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Carbon Dioxide Reforming of Tar During Biomass Gasification

Benedetta de Caprariis*[a],Claudia. Bassano[b], Paolo Deiana[b], Vincenzo Palma[c], Antonietta Petrullo[c], Marco. Scarsella[a], Paolo De Filippis[a]

[a]Department of Chemical Engineering, Sapienza University of Rome
[b]ENEA, Centro Ricerche Casaccia, Roma
[c]Department of Industrial Engineering, University of Salerno
benedetta.decaprariis@uniroma1.it

The energy demand increase and the necessity to contain CO_2 emissions lead to a growing interest on renewable and CO_2 free energy sources. Gasification has been identified as a key technology to enhance the environmental tolerability of low quality fuels such as biomass. The principal problem related with the use of biomass in gasification processes is the high quantity of tar released during the pyrolysis step of this fuel. Tar can account up to 50% of the total volatiles and contains a great part of the biomass energy. For this reason it is necessary to recover the tar and to transform it in combustible lighter gas species such as methane, carbon monoxide and hydrogen by means of catalytic processes. Another important issue is to lower the carbon dioxide content of the produced gas in order to increase its calorific value. The dry reforming represents an interesting solution. In this work the dry reforming of tar in a two stages bench scale reactor is proposed. In the proposed dry reforming process the tar reacts with the carbon dioxide released during the biomass pyrolysis to form carbon monoxide and hydrogen. It is thus possible to recover the tar energy converting it into CO and H_2 and to lower the syngas dilution using the CO_2 as a reagent. The dry reforming is a catalytic process and one of the major issues is the deactivation of the catalysts due to carbon deposition. The solution of this problem is very important in the case of tar dry reforming because of its high C/H ratio, which intensifies this phenomenon. Nickel has been extensively studied for the dry reforming but it is known that it suffers from carbon deposition. In this work Ce-promoted bimetallic Ni-Co catalysts with two different supports were tested.

1. Introduction

Biomass represents one of the most interesting alternatives to fossil fuels for energy purposes. In fact, biomass is a carbon neutral material and a renewable source of energy (Srirangan et al., 2012). Its exploitation towards traditional combustion processes is however limited due to the low energy density of the biomass with respect to that of fossil fuels and to its high water content which can reach up to 40 % of the weight. These aspects can cause problems to the stability of the flame in the combustion reactors. Thus, in order to make this kind of fuel more valuable, an interesting solution is to transform the solid biomass into gaseous or liquid fuels, which have higher energy density and are easier to handle and store. In this context gasification has been recognized as one of the most promising technologies to upgrade this low quality fuel into a gaseous fuel (Verdone et al., 2012). During gasification, biomass undergoes a partial oxidation to produce a gas, called syngas, that consists mainly in H_2, CO, CO_2, CH_4 and N_2 (if air is used) in different proportions. However high amount of tars are produced during the gasification along with the syngas. Tar is constituted by the condensable products of pyrolysis, composed of a complex mixture of organic compounds and can account up to 50 % of the weight of the former biomass. Tar represents a serious problem in biomass gasification since it can condense in pipes, filters and heat exchangers, causing obstruction of the downstream section of the plant and reduction of the heat transfer efficiency. For these reasons tars must be separated after the gasifier and before the further syngas treatment section where they can cause the deactivation of the catalysts used for the refining syngas processes. Several approaches for tar removal are available in literature such as physical treatments and chemical

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treatments (Shen and Yoshikawa, 2013). Among the chemical treatments catalytic reforming of tar into gas is one of the most promising, allowing the enhancement of the syngas quality increasing the amount of CO and H_2 (Peres et al., 2013). Another important issue is to lower the CO_2 content of the syngas in order to increase its calorific value. In this context the dry reforming represents an interesting solution since tar reacts with CO_2 to produce CO and H_2. The dry reforming was widely analysed in literature for the conversion of the biogas (mainly constituted by methane and carbon dioxide) into syngas and different catalysts have been tested (Fan et al., 2009). Nickel has been extensively used for catalytic reforming, however it is well known that it suffers from carbon deposition (Wang et al., 2011).

In this work the reforming of the tar produced by the pyrolysis of the residue of olive oil extraction over bimetallic nickel and cobalt catalyst promoted by cerium was studied in a two-stage bench scale reactor. The objective was to convert the tar into fuel gas, mainly CO and H_2, using as reforming agents the non-combustible compounds produced by the pyrolysis and gasification of the biomass, CO_2 and water. Cerium was added as a promoter since Ce improves the resistance to carbon deposition (Chen et al., 2013). The influence of two different supports, γ-Al_2O_3 and activated carbon (AC), on the process efficiency was evaluated. To better understand the reforming and the catalyst performances, experimental tests on methane and tar model compounds such as n-heptane and benzene were conducted.

