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Olive oil residue gasification and syngas integrated clean up system

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HIGHLIGHTS

- Innovative gasifier design to produce high quality syngas maximizing tar removal.
- Two steps of tar removal: a char moving bed followed by a catalytic reforming unit.
- Ni–Co/CeO_2–Al_2O_3 catalyst is used in the reforming to avoid catalyst deactivation.
- The obtained syngas is composed by 47% CO and 30% H_2.
- The syngas has a low tar amount and can be directly used in many applications.

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ABSTRACT

Gasification is one of the most promising technologies to convert low quality fuels into more valuable ones. The main problem in the use of biomass in gasification processes is the high amount of tar released in the pyrolysis step. It is thus necessary to recover the tar and to transform it in lighter combustible gas species such as CH_4, CO and H_2 by means of catalytic processes. In this work the gasification of olive husk is performed in order to produce a high quality syngas, composed mainly of carbon monoxide and hydrogen, using an innovative laboratory scale plant composed of a unique reactor divided into three sections. The first section is dedicated to the pyrolysis, the second to the gasification of char produced during pyrolysis and the third to the catalytic reforming of tar. In the reformer two catalysts were tested: a CeO_2 promoted bimetallic Ni–Co catalyst and a Ni catalyst, both supported on γ-Al_2O_3. This plant design allows one to minimize the heat dispersion enhancing the energy efficiency of the unit.

1. Introduction

The interest on the exploitation of biomass as source of energy has continuously increased in the last decade. Biomass has been recognized as one of the most attractive alternatives to fossil fuel, even if it is not yet competitive with it. The main problem in using biomass as feedstock in energy conversion processes relies in its low energy density and high water content, making it not convenient from an energetic point of view. Gasification is a promising method to produce energy with biomass. Gasification converts biomass into a gaseous product that is easier to treat than the biomass itself. The combustion of this gas allows one to obtain high rates of heat release and high burning efficiencies without particle emission. Another advantage is that burners with simple geometries are required [1,2].

Even though gasification is a well-established technology for coal, its adaptation to biomass feed is not straightforward. During gasification, biomass undergoes a partial oxidation and produces a gaseous mixture called "syngas" that consists mainly in H_2, CO, CO_2, CH_4 and N_2, in proportions that depend on the adopted gasifying agent and on the gasification system used. Additionally, a high amount of tar is produced. Tar is a complex mixture of condensable hydrocarbons, comprising single-ring to 5-ring aromatic compounds and other oxygen-containing organic molecules [3,4]. The presence of tar can cause operative problems to the gasification plants, such as obstruction of pipes and filters and reduction of the heat exchange efficiency due to its condensation in the downstream section. The tar tolerance limit varies depending on the application: it is $\sim$500 mg/Nm^3, $\sim$100 mg/Nm^3 and 5 mg/Nm^3 for compressors, internal combustion systems, and direct-fired industrial gas turbines, respectively [5]. Therefore the most difficult challenge in designing a reactor for biomass gasification consists in minimizing the tar contamination within the syngas.

To this aim different solutions have been studied. Primary methods provide tar removal directly into the gasifier itself, while secondary methods provide tar removal in a separate section [6]. The secondary methods include physical removal, for example by

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means of filters [7], and/or chemical conversion processes, which are more preferable since they allow to recover all the tar energy and enrich the syngas in valuable species [8–10]. The processes that occur during chemical conversion are cracking and reforming, where tar decomposes in lighter species such as methane, hydrogen and carbon monoxide. The principal reactions taking place in these processes are:

$$C_nH_m \rightarrow pC_nH_x + rH_2 \quad \text{cracking reaction}$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \quad \text{steam reforming reaction}$$

$$C_nH_m + nCO_2 \rightarrow 2nCO + \frac{m}{2}H_2 \quad \text{dry reforming reaction}$$

$$CO_2 + H_2 \Longleftrightarrow CO + H_2O \quad \text{reverse water gas shift reaction}$$

All these reactions are endothermic and occur at high temperatures ($T > 650$ °C). The use of a catalyst reduces the operative temperature and enhances the rates of both steam and dry reforming reactions. In order to maximize the efficiency of the process it is necessary that syngas from the gasifier is sent to the reforming at the highest available temperature. The design of the gasifier and its thermal integration, thus, has a key role in the minimization of the heat dispersion of the syngas [11].

In this work an innovative air gasifier is proposed and tested for olive husk gasification. The gasification system is composed of a unique reactor divided into three sections; this design allows one to minimize the heat dispersion and to enhance the energy efficiency and the syngas quality. In the first section of the plant the pyrolysis of the biomass takes place. In the second section the gasification reactions occur while the third section is dedicated to syngas clean-up by means of tar catalytic reforming. In particular, steam and dry reforming are supposed to occur in order to convert tar and at the same time to lower the CO_2 dilution of syngas.

