



Catalytic biomass gasification: Simultaneous hydrocarbons steam reforming and CO₂ capture in a fluidised bed reactor

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ABSTRACT

Tars and CH₄ generated from biomass gasification processes contribute significantly to the energy content of the producer gas: catalytic tar and CH₄ steam reforming allows to clean the gaseous fuel and improve the H₂ yield; in addition, the use of a CO₂ sorbent minimises carbon oxides. As a result of the whole process, a H₂ rich fuel gas may be obtained. This experimental work is addressed to study the practical feasibility of such concepts, choosing CH₄, toluene and 1-methyl naphthalene (1-MN) as biomass gasification key primary products. Ni is used as a catalyst for steam reforming, and dolomite as a sorbent for CO₂ capture. Two kinds of catalytic systems are tested as bed material: a mixture of dolomite and commercial nickel catalyst, and a new Ni/dolomite combined catalyst and sorbent. The experimental investigations have been carried out in a fixed bed microreactor and a bench scale fluidised bed reactor rig. Both combinations of catalyst and sorbent are found to be very effective in tar removing, with conversion values near to 100% for the compounds tested; simultaneous CO₂ sorption reveals itself as the key process step, improving significantly the performance of the catalytic system that may then decrease considerably after sorbent saturation.

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1. Introduction

It is well known that biomass is one of the most important primary and renewable energy sources, with a neutral balance in the carbon dioxide cycle. In order to obtain a readily usable energy vector from biomass, gasification is the conversion process closest to industrial exploitation [1]. Biomass gasification is a thermochemical conversion process utilizing air, oxygen and/or steam as gasification agents, which produces a fuel gas rich in hydrogen and carbon monoxide, with a significant content of methane and carbon dioxide. Steam and nitrogen are also present in the producer gas, in addition to organic (tar) and inorganic (H₂S, HCl, NH₃, alkali metals) impurities, and particulate. High molecular weight hydrocarbons (tar) are an undesirable and noxious by-product, with concentration ranging from 5 to 100 g/N m³ of the producer gas in fluidised bed gasifiers. Tar is a complex mixture of cyclic and polycyclic aromatic hydrocarbons [2] very harmful for toxicity and cancerous properties. Moreover, corrosive and pollutant characteristics of tar compounds prohibit direct utilization of the gas product stream.

Catalytic steam reforming seems to be the best way to eliminate tar compounds, converting them into syngas, and thus recovering their energy content. Steam reforming of model tarry compounds as well as toluene [3–6], phenol [7,8], naphthalene [7,9,5] and 1-methyl naphthalene [10] has been yet studied in literature, but further investigations are necessary for a successful application of biomass-derived producer gas [11]. It is also of practical interest to maximise the H₂ content in the fuel gas by simultaneous steam reforming of its CH₄ fraction.

Steam gasification processes are able to convert the chemical energy of biomass into a hydrogen-rich syngas containing up to about 50% by volume of hydrogen on dry basis [12]. Nowadays considerable interest is focussed on a pure-hydrogen energy vector, and biomass, is the only feedstock that could assure H₂ production in a sustainable way, without consumption of fossil fuels. In this respect, the steam gasification process appears as an optimum candidate, provided that a reliable and economically convenient process is developed to extract hydrogen from the producer gas. This can be obtained either by the utilization of selective membranes permeable to hydrogen small molecules, or by capture of carbon-containing gas components by means of an appropriate sorbent [13]. Both topics, steam reforming of hydrocarbons (methane and tar) and carbon dioxide capture, are therefore relevant to enhance the applicability of biomass gasification processes and to render them suitable for renewable hydrogen production.

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They are addressed in an innovative, unified perspective in this paper.

Recently, in the literature new developments have been reported to run a gasification process including CO₂ capture [14]. It has been proposed to add a CO₂ sorbent (a natural mineral substance, such as limestone or dolomite) to the FICFB (fast internally circulating fluidised bed [15]) reactor bed inventory. The sorbent circulates between a gasifier – CO₂ capture bubbling bed, and a combustor – calciner riser, in order to run the whole process continuously.

In the reactor chamber devoted to biomass gasification and CO₂ capture, the endothermic gasification and the exothermic solid carbonation processes combine well together and their coupling reduces the amount of the solid circulation rate required to sustain thermally the devolatilization and gasification reactions. On the other hand, the riser provides the calcined solid sorbent and the thermal loading, by combustion of residual char (and/or additional fuel). When this is performed utilizing pure oxygen, a CO₂ stream is easily obtained (by steam condensation), available for storage and sequestration.

The thermodynamic constraints of the reaction between CO₂ and CaO impose, at ambient pressure, a temperature level for gasification somewhat lower (650–700 °C) than the usual one (800–850 °C), as it is clear from the equilibrium equation [16,17] (Eq. (1)).

$$P_{\text{CO}_2\text{eq}} (\text{atm}) = 4.137 \times 10^7 \times \exp \left(-\frac{20,474}{T(\text{K})} \right) \quad (1)$$

where $P_{\text{CO}_2\text{eq}}$ (atm) is the equilibrium CO₂ pressure expressed in atmospheres, and T (K) the system temperature expressed in K.

However, the experimental evidence [14] does not show any negative effect on tar production in these conditions of reduced temperature.

The final goal of our research project is to optimise the granular, mineral solid material for a dual bed system with a CO₂ sorbent performing a calcination–carbonation loop. This is done in different steps, starting from the study of simultaneous hydrocarbon reforming and CO₂ capture by means of commercial, readily available materials (a nickel catalyst mixed with calcined dolomite), and progressively moving to improve the catalytic activity of dolomite for reforming reactions in order it to perform the double function of CO₂ sorbent as well as reforming catalyst.