2. Experimental section

2.1 Catalyst preparation

The γ-alumina supported Ni-Co/Ce catalyst (Ni-Co/Ce Al_2O_3) and the activated carbon supported Ni-Co/Ce catalyst (Ni-Co/Ce AC), both containing 10 wt% Ni, 3.33 wt% Co and 3.33 wt% Ce, were prepared by wet co-impregnation of commercial γ-Al_2O_3 (S_{BET}=230 m^2/g, pore volume=0.66 cm^3/g) and activated carbon (Acquacarb 207EA; S_{BET}=950/1100 m^2/g, methylene blue number=180-230, iodine number=900/100 mg/g), using an aqueous solution of $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and $Ce(NO_3)_3.6H_2O$. The wet solids were dried at 105 °C for 24 h under vacuum. The Ni-Co/Ce Al_2O_3 was calcinated for 6 h (2 h at 500 °C, 2 h at 600 °C and 2 h at 700 °C). To decompose the precursors of the active phase the Ni-Co/Ce AC was heated under a nitrogen flow with the same temperature program of the Ni-Co/Ce Al_2O_3. Before use, the catalyst were activated in situ in 0.5 NL/min flow of 50 % H_2/N_2 at 550 °C for 1 h and then held at 750 °C for 2 h.

2.2 Experimental setup

To test the catalysts performances, CH_4 and tar model compounds (n-heptane and benzene) dry reforming experiments were conducted on a laboratory scale plant. The plant consists of a feed section, of a tubular quartz reactor (i.d.= 0.8 cm, l= 25cm, heated by an external cable heater and equipped by a porous quartz disk to support the catalyst bed) and of a condenser to recover the condensable (unreacted heptane and benzene and the water that can be produced by the reverse water gas shift reaction). Tar model compounds are introduced in the gas stream by means of a saturation unit, controlling their flow rate by changing the saturation temperature. The gas composition is measured with a gas chromatograph. The experimental conditions used for both the catalysts are reported in Table 1. For the n-heptane and the benzene the inlet flow rate are chosen in order to obtain the 15 % of CO_2 in excess respect to the stoichiometric value.

Table 1: Experimental conditions used in the preliminary tests.

	CH_4	n-heptane	benzene
T (°C)	550;650;725;800	650;725;800	700;750;800
Gas flow rate (NL/min)	0.5	0.5	0.5
Feed gas composition			
CH_4 (%vol)	25	-	-
CO_2 (%vol)	25	40	40
N_2 (%vol)	50	60	60
Mass flow rate (g/min)	-	0.15	0.1
Catalyst bed height (cm)	2	2	2
Catalyst amount (g)	2	2	2

The tests on the tar produced by the olive residue biomass were conducted in a two-stage tubular quartz reactor (i.d.=4 cm; l=70 cm), shown in Figure 1.

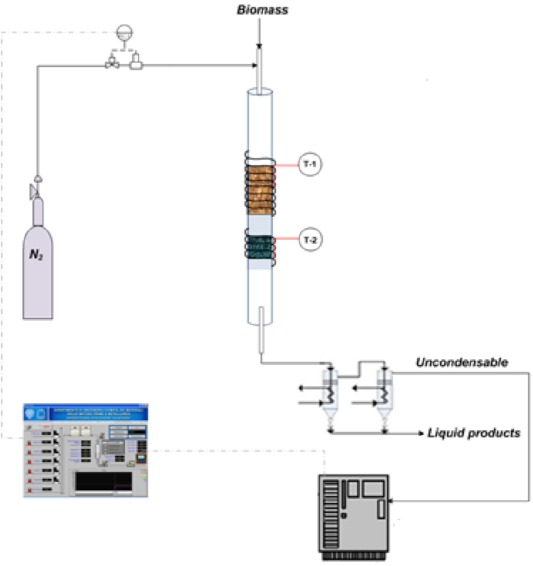

Figure 1: Tar reforming experimental setup.

In the first stage the biomass pyrolysis occurs, the produced gas and tar, then, pass through the second catalytic stage, where the reforming reactions take place. A layer of quartz wool, 5 cm height, divides the two sections of the reactor. The catalyst is loaded into the reactor over a porous quartz frit. The two sections are heated by two independent external cable heaters. The temperature of the catalyst bed is continuously measured by a K-type thermocouple, which is fitted in a small quartz pipe, placed in the center of the bed. The biomass is fed on the top of the reactor with a piston system at regular intervals of time in order to assure the continuity of the process. The solid is loaded for 30 min after the catalyst bed was heated to the set temperature. The produced gas passes through a series of water-cooled traps to condense the unreacted tar and then is sent to an on-line gas analyzer (Simens Ultramat 23) to measure the concentration of CO, CH_4, CO_2 and H_2. In all the tests nitrogen flow of 0.5 NL/min was fed above the biomass bed. In Table 2 the list of the operative conditions is reported.

