

EVALUATION AT LABORATORY-SCALE OF NICKEL-CATALYST PELLETS FOR IN-SITU TAR STEAM REFORMING IN BIOMASS THERMOCHEMICAL CONVERSION

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ABSTRACT: Ceramic filter candles, partially filled with pellets of a commercial nickel-based catalyst (about 600 g) for hydrocarbons reforming, were recently tested for in-situ syngas cleaning and conditioning in the freeboard of a fluidized-bed biomass steam gasifier, with positive results (Savuto et al. 2019). To get full insight into the performance of that device, characterizing more accurately the dependence of catalytic activity on the operating conditions, a more focused approach is needed; this work describes an experimental study utilizing a laboratory-scale tubular reactor containing a small packed bed with pellets of the same catalyst (3.9 g), and involving steam reforming tests of tar key-compounds (mixtures of naphthalene and toluene, optionally with the addition of thiophene, vaporized in an inert gas stream together with steam). The experimental data were used to infer a lumped kinetic law, referred to the steam reforming of a pseudo-component representing tars. This law was implemented in a mathematical model of the annular catalytic packed bed inside the filtering candle, obtaining numerical simulations in fair agreement with gasification experiments from Savuto et al. 2019, as far as tar removal from biomass product syngas was concerned.

Keywords: Tar removal, clean synthesis gas, gas cleaning, modelling

1 INTRODUCTION

Biomass steam gasification is a relevant route to produce syngas with a reduced environmental footprint; however raw gas cleaning – removal of particulate and tar – is a key, not yet fully assessed step in the whole process chain [1]. Tars in syngas produced by a fluidized-bed gasifier are in the order of magnitude of a few g Nm⁻³ [1], causing several drawbacks in downstream units: deactivation of catalysts in secondary reactors, fouling and corrosion in heat exchangers and turbines, obstruction of porous components in fuel cells [2]. Moreover, tars represent an inefficiency in gasification of carbon from biomass, depleting the syngas yield per unit mass of biomass.

Ceramic-catalytic porous candles were recently proposed as an innovative solution to face this issue; they are directly placed inside the freeboard of a fluidized-bed steam gasifier, acting simultaneously as an efficient particulate filter and a catalyst for tar steam reforming, and assuring at the same time noticeable thermal integration of gasification and syngas cleaning and conditioning processes [3,4]. Upgrading of raw product syngas is performed in-situ, with remarkable process intensification of downstream gas treatments, in relation to current practice of low temperature tar scrubbing. In fact, the related issue of tarry solutions disposal is avoided, and clean syngas is directly available at high temperature, improving overall energy efficiency of biomass utilization processes, such as production of chemicals [5,6] or power generation in fuel cells [7].

Ceramic-catalytic candles developed so far were made of an anisotropic porous support (particulate filtration is assured by an external film with very fine porosity) impregnated with nickel and/or integrated with a nickel-based ceramic foam, able to reduce tar content from a few g Nm⁻³ down to less than 0.2 g Nm⁻³ [3,8–11]. Recently, in order to avoid practical constraints related to the availability and feasibility of nickel-impregnated filtering candles, a simpler concept was proposed and tested with real biomass syngas in a pilot scale gasifier: a plain ceramic candle (filter) filled with pellets of a commercial nickel-based reforming catalyst (tar

reforming) [12]. However, the complexity and the high number of variables of a simultaneous gasification and syngas cleaning and conditioning test hinder a deeper insight into the intrinsic behavior of catalyst pellets placed inside the candle. In fact, in a gasification campaign, performed at sufficient scale to host in the gasifier a commercial ceramic filter candle operated at industrially relevant face velocities, the experimental results may be affected by a certain range of variability in the operating boundary conditions, certainly wider than that characterizing catalytic activity tests at micro-reactor scale, better controlled.