Monocyclic aromatic hydrocarbons are considered the most representative tar compounds, reaching 46% of overall biomass tar [2]. Two rings aromatic hydrocarbons represent about 28% of biomass tar [2]. So, the reactivity of about 75% of biomass tar can be studied by choosing the appropriate model tar compounds: in this work, toluene and 1-methyl naphthalene (1-MN). The results of methane, toluene and 1-methyl naphthalene steam reforming and water gas shift tests are reported. The experiments have been carried out in a bench scale rig, with a fluidised bed inventory allowing for simultaneous hydrocarbon reforming and CO₂ sorption by means of a commercial nickel catalyst mixed with calcined dolomite. In addition, toluene has been steam reformed in a fixed bed microreactor in presence of a 4 wt% Ni/dolomite supported catalyst.

It is worth mentioning here that dolomite is known to have a catalytic activity in tar reforming [18–21], and at the same time is a very attracting material to absorb CO₂ from syngas [13–15]. Nickel, on the other hand, is a well known, low-cost catalyst for steam reforming [4,22,23]. In this work, the activity of these materials is evaluated with different hydrocarbons (methane, toluene, 1-MN). The last two are representative of most tars formed during gasification, and the activity of methane is well known in steam reforming with Ni catalysts. The present contribution is only the first part of a more complex study including hydrocarbons reactivity in presence of all gas compounds produced during steam reforming of biomass.

Table 1

(a) Elemental analysis of fresh dolomite and (b) specific surface area of fresh and calcined dolomite.

	Fe	CaO	MgO
(a)			
Elemental analysis (wt% of fresh dolomite)	0.01	30.39	20.56
(b)			
Specific surface area of fresh dolomite			0.1 m ² /g
Specific surface area of calcined dolomite ^a			15.2 m ² /g

^a At 850 °C for 4 h in fluidised bed.

2. Experimental

2.1. Materials

Two different catalytic systems have been used. The former consists of a commercial nickel catalyst (Johnson Matthey Plc) mixed with dolomite kindly provided by Pilkington (see Table 1 for elemental analysis (a) and specific surface area (b) of dolomite).

The latter consists of the same dolomite as above, impregnated by nickel (Ni/dolomite); this catalyst contains 4% of nickel by weight. The preparation method is the following: a stirred suspension of calcined dolomite (pre-calcined at 900 °C for 4 h, 3 °C/min heating rate) in an aqueous solution of nickel nitrate (Sigma A) has been prepared, and heated at 110 °C. After solvent evaporation, the solid has been collected, dried overnight in an oven at 100 °C and then calcined at two different temperatures (900 and 1100 °C) for 4 h, with a heating rate of 3 °C/min.

2.2. Catalyst characterization

The Ni/dolomite catalyst has been characterized by X-ray diffraction (XRD) and temperature-programmed reduction (TPR).

2.2.1. XRD

The crystalline phases contained in the samples and the structural modifications occurring after reduction or catalytic tests were examined by powder X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer using a Ni detector side filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.2.2. TPR

To quantify the amount of reducible metal (nickel), we have followed the reducibility of the catalyst by temperature-programmed reduction performed on 50 mg of catalyst placed in a U-shaped quartz tube (6.6 mm I.D.). The reductive gas mixture (H₂ = 0.12 L h⁻¹ and Ar = 3 L h⁻¹) passed through the reactor heated from room temperature to 900 °C with a heating rate of 15 °C min⁻¹ and was then maintained at 900 °C until the end of H₂ consumption according to the baseline return. A thermal conductivity detector (TCD) was used for the quantitative determination of hydrogen consumption.

2.3. Reactivity tests

The experiments for catalytic steam reforming of tar components and CO₂ capture were carried out by using a fixed bed microreactor (Fig. 1) and a bench scale fluidised bed (Fig. 2). The former rig has been used for testing the new 4% Ni/dolomite catalyst for toluene-steam reforming, while the fluidised bed reactor has been used for testing the catalytic and sorption behaviour of dolomite mixed with the commercial nickel catalyst for methane, toluene and 1-methyl naphthalene steam reforming and water gas shift.

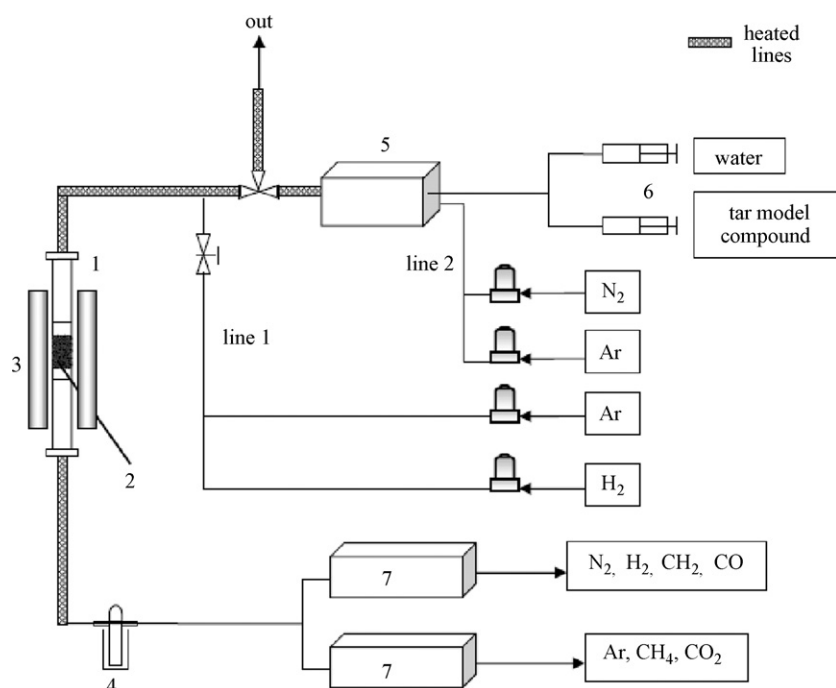


Fig. 1. Schematic diagram of the experimental apparatus (fixed bed microreactor): 1, quartz microreactor; 2, catalyst fixed bed; 3, furnace; 4, condenser; 5, evaporator; 6, motorised syringes for feeding liquids; 7, gas chromatographs.