Table 2: Experimental conditions used in the tar reforming tests.

	Ni-Co/Ce Al_2O_3	Ni-Co/Ce AC
T reforming(°C)	750	750
T pyrolysis (°C)	550	550
N_2 Gas flow rate (NL/min)	0.5	0.5
Biomass flow rate (g/min)	2.5	2.5
Catalyst bed height (cm)	5	5
Catalyst amount (g)	10	10

3. Results and discussion

3.1 Tar compounds results

The experimental tests were conducted at different temperatures in order to study the behaviour of the dry reforming reaction as a function of temperature and to calculate the kinetic parameters.

The reactions of dry reforming are reported below for the methane, n-heptane and benzene, respectively.

$$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2 \qquad \text{(Eq.1)}$$

$$C_7H_{16} + 7CO_2 \Leftrightarrow 14CO + 8H_2 \qquad \text{(Eq.2)}$$

$$C_6H_6 + 6CO_2 \Leftrightarrow 12CO + 3H_2 \qquad \text{(Eq.3)}$$

All these reactions are endothermic and so are promoted at high temperatures.

Other reactions occur during the process such as the reverse gas shift reaction, the reverse Boudouard reaction and the cracking reaction, which is the major responsible of coke deposition on the catalyst and of its deactivation. The occurring of the cracking reaction is promoted at temperature higher than about 550 °C, that is when the equilibrium constant becomes greater than 1 for the methane decomposition reaction (Chen et al., 2013). To avoid the carbon deposition it is, thus, preferable to work at temperature higher than 700 °C, that is when the reverse Boudouard reaction becomes thermodynamically favoured.

The conversions, *X*, were calculated as:

$$X = \frac{C_{out} - C_{in}}{C_{in}} \qquad \text{(Eq.4)}$$

where C_{in} and C_{out} are the inlet and outlet compound concentration, respectively.

The results obtained with the methane are reported in Fig. 2 for both the catalysts. It can be noted that the Ni-Co/Ce Al_2O_3 is more active with respect to dry reforming, leading to conversion of about 90 % at 800 °C. Ni-Co/Ce AC shows a much lower activity, reaching a maximum conversion of 41 % at 800 °C.

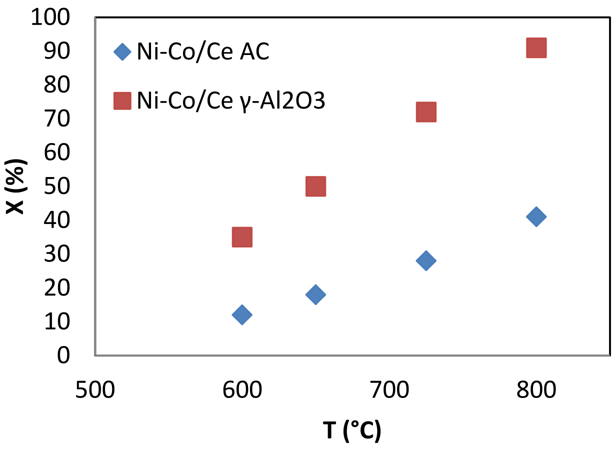

Figure 2: Dry reforming methane conversions as a function of temperature for both the catalysts.

In the Table 3 the results of the dry reforming of n-heptane and benzene at the different temperatures are reported. The results show the same behaviour observed for the dry reforming of methane, the activated carbon supported catalyst is less active and the conversion values are much lower. The conversion of n-heptane at 650°C is higher than that of methane at the same temperature. The methane molecule, in fact, is more stable and needs higher temperature to be broken. This result is also confirmed by the value of the kinetic parameters (Table 4); the Arrhenius pre-exponential factor for methane is higher than that for n-heptane. It means that at lower temperature the reaction is faster for n-heptane.

The results of the experimental tests on the benzene at 650 °C are not reported since at this temperature the quartz disk is immediately obstructed by the coke formation, so the results are shown for temperature higher than 700 °C.

Table 3: Conversion values of the dry reforming of n-heptane and benzene.

