtained from the retort of oil shale with particle sizes between 0 and 4 mm in a spouted bed. However, there is a lack of information about the catalytic combustion of biomass in spouted beds.

Although biomass is a renewable energy source with low CO_2 and sulfur emissions, incomplete combustion in some biomass combustion systems might lead to the emission of environmental pollutants such as CO, CH_4, polycyclic aromatic hydrocarbons (PAHs), and volatile and semi-volatile organic compounds (VOCs). Noble-metals based catalysts such as Pt and Pd have higher activities for the oxidative removal of VOCs from gaseous streams at temperatures lower than those for thermal destruction [17–19]. Pd is more resistant to thermal sintering in an oxidizing environment than is Pt [20–22]; however, there is controversy in the literature regarding the activities of Pt and Pd. For example, some authors reported that Pt-based catalysts have higher activity for the oxidation of hydrocarbons containing more than one carbon atom, and Pd-based catalysts have higher activity for CO and CH_4 oxidation [23–27]. Other authors reported that Pt-based catalysts have activity than Pd-based catalysts for the oxidation of both hydrocarbons and CO [28]. Larsson et al. [29], Ferrandon et al. [30], and Spivey et al. [31] suggested the use of heterogeneous catalysis for the cleaner combustion of biomass and for reducing pollutant emissions. For example, noble-metal based catalysts such as Pt and Pd supported principally on alumina can convert CO and VOCs into CO_2 and H_2O. Further, the activity of a Pd/Al_2O_3 catalyst can be regenerated by a quick temperature increase above 600 °C [32].

The mechanism underlying the catalytic oxidation of CO over Pd/Al_2O_3 is expressed by reactions (1)-(3). CO and the O_2 are chemisorbed at the active centers giving rise to the substrate-catalyst complexes as per the Langmuir-Hinshelwood mechanism, causing a decrease in the activation energy, as physisorption is negligible in heterogeneous catalysis. However, CO is adsorbed more strongly than oxygen

$$CO\ (g) + M \rightleftharpoons CO\text{-}M \quad (1)$$

$$O_2\ (g) + 2\,M \rightleftharpoons 2O\text{-}M \quad (2)$$

$$CO\text{-}M + O\text{-}M \longrightarrow CO_2\ (g) + 2M \quad (3)$$

where M is the sorption position on the surface of the catalyst

The overall reaction for the oxidation of CH_4 can be expressed by Eq. (4). Despite several reports from authors who studied the mechanism of catalytic oxidation of CH_4 over Pd/Al_2O_3, there is no general agreement with that reported the catalyst in the literature [33].

Some authors have reported that CH_4 oxidation occurrs by the Eley-Rideal mechanism, in which not all reactive are adsorbed on the surface of the catalyst [34]. However, other authors reported that CH_4 oxidation takes place by the Langmuir–Hinshelwood mechanism [35] with fast and irreversible adsorption of O_2 on the Pd catalyst and slow CH_4 adsorption [36,37]. Further, some authors proposed that CH_4 oxidation occurs via the Mars and van Krevelen redox mechanism, wherein CH_4 is oxidized by the catalyst and O_2 maintains the oxidation state of the catalyst [38–40].

$$2\ CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad (4)$$

Studies on the catalytic combustion of biomass are very limited in the literature. Some authors have investigated the effect of different catalysts on the ignition and combustion behavior of biomass by thermogravimetric analysis. Zhaosheng et al. [41,42] studied the catalytic combustion of wheat and rice straw with magnesia (MgO), nickel oxide (NiO), calcium oxide (CaO), and cuprum oxide (CuO) as catalyst. They reported that all the catalysts reduced the ignition temperature of wheat and rice straw and increased the combustible conversion degree in an air atmosphere. However, in an oxygen-enriched atmosphere, although the conversion degree of wheat straw was higher, the catalytic conversion degree of rice straw was lower irrespective of the catalyst amount. Wang et al. [43] investigated the combustion of wheat straw was using 2, 5, and 10 wt% of TiO_2, CuO and MnO_2 catalysts, and reported that the ignition and combustion temperatures were lower in the presence of the catalysts than in the absence of the catalysts in an air atmosphere. Vamvuka et al. [44] showed that transition metal oxides and alkali/alkaline earth catalysts (LiCl, NaCl, MgO, CaO, TiO_2, V_2O_5, Fe_2O_3, and CuO) increased the combustion reactivity of mixtures consisting of lignite and biomasses (olive tree pruning, cardoon, or sewage sludge) by increasing the reaction rate and lowering the peak and burnout temperatures. Cai et al. [45] explored the catalytic combustion kinetics of rice hull and bamboo biomasses after alkali metal (AM) pretreatment by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). They concluded that the AM catalysis of biomass combustion occurred in all processes and that the initial devolatilization temperatures decreased but the combustibility index increased. Peng et al. [46] investigated the efficiency of biomass catalytic combustion in a 1.2 MW circulating fluidized bed (CFB) combustor with metal nanoparticles (Al, Ni) via simulation using an Aspen Plus simulator and dedicated FORTRAN subroutines. Based on the results, lower emissions were predicted.

In a previous study thermal exploitation of vineyard pruning wastes was performed in a conical spouted bed combustor [9] and the favorable hydrodynamic performance of the catalyst particles was demonstrated in conical spouted beds of different geometries under different operating conditions in a stable regime, without noticeable segregation [47]. With the aim of improving combustion efficiency, thermal exploitation of vine shoots was carried out in batch mode by catalytic combustion using Pd/Al_2O_3 in the conical spouted bed combustor at different inlet gas temperatures. The gas velocity range over which the cyclic movement of the particles was observed, namely, the spouted bed regime, was determined for vine shoot combustion at different temperatures. The combustion yields of vine shoots with the Pd catalyst was calculated at different inlet gas temperatures from the flue gas concentrations and compared with those reported in the absence of a catalyst [9].

2. Experimental

Experiments were conducted on a pilot scale experimental unit (Fig. 1) described in detail in previous papers [9–11,48]. This experimental unit comprises a conical combustor, a blower that supplies a maximum air flow rate of 300 Nm^3/h at a pressure of 15 kPa, two high-efficiency cyclones, a mass-flow meter, and an electrical heater and thermocouples.

Fig. 1 The conical combustor used (Fig. 2) is made of AISI-310S heat-resistant stainless steel. The combustor consists of two sections, a conical bed (lower section) and a freeboard (upper cylindrical section). The combustor is externally insulated with quartz fiber in order to reduce heat loss. A viewfinder is used to visualize the particle regime, mainly the spouted bed regime. The geometric factors of the conical combustor are summarized in Table 1.

The air velocity used in the combustion process, between minimum spouting and 20% above this value, is determined from the air flow rate measured by a mass flowmeter located at the inlet pipe and controlled by a computer with an accuracy of ± 0.5% [49]. Inlet gas temperatures were measured by a K-type thermocouple (maximum relative error of ± 0.75% or ± 2.2 °C) located at the inlet of the combustor. In addition, the air moisture content at the inlet and outlet is measured by thermal conductivity detectors (Alhborn MT8636-HR6).

The bed pressure drop is measured by a differential pressure transducer (Siemens Teleperm) [50]. The bed pressure and air velocity data are registered and processed by means of the AMR-Control and the outputs are calibrated with U-type water manometer measurements.

The biomass wastes (Fig. 3) considered in this study were vine shoots with a density of $\rho_s = 540\ kg/m^3$ and moisture content of 25 wt % (dry basis), determined by thermogravimetry (Mettler Toledo HB43-S Halogen hygrometer, accuracy ± 0.01%). Several fractions with