2.3.1. Fixed bed microreactor experimental tests

Experiments in the fixed bed microreactor rig were carried out under atmospheric pressure in a quartz reactor (8 mm I.D.) placed in an electric furnace. The reactor was charged with 400 mg of the Ni/dolomite catalyst (particle size between 125 and 600 μm) inserted between two plugs of quartz wool, and then placed in the middle of the furnace. The catalyst bed temperature was monitored by a thermocouple located near to the catalyst bed.

The feeding system consists of two main lines (1 and 2 in Fig. 1). Line 1 (Ar with and without H_2), feeding directly the reactor, has been used to pre-reduce and just preserve the catalyst bed in a neutral atmosphere (purging the gas chromatographs downstream of the reactor, when necessary). Line 2 (Ar and N_2 mixture), acts as a carrier gas for steam and tar model compounds, passing through

an evaporation chamber where water and toluene are introduced as liquids, drop by drop, by motorised syringes. The temperature of the evaporation chamber, as well as the temperature of all feeding tubes, is kept above the dew point of toluene, to prevent condensation. The catalyst was tested under an overall feed flow rate of 3 NL/h with composition shown in Table 2.

The feeding gas mixture composition has been adjusted in order to obtain a tar concentration of 30 g/N m^3 , which corresponds to a representative value for the gas phase in a biomass gasifier. The steam/toluene ratio is slightly higher (18:1) than the stoichiometric value for complete toluene conversion into H_2 and CO_2 (14:1).

The inert nitrogen flow allows to normalize the area of gas-chromatographic peaks. The outlet gas has been analysed by two gas chromatographs equipped with TCD. The former indicating the

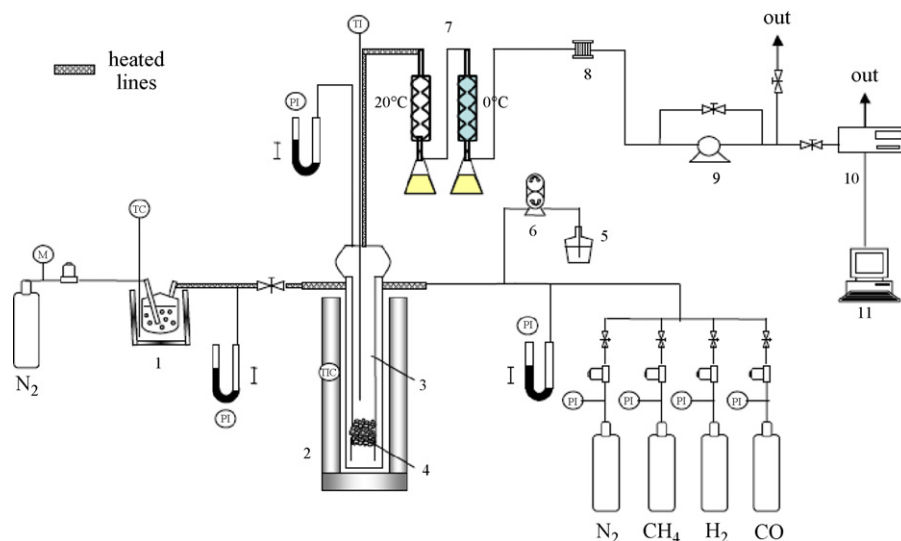


Fig. 2. Schematic diagram of the experimental apparatus (fluidised bed reactor): 1, model tar compound saturator; 2, furnace; 3, quartz reactor; 4, catalyst bed; 5, water flask; 6, peristaltic pump; 7, water and tar condenser; 8, particle filter; 9, pump; 10, analysis system; 11, acquisition system; TI, temperature indicator; PI, pressure indicator; TIC, temperature indicator controller.

Table 2
Feeding composition and test conditions for fixed bed microreactor test.

Parameter	Value	%V
Ar (NL/h)	2.02	67.2
H ₂ O (NL/h of steam)	0.36	12
Toluene (NL/h vapour)	0.02	0.8
N ₂ (NL/h)	0.6	20
Reactor temperature (°C)	640	
Bed inventory	4 wt% Ni/dolomite	
Particle size range (μm)	125–600	
Bed mass (mg)	400	
Contact time (s)	0.8	

amount of H₂, N₂, CH₄, CO separated on a molecular sieve 5 Å, and the latter quantifying Ar, CH₄ and CO₂ separated on a column Hayesep Q. The GC calibration has been done by employing a gas cylinder containing a reference mixture for CH₄ (19.58%), H₂ (22%), CO (18.83%), CO₂ (19.8%) and N₂ (19.81%).

In the Ni pre-reduction phase, a 10% H₂ (0.3 NL/h) in 2.7 NL/h Ar flow has been used. The catalyst has been reduced by heating the reactor up to the temperature level of 850 °C, with a heating rate of 5 °C/min.

2.3.2. Bench scale fluidised bed experimental tests

The schematic diagram of the fluidised bed experimental setup is shown in Fig. 2. A properly designed laboratory-scale quartz reactor (60 mm I.D. and 660 mm high) has been utilized, encased in an electrically heated cylindrical furnace. The gas distributor plate is made of sintered quartz glass with sufficient pressure drop to assure an even gas flow. An annular jacket where the reactants are mixed together and heated up to the reaction temperature surrounds the reactor wall. The entire apparatus has been conceived to carry out both gas and vapour reforming reactions, leading to a comprehensive understanding of methane and tar model compounds reactivity.

The whole test procedure includes six main steps:

1. pre-calcination of dolomite: the bed material (dolomite and catalyst) in the reactor is heated up to 850 °C, with a heating rate of 10 °C/min, with a total flow rate of 70 NL/h of nitrogen;
2. catalyst reduction: the bed material is heated up to 850 °C, with a heating rate of 10 °C/min, in 10% H₂ in N₂ gaseous flow, with total flow rate of 66 NL/h;
3. steam reforming and water-gas shift: see Tables 3–5, 6a and 6b for experimental conditions;

Table 3
Toluene-steam reforming experimental conditions.