This work aims to fill this gap by two complementary approaches: (i) investigating the activity of the nickel-based catalyst pellets recently utilized in a filter candle, by means of a bench-scale packed bed micro-reactor rig, purposely designed for steam reforming tests of tar mixtures, so to check the influence of inlet concentrations (10-30 mg Nm⁻³ dry), temperature (750-800 °C), sulfur poisoning (0-100 ppm_v of equivalent H₂S), when tar key-compounds (naphthalene and toluene) and steam are fed to the reactor; (ii) inferring a lumped kinetic law for tar steam reforming, assuming a unique carbonaceous pseudo-component whose carbon atoms (C_{tar}) are involved in the reforming process accompanied by Water Gas Shift (WGS), and validating this reaction kinetics with the experimental results of biomass gasification and syngas conditioning tests already mentioned [12]. The advantage of these approaches arises from the reduced scale of experiments: the catalytic bed inside a candle is made of about 600 g of catalyst pellets distributed on a candle height of about 40 cm, therefore it operates at a not well-defined temperature distribution, surely in the range between temperatures of gasification (fluidized bed) and that of syngas exiting at the top of the reactor (evaluated to be around 60 K less [12]); on the other hand, the bench-scale reactor requires a much lower quantity of catalyst (< 5 g), so that the active packed bed is confined in a smaller volume at a well-controlled temperature.

To the scope of validation, the lumped kinetic law for C_{tar} was implemented in the balance equations of an annular bed representing the catalytic inner packing of

filter candles tested in the previous study [12]; kinetic laws taken from the literature were used to describe the extent of additional reactions also involved in this process. Numerical simulations provided outcomes in fair agreement with experimental data, especially as far as tar reforming was concerned.

2 MATERIALS AND METHODS

2.1 Experimental

Commercial catalyst pellets were kindly supplied by Johnson Matthey together with relevant specifications. These pellets have a cylindrical shape with diameter 3 mm and height 3 mm; thanks to this small size, they could be used as such inside the catalytic-filtering candles, as well as in the bench-scale reactor described below. Nonetheless, in order to investigate diffusion resistance effects, some of these pellets were crushed by a ball mill and sieved, so to obtain a fine powder with particles diameter within the range 212-600 μm .

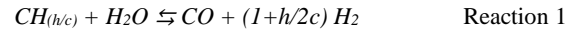
The experimental rig consisted of a vertical stainless-steel $\frac{3}{4}$ " pipe (internal diameter = 1.6 cm), 0.5 m long, containing in the middle the catalytic active packed bed (3.9 g). The reactor was heated by an electrical furnace and the temperature controlled by a thermocouple, the tip of which was located inside the catalyst bed. Water and a liquid solution of tar key-compounds were fed to a vaporization chamber (220 $^{\circ}\text{C}$) together with 600 Nl min^{-1} of N_2 as carrier gas, substituting other gaseous components of actual syngas (CO , CO_2 , CH_4 , H_2) so to isolate behaviors related to tar/catalyst interaction; proper flowrates were set for liquids and kept constant by syringe pumps, so to simulate closely steam and heavy hydrocarbon content of the raw syngas obtained in the biomass gasification tests discussed in [12]. Inlet steam to carbon molar ratio ranged between 6.5 and 19.4, with H_2O always in large stoichiometric excess with respect to tar key-compounds, as far as steam reforming and WGS are concerned. Tar solutions were made of toluene and naphthalene (with toluene/naphthalene molar ratio of 3.7, close to naphthalene solubility at ambient temperature [13]). In some tests, thiophene was also added, to investigate the influence of sulfur poisoning of catalyst activity (0-100 ppm_v of equivalent H_2S in the reactor feeding). Downstream, a condenser at about 0 $^{\circ}\text{C}$ separated condensable species from gaseous products; the overall flowrate of dry outlet stream was measured, as well as volumetric concentrations of H_2 , CO , CO_2 , CH_4 . Temperature was kept constant (750-800 $^{\circ}\text{C}$) over each test, at atmospheric pressure.

