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Biomass gasification and tar reforming in a two-stage reactor

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Abstract

Gasification is recognized as one of the most promising technologies to convert low quality fuels into more valuable ones. The principal problem related with the use of biomass in gasification processes is the high amount of tar released during the pyrolysis step. It is thus necessary to recover the tar and to transform it in lighter combustible gas species such as CH₄, CO and H₂ by means of catalytic processes. In this work the gasification of olive husk is performed in order to produce a high quality syngas, composed principally by carbon monoxide and hydrogen, using an innovative laboratory scale two-stage reactor. The first stage is used for gasification and the second for catalytic reforming. It is thus possible to recover the tar energy converting it into CO and H₂. Ce-promoted bimetallic Ni-Co catalyst was tested and compared with Ni catalyst, both supported on γ -Al₂O₃.

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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. The main problem related with the use of biomass in an energy conversion processes is the low energy density and the high water content of this material. Gasification is an interesting option for the production of energy from biomass. Even though coal gasification is a well-established technology, its adaptation to biomass is not straightforward. During gasification, biomass undergoes a partial oxidation to give a gaseous mixture, called “syngas”, that consists mainly in H₂, CO, CO₂, CH₄ and N₂ in different proportions, depending on the adopted gasifying agent. However high amount of tar is produced during the gasification along with the syngas. Tar is a complex mixture of condensable hydrocarbons comprising single-ring to 5-ring aromatic compounds plus other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs) [1]. The presence of tar can cause operative problems to the gasification plants,

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such as pipe and filters obstruction and reduction of the heat exchange efficiency due to its condensation on the downstream section. Therefore the most difficult challenge in designing a suitable reactor for biomass gasification is to avoid the presence of tar within the syngas.

Different solutions have been studied. Tar can be removed physically with filters or can be converted into light gas species such as CH_4 , H_2 and CO by means of catalytic processes. Catalytic reforming of tar allows to decrease the tar content of the syngas and to enrich it in valuable species.

In this work an innovative two-stage gasifier to enhance the syngas quality is proposed and tested for olive husk gasification. The first stage is used for the pyrolysis and gasification of the fuel and the second stage for the catalytic reforming of the released gasification products. In particular, steam and dry reforming are supposed to occur in order to convert tar and to lower the CO_2 dilution of the syngas. The water and the CO_2 needed for reforming are those produced from the pyrolysis of the biomass. A bimetallic Ni-Co catalyst promoted by Ce supported by Al_2O_3 is used. Ni was extensively used as catalyst for steam reforming applications but it is well known that it suffers from carbon deposition [2]. To limit this phenomenon Ce was added since it improves the resistance of the catalyst to carbon deposition [3].

2. Experimental section

2.1. Experimental set-up

The laboratory scale plant consists on a two-stage gasifier. In Fig. 1 the laboratory scale plant set-up is shown.

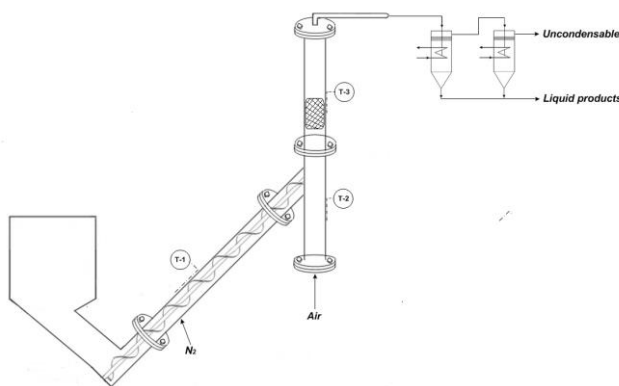


Fig. 1. Experimental laboratory scale plant.

Two reactors in series constitute the first stage. The first reactor is used for the pyrolysis, where tar, gas and char are produced. The char then falls in a second reactor where the gasification takes place. The pyrolysis reactor is built using a stainless steel tube (i.d.= 4 cm; L= 70 cm) with a tilt angle of 70° with respect to the ground. The tube contains a screw that allows 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. At the end of this reactor gas and tar flow toward the reforming reactor (i.d. = 4 cm; L=50 cm) while the char falls in the secondary gasification reactor (stainless steel tube, i.d.= 4 cm; L=30 cm). In the gasification reactor air is injected from the bottom (Equivalent Ratio = 0.4) 30 min after the beginning of the test to allow the formation of the char bed. The reforming reactor is equipped with steel net to support the catalyst bed; a thermocouple is used to measure the temperature of the 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 [4]. Three external cable heaters are used to heat the three reactors and to sustain the endothermic reactions. The char falling at high temperature into the gasifier allows maintaining the gasification step autothermal, so

that the external cable heater is required only to initiate the combustion reactions. At the exit of the reforming reactor three iced-cooled traps in series are used to condense the residual tar. A gas chromatograph is used to measure the concentration of H₂, CO, CH₄ and CO₂ into the produced syngas. The operative conditions used for the experimental tests are reported in Table 1.