Parameter	Value	%V
Primary N ₂ (NL/h)	30.7	41.2
Secondary N ₂ (NL/h)	28.5	38.2
Toluene (NL/h vapour)	0.69	0.9
H ₂ O (NL/h of steam)	14.7	19.7
Reaction temperature (°C)	645	
Catalytic system	Dolomite and commercial nickel catalyst	
Fresh dolomite particle size range (μm)	200–300	
Fresh dolomite mass (g)	125	
Commercial nickel catalyst particle size range (μm)	250–500	
Commercial nickel catalyst mass (g)	30	
Contact time (s)	6.1	

Table 4
1-MN steam reforming experimental conditions.

Parameter	Value	%V
Primary N ₂ (NL/h)	30.7	39.2
Secondary N ₂ (NL/h)	28.5	36.4
1-MN (NL/h vapour)	0.56	0.6
H ₂ O (NL/h of steam)	18.7	23.8
Reaction temperature (°C)	645	
Bed inventory	Dolomite and commercial nickel catalyst	
Fresh dolomite particle size range (μm)	200–300	
Fresh dolomite mass (g)	80	
Commercial nickel catalyst particle size range (μm)	250–500	
Commercial nickel catalyst mass (g)	20	
Contact time (s)	3.9	

Table 5
CH₄ steam reforming experimental conditions.

Parameter	Value	%V
Secondary N ₂ (NL/h)	40	44.45
CH ₄ (NL/h)	10	11
H ₂ O (NL/h of steam)	40	44.45
Reaction temperature (°C)	630 °C	
Bed inventory	Dolomite and commercial nickel catalyst	
Fresh dolomite particle size range (μm)	200–300	
Fresh dolomite mass (g)	90.2	
Commercial nickel catalyst particle size range (μm)	250–500	
Commercial nickel catalyst mass (g)	48	
Contact time (s)	6.8	

Table 6a

Water-gas shift experimental conditions using dolomite as bed material.

Parameter	Value	%V
Secondary N ₂ (NL/h)	70	63.3
CO (NL/h)	10	9.0
H ₂ O (NL/h of steam)	30.72	27.7
Reaction temperature (°C)	630 °C	
Bed inventory	Dolomite	
Fresh dolomite particle size range (μm)	200–300	
Fresh dolomite mass (g)	98.2	
Contact time (s)	3.68	

- calcination of dolomite after test: allows to quantify the CO₂ adsorbed at the end of steam reforming test. It has been carried out by using the same experimental conditions than those described in step 1;
- combustion (and quantification) of carbon deposited during the test: at about 830 °C, in a flow of 60 NL/h of nitrogen and 15 NL/h of air (4% O₂);
- analysis of total organic carbon in the condensed phase: to detect liquid hydrocarbons eventually present in the reactor outlet stream.

The outlet gas stream, after rapid cooling and steam and vapours condensation and separation, is fed to the analytical section, where H₂, CO, CO₂ and CH₄ are measured on-line by an ABB gas analyser. In each test N₂ has been always added to the reactant gases at a fixed and known molar flow rate, so that to allow for the desired fluidisation conditions and to provide a reference flow to evaluate the absolute yield of the reaction products.

Natural dolomite and the commercial nickel catalyst have been crushed and sieved separately to obtain fractions with average diameter of 200 and 300 μm, respectively. The minimum fluidisation velocity of dolomite and catalyst particle samples has been measured experimentally at ambient conditions according to a standardised method (bed pressure drop vs superficial velocity profile): for the dolomite sample, with a density of 1490 kg/m³, the measured minimum fluidisation velocity in air is 3.2 cm/s, while for the catalyst sample the corresponding value is 3.9 cm/s. On the basis of these measurements it is expected that the bed remained well mixed during the experimental tests.

2.3.2.1. Tar steam reforming. On the left hand side of the schematic diagram in Fig. 2, the tar model compound feeding system is shown: a nitrogen flow passes through a saturation unit (a heated flask), where the model tar compound (toluene or 1-MN) is located. The tar-saturated nitrogen stream is then fed to the reactor via a heated line. With such a system, by varying the temperature level of the saturation unit, mixtures of 1-MN or toluene with N₂ are obtainable in a broad range of partial pressures.

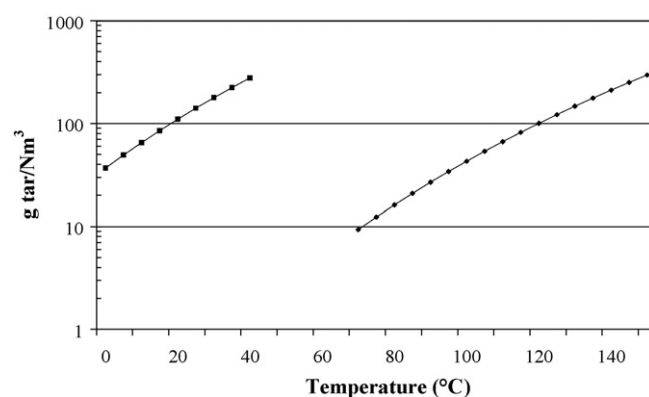


Fig. 3. Logarithmic plot of g tar/N m³ gas as a function of the saturation temperature, according to the Antoine Law, at ambient pressure, for 1-MN (♦) and toluene (■).

Theoretical toluene or 1-MN concentration in the reactor feeding stream are expressed by Antoine Law (Eqs. (2) and (3), Fig. 3):

$$\text{for toluene: } \ln P_{(\text{atm})} = 9.63 - \frac{3242.4}{-47.181 + T} \quad (2)$$

$$\text{for 1-MN: } \ln P_{(\text{atm})} = 9.64 - \frac{4265}{-75.47 + T} \quad (3)$$

In agreement with the equilibrium data, the temperature level in the saturation flask has been adjusted to 16 °C for toluene, to obtain a partial pressure corresponding to about 22,000 ppm (90 g of toluene/N m³), and 123 °C for 1-MN, which would assure a concentration of 18,000 ppm (114 g of 1-MN/N m³). The exact toluene and 1-MN concentration in the reactor feeding stream has been monitored by a MultiFID 14 analyser, before each test, to confirm the saturation level of the N₂ flow entering the reactor.