2.2 Lumped kinetic law for tar steam reforming

A tar mixture, made of N generic hydrocarbons C_nH_m , was modelled as a C_{tar} mono-carbonic pseudo-component with formula $\text{CH}_{(h/c)}$, where indexes h and c were calculated as weighted averages with respect to molar fractions of indexes m and n in all tar molecules of the mixture (Equation 1).

$$h = \sum_{i=1}^N x_{\text{tar},i} m_i \quad ; \quad c = \sum_{i=1}^N x_{\text{tar},i} n_i \quad \text{Equation 1}$$

As a consequence, Reaction 1 describes the lumped steam reforming of a tar mixture, in any case accompanied by WGS (Reaction 2).



For Reaction 1, a pseudo-first order kinetic law was postulated (Equation 2), as widely accepted in literature for the steam reforming of tarry molecules [14,15], with an adsorption term to consider sulfur deactivation (Equation 3) and an Arrhenius-type dependence on temperature for the specific reaction rate (Equation 4) [15].

$$r_{\text{CH}_{(h/c),1}} = k_1^{\text{app}} C_{\text{CH}_{(h/c)}} \quad \text{Equation 2}$$

$$k_1^{\text{app}} = \frac{k_1}{1 + K_S P_{\text{H}_2\text{S}}} \quad \text{Equation 3}$$

$$k_1 = k_1^0 \exp\left(-\frac{E_{a,1}}{RT}\right) \quad \text{Equation 4}$$

Under these assumptions, data collected by experiments in the packed bed rig allowed estimating the lumped kinetic parameters. The packed bed micro-reactor was modelled as a PFR: a mole balance for $\text{CH}_{(h/c)}$ was formulated (Equation 5) and then properly integrated with respect to variable packed bed mass (w); as a result, Equation 6 allowed calculating specific reaction rates. Arrhenius parameters in Equation 4 could be finally estimated, by the specific reaction rates determined from tests at different temperatures.

$$\frac{d\chi_{\text{CH}_{(h/c)}}}{dw} = k_{\text{tar}}^{\text{app}} \frac{\frac{P}{RT}(1 - \chi_{\text{CH}_{(h/c)}})}{F_{\text{CH}_{(h/c),\text{in}}}(1 + \alpha_{\text{in}}(1 + \beta_{\text{in}}) + \frac{h}{2c}\chi_{\text{CH}_{(h/c)}})} \quad \text{Equation 5}$$

$$\left(1 + \alpha_{\text{in}}(1 + \beta_{\text{in}}) + \frac{h}{2c}\chi_{\text{CH}_{(h/c),\text{out}}}\right) \ln(1 - \chi_{\text{CH}_{(h/c),\text{out}}}) + \frac{h}{2c}\chi_{\text{CH}_{(h/c),\text{out}}} = -k_1^{\text{app}} \frac{P}{RT} \frac{W}{F_{\text{CH}_{(h/c),\text{in}}}} \quad \text{Equation 6}$$

In each test, the average conversion at the packed bed outlet ($\chi_{\text{CH}_{(h/c),\text{out}}}$) was determined by a carbon balance, as the ratio between total carbon moles exiting as CO_x (no CH_4 was detected in the outlet stream, for all tests) and total carbon moles fed to the reactor, on a proper time interval during which the process took place in a steady state (Equation 7):

$$\chi_{\text{CH}_{(h/c),\text{out}}} = \frac{\int_{t_{\text{start}}}^{t_{\text{fin}}} (F_{\text{CO},\text{out}} + F_{\text{CO}_2,\text{out}}) dt}{\int_{t_{\text{start}}}^{t_{\text{fin}}} F_{\text{CH}_{(h/c),\text{in}}} dt} \quad \text{Equation 7}$$

The validity of this approach was corroborated by the deposition of condensed organic phases on the inner cold wall of downstream heat exchanger, i.e. tar un-converted to CO_x .