	T (°C)	Ni-Co/Ce Al_2O_3	Ni-Co/Ce AC
n-eptane	650	63%	23%
	725	72%	31%
	800	78%	36%
Benzene	700	44%	16%
	750	52%	22%
	800	65%	28%

The apparent kinetic parameters were carried out as (Fuentes-Cano et al., 2013):

$$-r_{app} = k_{app} C_i \qquad \text{(Eq.5)}$$

$$k_{app} = \frac{-\ln(1-X)}{\tau} \qquad \text{(Eq.6)}$$

where r_{app} is the rate of conversion [kmol/m^3 s], k_{app} is the apparent kinetic constant [1/s], C_i is the compound concentration [kmol/m^3], X is the conversion and τ is the resident time in the catalyst, calculated as:

$$\tau = \frac{V_{R,cat}}{Q_{in}(T,P)} \qquad \text{(Eq.7)}$$

where $V_{R,cat}$ is the of catalyst bed volume with respect to the volume of empty reactor and $Q_{in}(T,P)$ is the inlet volume flow rate.

The kinetic parameters are reported in Table 4 only for the Ni-Co/Ce Al_2O_3 catalyst, which is the most active.

Table 4: Kinetic parameters using Ni-Co/Ce Al2O3 and τ=0.6 s.

	A (1/s)	E (kJ/mol)
CH4	22471	76
n-heptane	33	24
Benzene	608	57

3.2 Tar dry reforming

In the tar dry reforming tests the catalyst bed is held at 750 °C since this temperature seems to be sufficient to obtain a quite good conversion of the aromatic species contained in the tar as it can be deduced from the tests performed on the benzene. In Table 5 the amounts of tar produced with the two-stage reactor are compared with that obtained with the traditional one-stage fixed bed pyrolysis. For the Ni-Co/Ce Al_2O_3 catalyst the tar percentage decreases when the second stage is used by up to 78 % weight. The activated carbon supported catalyst leads to a minor reduction of about 56 %, as expected.

Table 5: Tar weight fractions.

	Tar (wt. %)
Pyrolysis	16.1
Ni-Co/Ce Al_2O_3	3.5
Ni-Co/Ce AC	7.2

The gas composition is reported on Fig. 3. The use of the second stage allows an improvement of the gas quality. In fact, the CO_2 concentration decreases, lowering the syngas dilution. With Ni-Co/Ce Al_2O_3 catalyst the fraction of H_2 raises of about 50 % due to the occurring of dry reforming and steam reforming reactions. During the steam reforming the tar reacts with the water produced by the pyrolysis to form hydrogen and carbon monoxide. This result is confirmed by the decrease of the water content of about 9% in the products, this reduction of water is not observed with the activated carbon supported catalyst.

Furthermore with both the catalysts the CO fraction increases considerably. It must be noted that in the case of activated carbon supported catalyst the CO concentration increases without a significative increment of H_2 concentration, this can be justified by the Boudourd reaction, which consumes the carbon of the support.

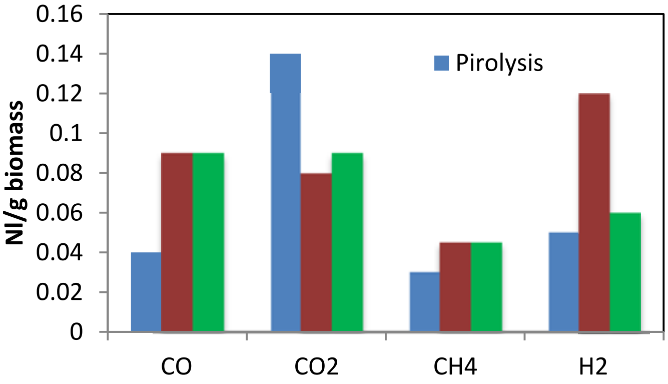

Figure 3: Yield of the monitored gas species for the pyrolysis and pyrolysis with reforming using Ni-Co/Ce γ-Al2O3 and Ni-Co/Ce AC.

4. Conclusions

In this work the possibility of improving the syngas quality with a contemporary reduction of the tar production in a pyrolysis process was tested using a catalytic stage. In this catalytic stage steam and dry reforming of tar occurs, leading to a decrease of its concentration and enhancing the gas production and quality. The influence of the catalytic support was investigated: Ni-Co bimetallic catalyst promoted with Ce, supported on γ-Al_2O_3 and on activated carbon were tested. The Ni-Co/Ce Al_2O_3 was found to be the most active, with a reduction of tar of 78 % and an increase of 65% and of 85% of CO and H_2, respectively. The CO_2 concentration decreases in both the setups tested, lowering the syngas dilution and so increasing its calorific value. The addition of a second stage of reforming can be a solution for the purification of the syngas from tar, converting it into CO and H_2.

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