Syngas Cleaning by Chemical Looping Conversion of Tars from Hazelnut Shells Pyrolysis/Gasification

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Syngas tars are responsible for clogging and corrosion of pipelines and equipments due to their high condensation temperatures. At the same time, considering their energy content they cause a reduction in the energy efficiency of the conversion process. To overcome these drawbacks, the addition of a downstream reactor to perform hot catalytic gas cleaning has been proposed. However, the occurrence of significant carbon deposition and sulphide formation on the catalytically active surfaces can easily lead to early deactivation of the catalyst. Chemical looping tar reforming is based on a solid material, known as oxygen carrier, that undergoes two reactions steps: (1) reduction by interaction with the gas and tar streams; (2) regeneration by oxidation with ambient air, which also involves the combustion of any deposits on the particle surface. In this work, the first reaction step of the process is investigated in an integrated setup involving the pyrolysis or the gasification of hazelnut shells and the reaction with the oxygen carrier for tar abatement. Two reactor configurations have been considered: (1) single reactor, where the biomass and the oxygen carrier beds are loaded in series into the same reactor; (2) two reactors, where the two beds are loaded into different reactors in series. Blank tests for pyrolysis and gasification are also carried out for comparison. The results indicate that the two beds configuration enables higher tar conversion (89% wt for pyrolysis and 75% wt for steam gasification), though the presence of the oxygen carrier causes a reduction in the energy content of the syngas, especially in terms of H_2 concentration, which is reduced from around 34% to 21% mol for pyrolysis and from 28% to 21% mol for steam gasification.

1. Introduction

Biomass gasification and pyrolysis represent promising routes for the production of carbon neutral and high quality syngas (i.e. with high H_2 and CO molar concentration), that can be used in the energy sector, for example in power production or district heating, and in the chemical sector for the production of liquid fuels and chemicals such as methanol, ammonia, dimethyl-ether, formaldehyde etc.

To date one of the main drawbacks of this technology is represented by tars formation, which account for 5%-15% of the total energy of the products (Z. Huang et al., 2020). Tars are organic pollutants with a molecular weight higher than benzene that condense at high temperatures causing clogging of pipelines and equipment corrosion. Efficient syngas cleaning and upgrading is crucial for the development of this technology and, in this sense, high temperature gas cleaning is an interesting pathway to preserve the enthalpic content of the syngas from gasification/pyrolysis. The catalytic cracking of tars by steam reforming enables syngas cleaning with simultaneous energy upgrading, since additional CO and H_2 are produced, but it is affected by significant carbon deposition on the catalyst surface which inhibits the performance of the process over time.

Chemical looping tar reforming has been recently proposed as an alternative technology that can overcome these drawbacks. Chemical looping reforming (CLR) involves an oxygen carrier (OC) that undergoes two successive reaction steps: reforming, in which the oxygen carrier reacts with a gaseous fuel and produces CO,

CO_2, H_2O and H_2, by exchange of lattice oxygen with the solid material; oxidation where the reduced oxygen carrier is oxidized by a stream of ambient air. The available literature on this specific application of chemical looping is limited. Catalysts currently employed for tar cracking are natural ores, alkali metals, transition metals, and carbon-based catalysts. In Cuiping et al. (Cuiping et al., 2020) a composite oxygen carrier with Fe_2O_3, Al_2O_3, and CaO has been synthesized by the impregnation method. At 900 °C, oxygen carrier to carbon molar ratio of 3, and steam to carbon molar ratio of 0.5, a tar conversion above 90% has been demonstrated in a lab-scale fluidized bed reactor where tar has been directly injected. In Luo et al. (Luo et al., 2023) three oxygen carriers are tested (NiO, CuO-NiO, Fe_2O_3-NiO) and compared for the removal of toluene, which is used as tar model, given that toluene accounts for around 15-25% of biomass tar composition. The synergistic effect of Ni and Fe has been observed to promote toluene conversion (94.4%) and syngas production (3.3 Nm^3/kg) at 900 °C and at a steam to carbon ratio of 2. Fe-based oxygen carriers represent promising materials due to their high availability, resistance to attrition, thermal stability, and environmental friendliness (Palone et al., 2024). The combination of Fe with alkaline earth metals, such as Ca, has been proved to improve syngas yield during chemical looping gasification processes compared to iron oxides (X. Huang et al., 2020). Moreover, CaO is inexpensive, environmentally friendly, and is a catalyst for tar cracking.