3 EXPERIMENTAL RESULTS AND LUMPED KINETIC PARAMETERS

Tab. I summarizes conditions and experimental results characterizing tests of tar steam reforming in the bench scale packed bed rig.

Tests A and B were carried out at the same process conditions, except for the shape of the catalyst; their comparison allowed to exclude severe effects from diffusion resistances inside catalyst pellets for reforming

Table I: Experimental conditions and resulting carbon conversion from tar reforming tests in the packed bed rig

	TEST A	TEST B	TEST C	TEST D	TEST E	TEST F
Pressure, P [atm]	1	1	1	1	1	1
Temperature, T [°C]	800	800	800	750	800	800
Catalyst shape	Powder	Pellets	Pellets	Pellets	Pellets	Pellets
Catalyst mass, W [g]	3.9	3.9	3.9	3.9	3.9	3.9
N ₂ inlet, $F_{N_2,in}$ [Nm ³ min ⁻¹]	600	600	600	600	600	600
Inlet tar concentration [g Nm ⁻³ dry]	10	10	30	30	10	30
Inlet H ₂ S equivalent [ppm _v]	0	0	0	0	100	100
Inlet steam to carbon ratio, α_{in} [mol/mol]	19.4	19.4	6.5	6.5	19.8	6.5
Inlet N ₂ to steam ratio, β_{in} [mol/mol]	3	3	3	3	3	3
Carbon to CO _x conversion, $\chi_{CH(h/c),out}$ [%]	93.6	92.7	91.5	76.6	30.5	29.2

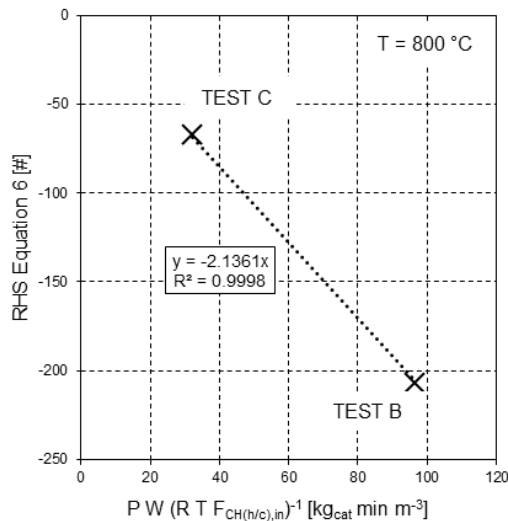
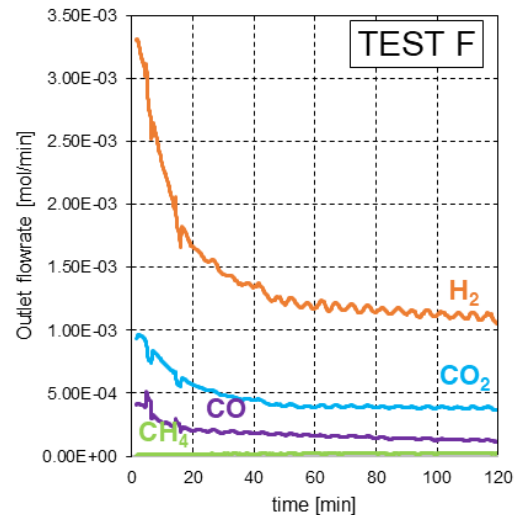
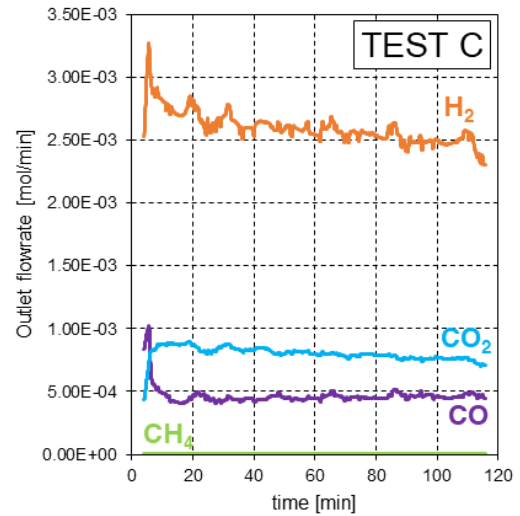
of considered tarry molecules, as carbon conversions resulted very close between each other.