The steam feeding flow rate corresponds to about 1.5 times the stoichiometric value required for total conversion of the model tar compounds.

Tables 3 and 4 show the overall experimental conditions for toluene and 1-MN steam reforming tests, respectively.

The contact time is given by the ratio between the volume occupied by solids in the reactor, measured in fixed bed conditions before test, and the overall volumetric flow rate entering the reactor, evaluated at normal conditions.

2.3.2.2. Methane-steam reforming and water-gas shift reactions. A gas cylinders station is connected to the reactor, together with a water inlet flow controlled by means of a dosing pump with variable speed; water is then vapourised and mixed with the gas stream inside the reactor jacket. The flow rate of the gaseous compounds is measured by mass flow meters. In this way, methane-steam reforming has been carried out by using the conditions shown in Table 5, whereas experimental conditions for water-gas shift reaction tests are shown in Tables 6a and 6b.

Table 6b

Water-gas shift experimental conditions using Ni catalyst and dolomite as bed material.

Parameter	Value	%V
Secondary N ₂ (NL/h)	70	63.3
CO (NL/h)	10	9.0
H ₂ O (NL/h of steam)	30.72	27.7
Reaction temperature (°C)	630 °C	
Bed inventory	Dolomite and commercial nickel catalyst	
Fresh dolomite particle size range (μm)	200–300	
Fresh dolomite mass (g)	92	
Commercial nickel catalyst particle size range (μm)	250–500	
Commercial nickel catalyst mass (g)	49.4	
Contact time (s)	5.5	

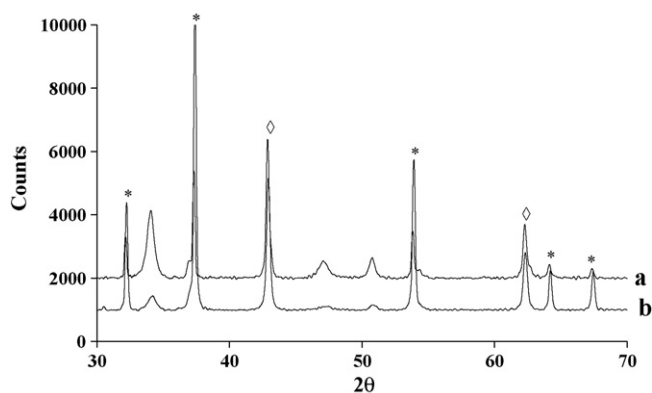


Fig. 4. X-ray diffraction for the Ni/dolomite catalyst (a) compared with calcined dolomite (b) (\diamond = CaO; * = MgO).

2.3.3. Multi-cycle experimental conditions

When alternate calcination–carbonation tests are performed successively, to check the sorbent behaviour under multi-cycle operating conditions, the main steps of the experimental procedure are:

- initial pre-calcination of dolomite and reduction of catalyst, as described in Section 2.3.2 (point 1 and 2);
- steam reforming test and calcination of dolomite after test (point 3 and 4, Table 5), performed iteratively. Catalyst reduction is not repeated between cycles.

3. Results and discussion

3.1. Catalyst characterization

The characterization of Ni/dolomite catalyst, prepared according to the methodology explained in Section 2.1, highlights the interactions between NiO and CaO–MgO dolomite substrate.

When calcined dolomite and Ni/dolomite samples are compared, the X-ray diffraction analysis (Fig. 4) shows that there are not new phases in the Ni/dolomite catalyst with respect to the raw calcined dolomite.

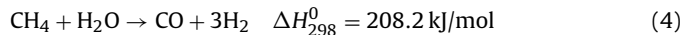
This means that a solid solution between calcined dolomite and NiO is produced, and in particular, due to the slight difference on atomic radius between Mg and Ni (about 10%) we can infer that a solid solution MgO–NiO is obtained. This interaction is known from previous works [24] to have beneficial effects on increasing carbon deposition resistance.

TPR analysis of the sample calcined at 900 and 1100 °C shows a key difference in the behaviour of this NiO–MgO solid solution with respect to calcination temperature. For both catalysts, a high reduction temperature (900 °C) has been observed, that may be identified as the reduction zone of NiO in the NiO–MgO solid solution. In fact, NiO in the crystal lattice of MgO is strongly bounded with the substrate and therefore less available for the reduction. However, the sample calcined at 900 °C shows a reducibility of about 25% calculated by the calibration method; on the other hand, the sample calcined at 1100 °C evidences only a very small peak (about 4%) near 900 °C for NiO reduction. This information is very important considering that reduction is the key step to activate a nickel based catalyst. As a matter of fact, the sample calcined at 1100 °C did not exhibit any catalytic activity, and only data related to the Ni/dolomite sample calcined at 900 °C are shown here. Some similar tendency has been previously obtained between Ni/olivine calcined at 1100 and at 1400 °C for methane and toluene reforming [24,25].

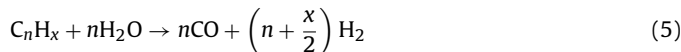
3.2. Catalytic tests with commercial nickel catalyst and dolomite in the fluidised bed reactor

In the presence of nickel catalyst and dolomite as CO₂ sorbent, the main reactions that take place into the raw syngas generated by coal or biomass steam gasification are:

Steam reforming of methane:

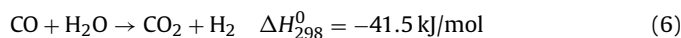


Steam reforming of hydrocarbons:

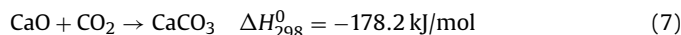


(in this case, the enthalpy of reaction is related to different molecular structures)

Water-gas shift:



CO₂ capture:



Some hydrocarbon dry reforming and cracking are also possible; coke deposited on the solid surface can eventually react with steam or carbon dioxide.

