Toluene steam reforming properties of CaO based synthetic sorbents for biomass gasification process

A. D'Orazio [a,*], A. Di Carlo [a], N. Dionisi [b], A. Dell'Era [a,b], F. Orecchini [a,b]

[a] CIRPS – Interuniversity Research Centre for the Sustainable Development, Sapienza University of Rome, Piazza S. Pietro in Vincoli 10, Via Cavour 256, 00184 Roma, Italy
[b] DME – Mechanical and Energy Engineering Department, Guglielmo Marconi University, Via Plinio 44, 00192 Roma, Italy

ARTICLE INFO

ABSTRACT

Biomass gasification process generates undesired Topping Atmosphere Residue (TAR), removable by catalytic steam reforming. The use of a CO_2-sorbent powder inside the reactor bed can minimize the content of carbon dioxide and carbon monoxide by enhancing the *water gas shift* (WGS) reaction, offering a fuel gas rich of H_2. The present study addresses the practical feasibility of such concepts, using toluene as a representative TAR and a hybrid compound $Ni/CaO–Ca_{12}Al_{14}O_{33}$ as reactor bed material, simultaneously acting as reforming catalyst and CO_2 sorbent. In fact, the CaO is the effective sorbent, whereas the $Ca_{12}Al_{14}O_{33}$ is a support for both the CaO and the active metallic Ni particles. A different synthesis route with respect to the literature has been developed for the production of the $Ni/CaO–Ca_{12}Al_{14}O_{33}$ and a total of three different bed reactor powders have been tested and compared: (i) a mixture of olivine and commercial nickel catalyst, (ii) a mixture of $CaO–Ca_{12}Al_{14}O_{33}$ and commercial nickel catalyst, and (iii) the $Ni/CaO–Ca_{12}Al_{14}O_{33}$ combined catalyst and sorbent. The best performances have been observed in the latter, with toluene conversion close to 99%, and the volume fraction of hydrogen in the gas over 95%. During multi-cycle tests, the synthetic $Ni/CaO–Ca_{12}Al_{14}O_{33}$ combined catalyst and sorbent exhibited superior resistance to carbon deposition and stability in toluene conversion compared to the other bed materials that suffer from decreased conversion efficiency after few cycles.

1. Introduction

Steam gasification processes are able to convert the chemical energy of the biomass into a syngas which can be used for the electrical power generation. At the moment one of the most efficient technologies for the gasification is the fluidized bed technology. Fluidized-bed reactors are common in those processes where catalysts must be continuously regenerated, also facilitating heat transfer, temperature uniformity, and

higher catalyst effectiveness factors [1,2]. Gasification of biomass with steam produces a fuel gas rich in hydrogen and carbon monoxide, with a significant content of methane and carbon dioxide but also organic impurities, generally indicated as Topping Atmosphere Residue (TAR). TAR is a complex mixture of cyclic and polycyclic aromatic hydrocarbons: it is an undesirable and noxious by-product very harmful, known for its toxicity and cancerous properties. In fluidized bed gasifiers, the concentration of TAR is typically ranging from 5

---

to 100 g/Nm^3 of the produced gas. Moreover, corrosive and pollutant characteristics of TAR compounds prohibit direct utilization of the produced gas stream. Eliminating the TAR compounds by the catalytic steam reforming and converting these into syngas, is a way to recovering their energy content. There are different reports on the steam reforming of representative TAR compounds, as well as toluene [3—11], but further investigations are necessary for a successful application of the biomass-derived gas [11] because of the high degradation of the catalyst due to, for example, the carbon deposition or sintering.

Taking into account that nowadays considerable interest is focused on a pure-hydrogen energy vector, the steam gasification process appears as an optimum candidate, provided that a reliable and economically convenient process is developed to extract hydrogen from the produced gas. This can be obtained for example by the capture of carbon-containing gas components by means of an appropriate sorbent [12]. Both the topics, the steam reforming of hydrocarbons (methane and TAR) and the carbon dioxide capture, are therefore relevant to enhance the applicability of biomass gasification processes and to render them suitable for renewable hydrogen production.

During last years new developments have been reported to run a gasification process including CO_2 capture [13,14]. In particular it has been proposed to add a CO_2 sorbent (a natural mineral substance, such as limestone or dolomite) to the reactor bed inventory [15—17]. Furthermore, using Ni as metal catalyst, good results have been reported in the Sorption Enhanced Steam Methane Reforming [18—24] with hydrogen molar fraction higher than 95% and CH_4 almost completely reformed with an operative temperature that varied between 600 and 700 °C. The use of Ni catalyst is effective also in the TAR reforming process and different studies to impregnate the dolomite with Ni were conducted successfully for example by Di Felice et al. [25,26].