Table 1. Experimental operative conditions

Operative conditions	
Pyrolysis T (°C)	600
Reforming T (°C)	600
Air flow rate (L/h)	0.05
Catalyst amount (g)	50
Residence time during pyrolysis (h)	0.25
Biomass feeding rate (g/h)	700

2.2. Catalyst preparation

The γ -alumina supported Ni-Co/Ce catalyst (Ni-Co/Ce Al₂O₃), containing 10 wt % Ni, 3.33 wt % Co and 3.33 wt % Ce, and Ni catalyst (Ni Al₂O₃), containing 10 wt % Ni, were prepared by wet co-impregnation of commercial γ -Al₂O₃ (S_{BET}=230 m²/g, pore volume=0.66 cm³/g), using aqueous solution of the precursor salts. The used salts were Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O. The obtained wet solids were dried at 105 °C for 24 h under vacuum and calcinated for 6 h (2 h at 500 °C, 2 h at 600 °C and 2 h at 700 °C). Before use the catalysts were activated in situ in 0.5 NL/min flow of 50 % H₂/N₂ at 550 °C for 1 h and then held at 750 °C for 2 h.

3. Results and discussion

To study the performances of the plant and the activity of the catalytic stage, four different experimental tests were performed. The amount of tar released during the pyrolysis was measured using the plant as a simple pyrolyzer. To test the catalysts activity and the improvement achieved when Co and Ce are added to the traditional Ni catalyst, pyrolysis tests were conducted using the two catalysts. Then a complete gasification test was performed using Ni-Co/Ce-Al₂O₃ catalyst in the second stage. In Table 2 the amounts of tar and water recovered during the experimental tests are reported.

Table 2. Tar and water amounts recovered in the experimental tests.

	%wt			
	Pyrolysis	Pyrolysis Ni	Pyrolysis Ni-Co/Ce	Gasification
Tar	16	3.5	3.2	3.0
Water	25	21	16	15

The reduction of the amount of tar is about 75 %, almost the same for both the catalysts. The reduction of the water quantity is considerably higher using the Ni-Co/Ce Al₂O₃ catalyst. Looking at the gas composition (Table 3), it is clear that the Ni-Co/Ce Al₂O₃ is more active with respect to the steam reforming reaction, in fact in addition to the water decrease the H₂ concentration increases of about 140 %. The tests conducted in pyrolysis condition do not show remarkable differences for the other gases.

In the gasification test the CO concentration is much higher, leading to a high quality gas composed principally by CO and H₂.

Table 3. Gas composition expressed on free N₂ basis and total gas yield for each test.

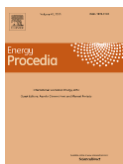
% vol.	Pyrolysis	Pyrolysis Ni	Pyrolysis Ni-Co/Ce	Gasification
CO	20.9	18.3	15.2	32.3
CO ₂	39.5	36.5	35.5	24.5
CH ₄	16.2	16.5	17.5	12.3
H ₂	23.4	28.7	31.8	30.9
Total gas yield (l/g biomass)	0.25	0.34	0.47	0.54

4. Conclusions

In this paper an innovative two-stage gasification laboratory plant is studied in order to produce a high quality syngas. The reactors configuration allows to make the gasification step autothermal and to avoid tar condensation between the gasifier and the catalytic stage. The Ni-Co/Ce Al₂O₃ catalyst allows to reduce the tar content up to 75 % and to increase the H₂ concentration, so enhancing the syngas quality. The syngas produced is composed principally by H₂ and CO, which are the most valuable species.

References

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Biography

Benedetta de Caprariis received her PhD degree at the Department of Chemical Engineering at the University of Rome ‘La Sapienza’ in 2013 and now she is a post doc at the same department. Her research activity concerns the development of alternative energy processes, in particular biomass pyrolysis and gasification.