Endothermic and exothermic reactions are therefore combined together, and the global reaction enthalpy term in the energy balance will depend on the gas composition. On the other hand, the equilibrium conditions (CO₂ partial pressure as a function of temperature) for CO₂ capture impose to operate over a limited temperature range: the fluidised bed reactor, thanks to good solid and gas phase mixing, allows temperature homogeneity and therefore a careful control of the effective temperature level across the whole reaction volume.

Some representative reactions taking place in the gas phase have been studied separately, in presence of a commercial Ni catalyst and dolomite, following the procedures described above. Each test has been performed after calcination of dolomite and reduction of catalyst in the bed inventory. Once the dolomite sorption capacity is exhausted, a further calcination is performed to regenerate the CO₂ sorbent. Typical results obtained as a function of time for the above fixed conditions are shown in Figs. 5, 6, 8 and 9 for methane, toluene, 1-methyl naphthalene steam reforming and water-gas shift, respectively. It is observed that two different steady state conditions are clearly established at the reactor outlet, with or without CO₂ sorption by dolomite, separated by a rather narrow breakthrough zone, corresponding to the exhaustion of the CO₂ absorption capacity of dolomite.

3.2.1. CH₄ steam reforming

In this case, the main reactions taking place into the system are (4), (6) and (7). The experimental data (Fig. 5) show clearly two dis-

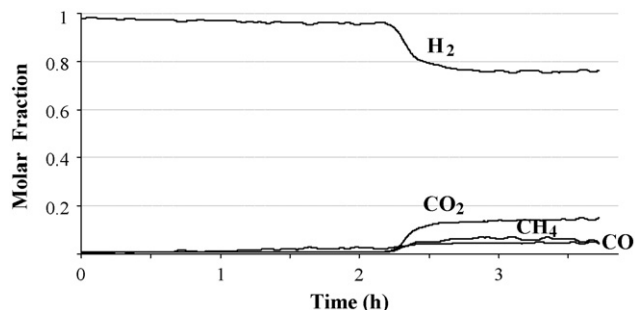


Fig. 5. Methane-steam reforming and CO₂ capture experimental test: experimental gas concentrations (dry and nitrogen-free basis) as a function of time.

tinct equilibrium zones, as described above, with and without CO₂ capture reaction (7). In the pre-breakthrough time period, CO₂, CO and CH₄ concentrations are almost brought to zero, and H₂ content in the product gas is very high (97.5%, on dry and nitrogen-free basis); then the H₂ concentration decreases to a value of 76.7% (dry and nitrogen-free basis), whereas the CH₄, CO₂, CO concentrations increase. The influence of the CO₂ capture step on enhancing CH₄ conversion and H₂ yield is well evident from the experimental data. CO₂ partial pressure during the capture phase is close to thermodynamic equilibrium predictions (Eq. (1)). This has also been observed for toluene and 1-MN steam reforming.

3.2.2. Toluene-steam reforming

Similar results have been obtained for toluene-steam reforming (Fig. 6). In this case, the main reactions are the following:



In the pre-breakthrough time period, a high toluene conversion is evaluated from the H₂ content in the gas exiting the reactor (16.5 vol.%, 92% on dry, nitrogen-free basis). This value corresponds to a nearly total conversion of the toluene feed. The CO and CO₂ concentrations are much lower during the CO₂ absorption phase than the corresponding values after saturation of dolomite. A high toluene conversion is confirmed also by total organic carbon (TOC) analysis in the condensed phase collected at the reactor outlet, which indicates a very low carbon concentration level (about 1 g/L in 40 g of condensed phase). After saturation of dolomite, the toluene conversion drops to about 75%, and a H₂ concentration of 12.5% is detected (72% on dry, nitrogen-free basis), 1.3% of CO (7.3% on dry, nitrogen-free basis), 3.6% of CO₂ (20.7% on dry, nitrogen-free basis). No methane formation is detected.

At the end of the toluene reforming step, carbon is trapped in the reactor bed either as CaCO₃, and in the form of coke deposited on the solid surface as a result of secondary cracking processes. To allow an estimate of such quantities, calcination in nitrogen atmosphere, and combustion with air are performed sequentially.

During the former step, CaCO₃ decomposition produces CO₂ (labelled as CO_{2calc}) that is partially converted in CO (CO_{calc}) by coke dry reforming (Fig. 7):



In the subsequent combustion, the remaining coke is converted into CO₂ (labelled as CO_{2comb}) and CO (CO_{comb}).

As a result, the CaCO₃ moles formed in the toluene reforming step can be estimated as follows:

$$\text{mol}(CaCO_3) = \frac{1}{2} \text{mol}(CO)_{calc} + \text{mol}(CO_2)_{calc} \quad (10)$$

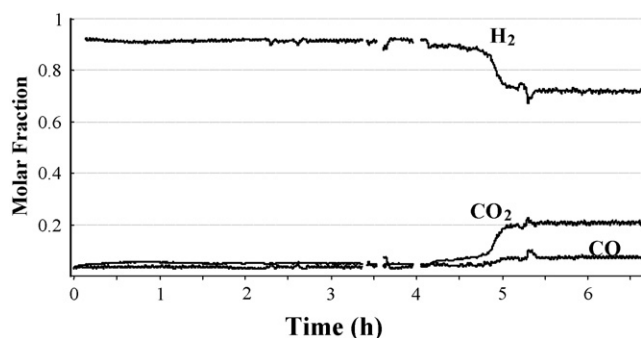


Fig. 6. Toluene-steam reforming and CO₂ capture test: experimental gas concentrations (dry and nitrogen-free basis) as a function of time.