The aim of this work is to analyse the effect of a Fe and Ca-based oxygen carrier bed on tar removal from a real syngas stream. No tar model compounds have been used, but biomass pyrolysis/gasification has been performed online with the subsequent tar removal by an oxygen carrier bed. Comparison with conventional fixed bed biomass pyrolysis or gasification is undertaken to assess the impact of the oxygen carrier presence on tar removal efficiency and insights from the preliminary results are discussed.

2. Method

2.1 Oxygen carrier preparation

The calcium ferrite is prepared via the sol-gel method. First $Fe(NO_3)_3.9(H_2O)$ and $Ca(NO_3)_2.4(H_2O)$ provided by Sigma Aldrich are weighed so that Fe^{3+}:Ca^{2+} = 2:1 and dissolved in distilled water. Stirring at 80 °C for 10 min is performed to reach a homogeneous solution, then citric acid is added according to an acid/Ca molar ratio of 1:1 and finally the pH is adjusted to 7 by the addition of aqueous ammonia. Subsequently, water is evaporated for 6 h at 80 °C and a gel is formed. The gel-like substance is put for 24 h in an oven at 100 °C to evaporate residual water and then calcined in a muffle furnace at 900 °C for 3 h. The resulting powder is then sieved with a sieve of nominal aperture of 710 μm.

2.2 Experimental setup and procedure

The experiments are carried out with two reactor configurations. In the first configuration a single stainless-steel tubular reactor of 2 cm diameter and 40 cm length is used. The reactor is loaded with two particle beds in series separated by quartz wool and containing 2 g biomass and 0.5 g Ca ferrite (i.e. 0.25 OC/B in mass), respectively. A simplified scheme of the setup is reported in Figure 1-(a). An argon flow rate of 0.25 nl/min is injected into the reactor and then heating by an external tubular resistance is started with a first step at 200 °C for 5 min to release the residual moisture in the biomass (to avoid clogging), and then a second step at 750 °C for 20 min.

In the second configuration, an additional quartz reactor (1 cm diameter and 20 cm length) containing the oxygen carrier is added downstream to the first one (where only biomass is loaded). A simplified scheme is provided in Figure 1-(b). The second reactor is heated by an external resistance to 730 °C and then the biomass reactor is heated according to the previous procedure to 750 °C. This is expected to promote tar cracking by the oxygen carrier, which is more active at higher temperatures.

Each reaction step is evaluated for a total of 20 minutes after which the reactor is cooled down by the Ar flow. In the gasification tests, liquid water is mixed with the Ar flow by injection with a syringe pump and electrically heated to 250°C before entering the first reactor. The resulting mixture is composed of 10% vol H_2O and 90% vol Ar. The gaseous products are analyzed by online mass spectrometry (QGA, Quantitative Gas Analyzer), while the liquid products are condensed and collected in a balloon flask immersed in an ice bath. Gas chromatography–mass spectrometry (GC-MS) is also used for qualitative characterization of the collected tars. However, the associated results will not be displayed in this paper.
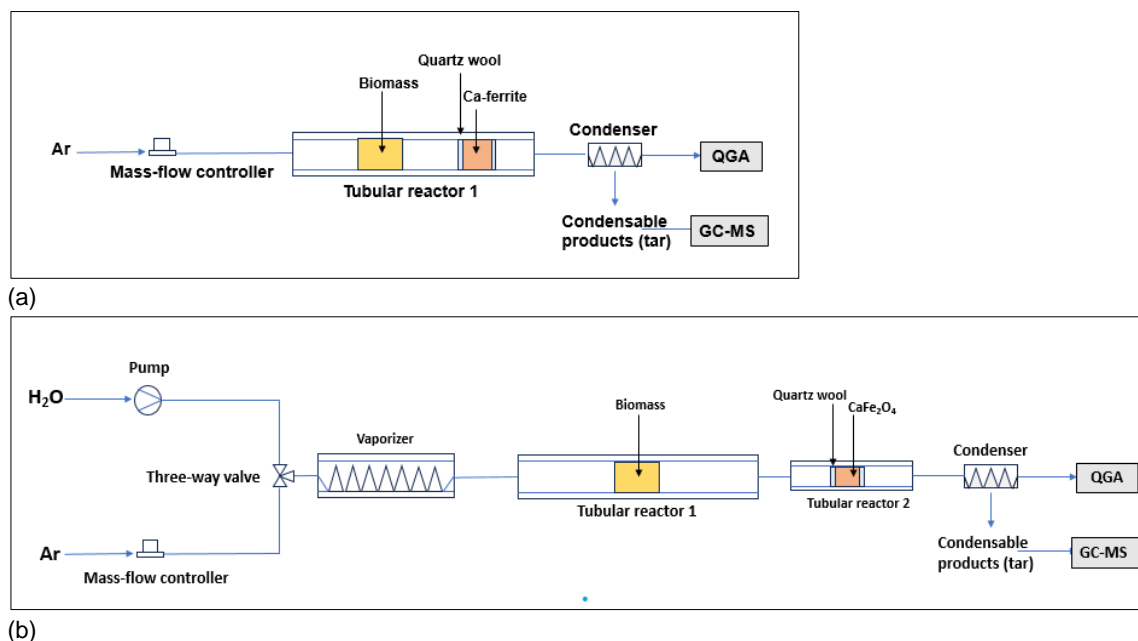
(a)