In the proposed system the tar abatement occurs into two steps. In the first step the pyrolysis volatile products are forced to pass through a char bed where part of the tar is converted into lighter species. It is known from literature, in fact, that char is a very active catalyst for tar cracking. Its high porosity allows increasing the residence time of the gas in the reactor, thus favouring cracking reactions; furthermore the alkali content of the char ash acts as catalysts promoting tar conversion [12,13]. The second step of tar abatement consists in a catalytic reformer where the activity of Ni catalyst, promoted with Co and CeO_2, was studied.

2. Experimental section

2.1. Experimental set-up

A laboratory scale, semi-continuous, gasification plant was used for the tests. The plant, which capacity is of 500 g/h, is divided in three zones: a feeding system constituted by a hopper and screw conveyor, a reaction unit and a collection system.

The reaction unit can be further divided into three sections: a first section, where pyrolysis occurs, a second section for tar cracking and gasification and a third section for tar catalytic reforming. In Fig. 1 is reported the conceptual flow scheme of the plant.

The entire plant is built in AISI 310L stainless steel. The pyrolysis section is constituted by a tube of 40 mm i.d. and 700 mm length with a tilt angle of 70° with respect to the ground. The tube, externally heated by means of an electrical heater, contains a screw that allows one to control the residence time of the biomass into the reactor. Four K-type thermocouples are placed at different reactor heights to measure the inner temperature. The upper part of this reactor is filled with the char produced by the pyrolysis before it falls into the gasification section. The bed of char at the top of the pyrolyzer is about 100 mm high and it constitutes the first step of tar abatement. The tar, in fact, passing through the char bed, undergoes cracking reactions, being in part converted into lighter species. At the end of this section the char falls in the connected vertical gasification reactor (stainless steel tube, i.d. = 40 mm; L = 400 mm). Then the gas and the remaining tar flow through the reforming reactor (i.d. = 40 mm; L = 500 mm) and finally reach the collection system. The reforming reactor is equipped with a cable heater to minimize the heat loss from the reactor walls and to sustain the endothermic reactions, and with a steel net to support the catalyst bed and a thermocouple to measure the temperature of the bed.

Two different configurations of the reaction section were tested, which differ for the position of the reforming unit, as shown in Fig. 2. In the configuration "a" the gasification reactor can be considered as an up-draft gasifier while in the configuration "b" it can be considered as a down-draft [14].

During the experimentation in the "a" configuration the gasifying agent (air in the performed tests) is injected from the bottom of the gasifier 30 min after the beginning of the test to allow the formation of the char bed. The advantage of this configuration, with respect to the traditional up-draft gasifier, is that tar and gas are immediately sent to the reforming reactor without cooling them, so avoiding tar condensation [15]. In traditional up-draft gasifiers, in fact, the solid fuel and the gas flow in counter-current, so that the hot gases, produced during gasification, give the majority of their heat to the fresh feedstock that is heated up, dried and then pyrolyzed [16]. In this way the produced gases exiting from the reactor are cooled down even up to 300 °C. This temperature is too low to allow the occurring of the reforming reactions without heating up again the gas.

In the adopted experimental set-up, however, the char bed is cooled down by the injected air and so the temperature in the gasifier became too low to ignite the endothermic gasification reactions. To overcome this problem a rod heater is used to trigger the combustion reaction. The heater is activated when the char bed is formed on the gasifier and it is kept switched on only for the time needed for the initiation of the char combustion. After that time the process proceeds in an autothermal regime.

In the second configuration, as already said, the gasifier behaves like a down-draft gasifier, with the air and the char fed from the top of the gasifier and flowing in the same direction. In this way

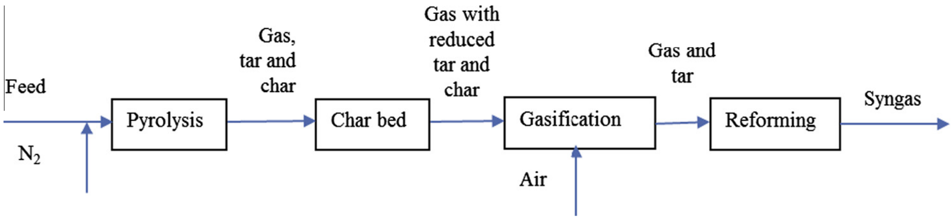

Fig. 1. Conceptual flow scheme of the experimental plant.