Unfortunately calcium oxide based sorbents are vulnerable to the conditions reached in the fluidized bed systems (high temperature, mechanical friction etc), therefore exhibiting quick activity loss. Abanades and Alvarez [27] reported that the absorption capacity for Ca-based sorbents decays as a function of the number of calcination—carbonation cycles. They collected experimental data from different authors and concluded that the initial highest carbonation capacity of CaO equal to 14 mol/kg decreases to 3.78 mol/kg after 20 cycles and keeps decreasing. Li et al. [28,29] used $Ca_{12}Al_{14}O_{33}$ as a binder to improve the stability of CaO. The tests carried out in a thermo-gravimetric instrument showed an efficiency of adsorption equal to 41% after 50 carbonation—calcination cycles. Manovic and Anthony [30,31] also worked on the same direction using calcium aluminate cements to support CaO for high temperature applications. Martavaltzi et al. [32] impregnated the $CaO—Ca_{12}Al_{14}O_{33}$ sorbent with Ni catalyst presenting the development and the evaluation for application in methane sorption enhanced reforming of the hybrid material. This $Ni/CaO—Ca_{12}Al_{14}O_{33}$ functions simultaneously as reforming catalyst and CO_2 sorbent. $CaO—Ca_{12}Al_{14}O_{33}$ acts as an effective CO_2 sorbent and also as a support for the active metallic Ni particles. Li et al. [33] demonstrated the high resistance to coke formation by the $Ni/Ca_{12}Al_{14}O_{33}$ during steam reforming of TAR compound.

In the present work: a) a different synthesis route (with respect to the literature [32]) has been developed for producing the hybrid material $Ni/CaO—Ca_{12}Al_{14}O_{33}$ in order to make it more resistant and efficient for what concerning the features related to the biomass gasification and TAR removal (i.e. CO_2 adsorption, catalyst resistance to the poisoning due to the carbon deposition, resistance to the cycling) and material characterization has been carried out by different techniques (XRD, SEM, BET); b) the powder has been used in toluene steam reforming process for testing its effectiveness in the TAR removal. In particular, three different powders (S1, S2 and S3) for the bed material have been analyzed and compared: (i) S1 was olivine with the mixing of commercial catalyst Hifuel R110 provided by Alfa Aesar, for evaluating the effect of the catalyst alone on the process; (ii) S2 was home made $CaO—Ca_{12}Al_{14}O_{33}$ with the mixing of commercial catalyst Hifuel R110 provided by Alfa Aesar, for evaluating the effect of the combined catalyst and sorption on the process; (iii) S3 was home made $Ni/CaO—Ca_{12}Al_{14}O_{33}$ for evaluating the effect of the synthesis procedure in the catalytic effect of the powder. All the powders have been prepared keeping constant the amount of nickel available for the catalyst action, equal to 5% weight of $CaO—Ca_{12}Al_{14}O_{33}$. Toluene has been selected as TAR representative because is one of the organic hydrocarbons present on major amount (with benzene and naphthalene) generated during the pyrolysis of the biomass and more difficult to remove due to the stability of its single ring molecule [6,35]. The efficiency in TAR steam reforming and also hydrogen purification by CO_2 capture and coke formation were evaluated during multi-cycle test.

2. Experimental

2.1. Chemicals

The synthesis of the $CaO—Ca_{12}Al_{14}O_{33}$ and $Ni/CaO—Ca_{12}Al_{14}O_{33}$ has been carried out by different steps. Calcium carbonate $CaCO_3$ (CarloErba, technical grade) and acetic acid CH_3COOH (Sigma Aldrich, >99.7%) were adopted to produce the calcium acetate $Ca(CH_3COO)_2$ (that is the calcium oxide CaO precursor). Aluminum nitrate nonahydrate $Al(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich — ACS reagent, ≥98%) and Nickel(II) nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich purum p.a., crystallized, ≥97.0% KT) have been used to obtain mayenite and nickel oxide catalyst. For the test with commercial catalyst, the commercial Ni based pellets (HiFUEL R110) provided by Alfa Aesar-Johnson Matthey Company is used. For the laboratory scale sorption enhanced reforming experiments the following chemicals were used: anhydrous toluene (Sigma Aldrich, 99.8%), anhydrous 2-propanol (Sigma Aldrich, 99.5%), hydrogen/nitrogen/air (SIAD, 5.5 purity) and distilled water.

2.2. Synthesis of CaO—Ca$_{12}$Al$_{14}$O$_{33}$

Unlike the literature (Martavaltzi et al. [32]), where the Ni/ $CaO—Ca_{12}Al_{14}O_{33}$ powder has been produced mixing in one step $(Al(NO_3)_3 \cdot 9H_2O)$, $(Ni(NO_3)_2 \cdot 6H_2O)$ and the CaO obtained from commercial $Ca(CH_3COO)_2$, in the present work the Ni/