(b)

Figure 1. Scheme of the two configurations: (a) one reactor with separate biomass and oxygen carrier beds, (b) two separate reactors with single beds in series

2.3 Material characterization

Material characterization is carried out by X-Ray Diffraction (XRD) using a Philips Analytical PW1830 diffractometer (Malvern, UK) equipped with a Ni β-filtered Cu Kα (1.5418 A) with applied voltage and current of 40 kV and 30 mA, respectively.

As shown in Figure 2, the synthesized material is composed of a mixture of $Ca_2Fe_2O_5$ and $CaFe_2O_4$. Peaks of residual Fe_2O_3 are also detected.
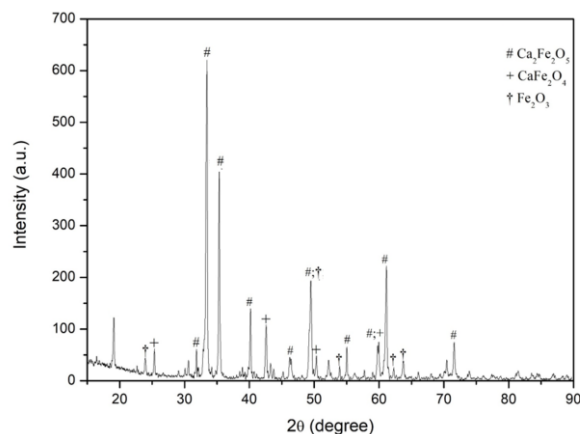
Figure 2. Diffractogram of the synthesized Ca ferrite powder

The oxygen carrier surface properties are analyzed by the Brunauer-Emmett-Teller (BET) method using a Micromeritics Triflex Analyzer (Micromeritics Instrument Corp., Norcross, Ga, USA) with N_2 adsorption-desorption isotherms at -196 °C in a p/p_0 range from 0.01 to 0.99. Before analysis, the samples are outgassed for 4 h at 300 °C.

The results are collected in Table 1. Very low surface area (< 1 m^2/g) and pore volumes are detected, as shown in the literature for unsupported iron ores (Luo et al., 2021) or calcium ferrites (Hu et al., 2020).

Table 1. BET analysis of the synthesized Ca ferrite providing specific surface area (m²/g), mean pore width (nm), and total pore volume (cm³/g)

Material	Specific surface area (m²/g)	Mean pore width (nm)	Total pore volume (cm³/g)
Ca ferrite	0.48	7.48	0.0011

The selected biomass, hazelnut shells, is characterized with an Eurovector EA3000 elemental analyzer. Three samples have been analyzed to obtain statistically relevant data. The oxygen mass fraction is calculated per difference assuming the absence of any sulfur content in the biomass. The results shown in Table 2 indicate that around 51% wt of carbon and 6% wt of hydrogen are present in the biomass.