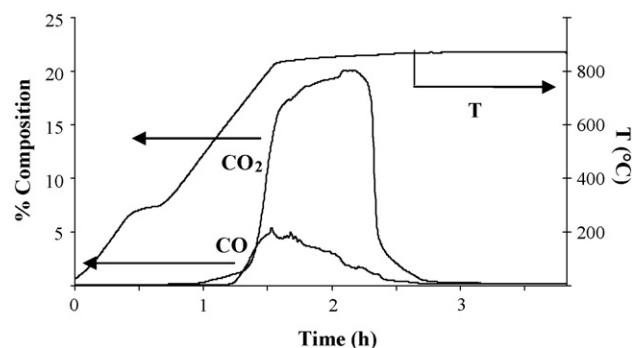


Fig. 7. CO and CO₂ produced during re-calcination of dolomite after toluene-steam reforming: experimental gas concentrations as a function of time.

while carbon deposited on dolomite and catalyst surface is given by:

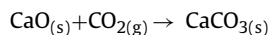
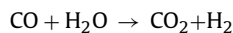
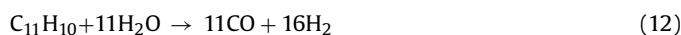
$$\text{mol}(C) = \frac{1}{2} \text{mol}(CO)_{calc} + \text{mol}(CO)_{comb} + \text{mol}(CO_2)_{comb} \quad (11)$$

The value calculated introducing the experimental data in the balance relation (11) allows to estimate that about 1.4 g of coke are produced during the test, that is 8.7% of toluene feed is cracked.

On the other hand, CO₂ moles absorbed on dolomite, as results from Eq. (10), are equal to 0.7, in good agreement with CaO moles initially present in the reactor, confirming an absorption efficiency near to 100%.

3.2.3. 1-MN steam reforming

The key reactions that occur in 1-MN steam reforming are:



Two ring compounds have been indicated as the most suitable for use as model tar compounds exhibiting a lower reaction rate with respect to steam reforming [26]. However, absorption enhanced reforming evidences once again an excellent efficiency (Fig. 8), with a high conversion of 1-MN. Hydrogen produced during the CO₂ absorption phase corresponds initially to an average volumetric concentration of 19.2% in the total flow (92% on dry, nitrogen-free basis), that means a nearly total conversion of 1-MN. However, it is observed a progressive slight decrease as a function of time of the H₂ concentration at the exit of the reactor, and a corresponding steady increase of CO and CO₂ before the breakthrough conditions is reached. In comparison with the previous reforming test

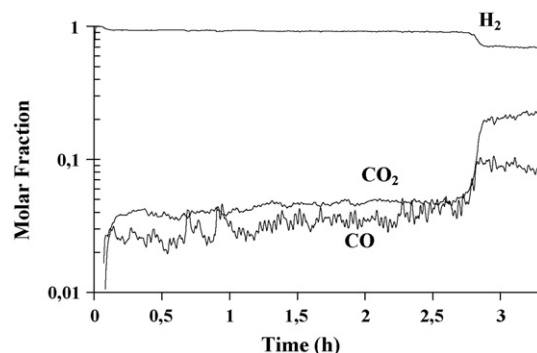


Fig. 8. Logarithmic plot of 1-MN steam reforming and CO₂ capture test: experimental gas concentrations (dry and nitrogen-free basis) as a function of time.

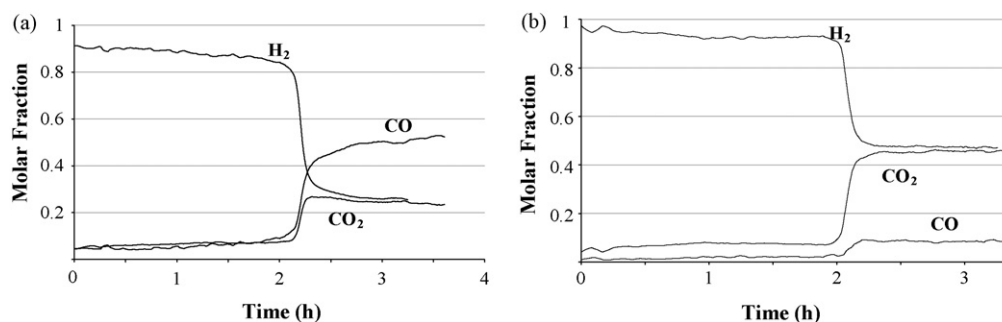


Fig. 9. Water-gas shift reaction using: (a) dolomite and (b) dolomite and nickel catalyst as bed inventory: experimental gas concentrations (dry and nitrogen-free basis) as a function of time.

Table 7

Experimental gas concentrations (% dry and nitrogen-free basis) and breakthrough time obtained in multi-cycle CH₄ steam reforming test, for the 1st and 12th cycle.

Cycle	1st			12th		
	Pre-breakthrough	Post-breakthrough	Breakthrough time (h)	Pre-breakthrough	Post-breakthrough	Breakthrough time (h)
H ₂	97.5	76.7	2.3	98	79.0	1.9
CO	0.7	4.6		0.6	3.7	
CO ₂	0.9	13.9		0.6	11.6	
CH ₄	0.9	4.8		0.8	5.7	

with toluene, the required carbon absorption rate per unit mass of dolomite is now substantially increased, and this may help to explain the observed behaviour in terms of kinetic considerations. Dolomite carbonation degree increases progressively with time, making more difficult a further absorption of CO₂, for a number of reasons: among these, reduction of internal particle pore volume, and increase of the thickness of the product layer (CaCO₃) built up around each CaO grain.

After saturation of dolomite, the H₂ yield decreases abruptly, simultaneously to an increase in CO and CO₂ concentrations at the reactor outlet: a 1-MN conversion of about 80% is evaluated in this new equilibrium zone, from a measured H₂ content of 15.7% (70% on dry, nitrogen-free basis), CO 2.05% (10% on dry basis) and CO₂ 4.65% (20% on dry basis).

Total organic carbon (TOC) analysis in the condensed phase collected at the reactor outlet, indicates once again a very low carbon concentration level, about 0.9 g C in 20 g of water.