Table 2. Elemental analysis of the hazelnut shells

Mass fraction (%)	N	C	H	O (diff.)
Mean	0.61	50.55	5.99	42.85
Standard deviation	0.10	0.47	0.06	0.06

3. Results analysis

3.1 Single reactor configuration

In the first configuration a single reactor is tested with two particle beds in series containing the biomass and the Ca ferrite particles. In this case the objective is to realize a compact configuration where the tars released by the biomass interact with the oxygen carrier bed and are partially oxidized. A comparative analysis is performed with the blank test involving the sole biomass bed. The QGA results on gas compositions are integrated over the whole duration of the tests and collected in Table 3.

Table 3. Average gas compositions (% mol) in the single reactor configuration after blank pyrolysis and with oxygen carrier

	H_2	CO_2	CO	CH_4	C_2H_4	Tot
Blank	28.2%	27.0%	28.4%	14.5%	1.9%	100%
Oxygen carrier	19.1%	24.4%	27.9%	13.5%	15.2%	100%

The presence of the oxygen carrier bed causes a decrease in the H_2, CO, and CH_4 concentrations, while the C_2H_4 content rises from 1.9% to 15% mol. This result can be associated with the simultaneous occurrence of material reduction by the fuel gases (H_2, CO, and CH_4) released during pyrolysis and the tar cracking with C_2H_4 production. The mass balance for the three product phases in Table 4 corroborates these findings by reporting a 10% wt decrease in tar production and an increase in the gas phase. The balance is performed by weighing the collected char and tar, while the gases mass yield is derived by mass difference. As expected, the char mass yield remains unaltered.

The results are however not satisfactory in terms of tar conversion. This outcome can be attributed to the oxygen carrier bed limited reactivity during tar release, which is expected to occur from around 300 °C during the reactor temperature ramp (Mahmood and Ceylan, 2022).

Table 4. Mass balance for the three product phases (solid, liquid, and gas) in the single reactor configuration after blank pyrolysis and with oxygen carrier

	Char (g)	Tar (g)	Gas (g)	Tot (g)
Blank	0.49	0.33	1.17	2.00
Oxygen carrier	0.49	0.30	1.20	2.00

3.2 Two reactors configuration: pyrolysis

In the two reactors configuration the tars released by the biomass during the temperature ramp encounter the oxygen carrier bed at high temperature (730 °C). As shown in Table 5, with respect to the blank test the CO concentration increases from 28.4% mol to 39.1% mol, the CH_4 concentration increases to 16.4% mol, and the C_2H_4 increases to 6.4% mol. On the contrary, the CO_2 and H_2 decrease with respect to the blank test and, in particular, the H_2 content is reduced by around 13 percentage points because of the high reactivity with the material. The product phases mass balance in Table 6 corroborates the results, indicating tar conversion by 89% wt, which is mainly converted to syngas.

Table 5. Average gas composition (% mol) in the two reactors configuration after blank pyrolysis and with oxygen carrier

	H_2	CO_2	CO	CH_4	C_2H_4	Tot
Blank	34.3%	21.0%	28.4%	14.1%	2.3%	100%
Oxygen carrier	21.4%	16.7%	39.1%	16.4%	6.4%	100%

Table 6. Mass balance for the three product phases (solid, liquid, and gas) in the two reactors configuration after blank pyrolysis and with oxygen carrier

	Char (g)	Tar (g)	Gas (g)	Tot (g)
Blank	0.49	0.28	1.31	2.08
Oxygen carrier	0.51	0.03	1.55	2.09

3.3 Two reactors configuration: steam gasification

A biomass gasification test with H_2O as enhancer has been carried out in the two reactors configuration. Liquid water is mixed with an Ar flow to reach 10% vol in the final mixture (0.02 ml/min of H_2O) and then heated by a resistance to 250 °C for steam production.

Comparison with the blank test results is given in Table 7. Except for a slight increase in CH_4 and C_2H_4 in the oxygen carrier case, which can be ascribed to tar cracking, in general the syngas energy content decreases due to the oxygen carrier reduction. In particular, the H_2 concentration in the final syngas decreases by about 5 percentage points. The combined effect of H_2 reduction and H_2O oxidation of the material can be responsible for this relatively limited drop in the concentration, if compared to the results for pyrolysis. However, tar conversion by 75% wt is achieved, as indicated by the results in Table 8. Compared to the pyrolysis tests of Table 5, in the two reactors configuration with the oxygen carrier the H_2 concentration rises from 21.4% to 33.4% mol while the CO, CH_4, C_2H_4 concentrations are reduced, due to a combination of water gas shift and hydrocarbons steam reforming. Especially the CO concentration decreases substantially, shifting from around 39% mol in the pyrolysis test to about 28% mol in the steam gasification test. Therefore, as expected, the positive effect of the oxygen carrier in terms of tar conversion and hydrogen intensification in the final syngas is more evident in the steam gasification case. On the contrary, the residual tar after gasification and pyrolysis is almost unchanged (0.03 mg), while the char reduction after gasification is also limited (0.02 mg).

From the observed results the following adjustments and implications can be drawn to maximize tar conversion and syngas upgrading: (1) by increasing the second reactor temperature above 800 °C material activity can be improved; (2) by optimizing the steam to carbon ratio hydrogen production can be intensified by the combined effect of water gas shift, hydrocarbons reforming, and oxygen carrier oxidation; (3) by optimizing material synthesis with the addition of a support can provide higher specific surface areas and facilitate tar conversion.

Table 7. Average gas composition (% mol) in the two reactors configuration after blank gasification and with oxygen carrier

	H_2	CO_2	CO	CH_4	C_2H_4	Tot
Blank	38.9%	14.8%	30.8%	12.3%	3.3%	100%
Oxygen carrier	33.4%	20.9%	28.3%	13.7%	3.7%	100%

Table 8. Mass balance of the three product phases (solid, liquid, and gas) in the two reactors configuration after blank gasification and with oxygen carrier

	Char (g)	Tar (g)	Gas (g)	Tot (g)
Blank	0.47	0.12	1.47	2.05
Oxygen carrier	0.47	0.03	1.55	2.05

4. Conclusions

Chemical looping tar reforming by a calcium ferrite oxygen carrier is evaluated in an integrated system under hazelnut shells pyrolysis or gasification conditions. Two configurations are compared: (1) single reactor with two particle beds in series; (2) double reactor with one particle bed per reactor.

The results for the pyrolysis tests in the first configuration indicate limited tar conversion (10% wt) and a decrease in the H_2 concentration in the final syngas, likely due to the oxygen carrier reduction by H_2. The main limitations in the first configuration lie in the tars being released at low temperatures (from 350 °C according to literature), at which the oxygen carrier is not active.

Therefore, a second configuration has been developed where the oxygen carrier is located in a second reactor which is kept at high temperatures (730 °C) during the whole test. With respect to the blank pyrolysis, in the two reactors configuration the CO concentration increases by around 11 percentage points and the tars are significantly reduced (around 89% wt conversion). Given the promising results of the two reactors configuration, steam gasification tests are performed for H_2 intensification in the final syngas with respect to pyrolysis. Compared to the blank gasification test, a general reduction in syngas energy quality is observed except for a slight increase in C_2H_4 and CH_4 concentrations, while tar conversion is promoted and reaches a conversion of around 75% wt. In general, the final tar mass in unchanged between pyrolysis and steam gasification with the oxygen carrier, while as expected the H_2 content is intensified in the latter case by the combined effect of hydrocarbons reforming, water gas shift, and oxygen carrier steam oxidation.

Based on these promising results, future optimization of the oxygen carrier composition and of the reaction conditions, such as the steam to biomass ratio and the total temperature in the two reactors, will be crucial to minimize the observed syngas energy downgrading in the presence of the oxygen carrier while maximizing tar conversion.

Nomenclature

Brunauer-Emmett-Teller	BET
Chemical looping reforming	CLR
Gas Chromatography–Mass Spectrometry	GC-MS
Oxygen Carrier	OC
Quantitative Gas Analyzer	QGA
X-Ray Diffraction	XRD

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