In the same manner as in toluene-steam reforming, the amount of CO₂ absorbed on dolomite and the carbon deposited in the bed have been detected by means of calcination and combustion steps. The former results very close to the theoretical absorption capacity of dolomite loaded in the reactor, altogether 0.43 mol of CO₂. The latter is found to be much less than carbon deposited in the toluene reforming test (corresponding to about 0.5% of 1-MN feed), showing a superior thermal stability or an enhanced resistance to catalytic cracking with catalyst of 1-MN at the process temperature. No methane formation is detected during the whole process.

3.2.4. Water-gas shift reaction

Water-gas shift has been studied experimentally with and without Ni-catalyst, however always in presence of dolomite, and at the same temperature level as that of methane-steam reforming tests. Fig. 9a shows that it is possible to obtain high reaction conversion and hydrogen content using a reactor bed of dolomite alone, and the addition of a pre-reduced Ni-catalyst in the bed increases slightly hydrogen concentration (Fig. 9b). On the other hand, when the sorption capacity of dolomite is exhausted (post-breakthrough), the water-gas shift reaction is considerably enhanced by the presence of catalyst (CO, CO₂ and H₂ concentrations are close to equilibrium conditions – Fig. 9b), in comparison to test without Ni-catalyst

(Fig. 9a). In both cases H₂/CO₂ ratio is equal to 1 after dolomite saturation, in accordance with stoichiometry of reaction (6).

3.3. Catalytic tests with the 4% Ni/dolomite combined catalyst and sorbent

Finally, the newly prepared, combined catalyst and sorbent, made of 4% Ni impregnated on dolomite, has been tested in the microreactor using toluene as model tar compound (see Table 2 for experimental conditions and Fig. 10 for experimental results). In this case, the contact time is very low (0.8 s) in comparison to fluidised bed tests, the aim being to assess catalytic activity rather than equilibrium approach at process conditions. Moreover, the broad range of particle size used in this preliminary test does not allow to exclude diffusion limitations.

The composition of the gas exiting from the microreactor, monitored by GC injections every 20 min, is characterized by the following average values: 12% H₂, 2% CO₂, 1.3% CO before breakthrough, and 11.5% H₂, 3.3% CO₂, 1.5% CO after breakthrough. No methane formation is detected. These values are shown in Fig. 10 on dry and nitrogen-free basis: 79% H₂, 12.8% CO₂, 8.2% CO on average before breakthrough, and 71% H₂, 19.7% CO₂, 9.3% CO after

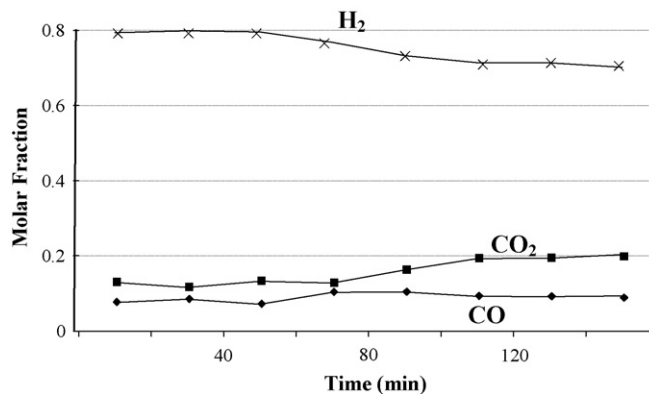


Fig. 10. Toluene-steam reforming using the 4% Ni/dolomite catalyst and sorbent: experimental gas concentrations (dry and nitrogen-free basis) as a function of time.

breakthrough. They correspond to a high toluene conversion in the pre-breakthrough range (90%), and in the post-breakthrough (85%).

3.4. Multi-cycle operation

Re-calcination of dolomite allows to obtain a regenerated sorbent and to run a multi-cycle steam reforming and CO₂ capture test. This step is essential for evaluating the possibility of making the whole process continuous and amenable to industrial exploitation, as it is recalled in Section 1. Twelve calcination-steam reforming and CO₂ capture cycles have been carried out in the fluidised bed rig, for methane reforming (experimental conditions are described in Section 2.3.3). It is observed (Table 7) that concentration of H₂, CO, CO₂ and CH₄, during pre- and post-breakthrough, are quite constant throughout the cycles, respectively, evidencing that equilibrium is reached for each cycle, as reported in a previous work [27]. Moreover, the observed breakthrough time, that is the time required for saturation of dolomite, is close to that corresponding to the theoretical value in the 1st cycle, while is reduced to 80% of its initial value in the 12th cycle, evidencing a progressive (although rather limited) loss of sorption capacity during cycles, a phenomenon quite well known in the literature and often related to structural modifications of the sorbent particles [28].

4. Conclusions

The results obtained for methane reforming and simultaneous CO₂ capture confirm those reported in the literature [27] and indicate a promising sorption performance of dolomite in cyclic operation, while those related to water-gas shift, toluene and 1-MN reforming allow to extend to a biomass syngas the experimental evidence on simultaneous CO₂ capture and heavy hydrocarbons (tar) reforming, showing the potential of generating a hydrogen energy vector by using a particulate solid acting as CO₂ sorbent.

Mixtures of a commercial nickel catalyst and calcined dolomite perform very well in catalytic steam reforming of methane, toluene and 1-MN carried out in a fluidised bed reactor, with conversion reaching nearly 100% during the pre-breakthrough time period. A newly developed Ni/dolomite combined catalyst and sorbent has been prepared and characterized; preliminary tests in a fixed bed microreactor show a toluene conversion comparable to that obtained with the commercial nickel catalyst.

Further investigations will be addressed to test the new Ni/dolomite catalyst in the bench scale fluidised bed rig, in CH₄,

toluene and 1-MN steam reforming, in order to verify the feasibility of a one step, combined process of steam reforming, CO₂ capture and water-gas shift using a single mineral solid phase.

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