Tests B, C and D were carried out on catalyst pellets in the absence of sulfur: at 800 °C, notwithstanding a substantial difference in the inlet tar fraction (30 and 10 mg Nm⁻³ dry gas), the catalyst pellets were similarly very active, since they converted more than 90 % of tarry carbon to CO_x, showing a behavior that confirms the assumption of first order kinetics with reference to tar concentration; at 750 °C, a reduction in tar conversion of 14.9 % occurred.

These results were exploited to estimate lumped kinetic parameters k_T^0 and $E_{a,T}$ (Tab. II); the latter is included in the range of values reported in the literature for the steam reforming over Ni-based catalysts of benzene (177 kJ mol⁻¹ [15]), toluene (196 kJ mol⁻¹ [14]) and naphthalene (94 kJ mol⁻¹ [15]). At 800 °C, the corresponding calculated value of k_T (2.15 m³ kg_{cat}⁻¹ min⁻¹) was in fair agreement with the linear regression of data at different inlet tar fraction (Fig. 1) and close to the specific rate of naphthalene steam reforming at 800 °C reported in [16] (as pseudo-first order kinetic law).

Table II: Parameters of lumped kinetic law for tar reforming, obtained from experimental data in Tab. I

k_T^0 [m ³ kg _{cat} ⁻¹ min ⁻¹]	297152
$E_{a,T}$ [kJ mol ⁻¹]	105.6
$K_S(800\text{ °C})$ [atm ⁻¹]	63225

**Figure 1:** Linear regression of results from Test B and C, with vertical intercept = 0, according to Equation 6**Figure 2:** Outlet molar flowrates from TEST C and TEST F, same test conditions except for sulfur poisoning (absent in A, 100 ppm_v (equivalent) H₂S in F) as detailed in Tab. I

Test E and F involved adding thiophene to the tar mixture, in order to develop a H₂S concentration corresponding to 100 ppm inside the reactor, at 800 °C and with both explored inlet tar fractions; comparisons with corresponding cases without sulfur poisoning (Test B and C, respectively) confirmed a first order kinetic law for tar steam reforming, this time with an evident

Table III: Conditions and results of gasification tests carried out in the pilot plant of University of Teramo [12] (tar and benzene by average from Table 3 in [12])

	Empty candle	Partially-filled-candle 1	Partially-filled-candle 2
Pressure, P [atm]	1	1	1
Average candle temperature, T [°C]	790	820	775
Catalyst pellets mass, W [g]	0	561.25	563.80
Face filtration velocity, [cm s ⁻¹]	2.8	3.2	3.1
N ₂ inlet, $F_{N_2,in}$ [mol h ⁻¹]	48.9	/	/
Steam inlet, $F_{H_2O,in}$ [mol h ⁻¹]	15.2	/	/
Tar outlet concentration [g Nm ⁻³ _{dry, N2 free}]	3276	254	357
Benzene outlet concentration [g Nm ⁻³ _{dry, N2 free}]	2439	133	74
H ₂ outlet concentration, Y_{H_2} [vol% _{dry, N2 free}]	40.6 ± 0.6	53.5 ± 1.1	54.0 ± 0.6
CO outlet concentration, Y_{CO} [vol% _{dry, N2 free}]	29.2 ± 0.4	31.9 ± 0.7	29.8 ± 0.2
CO ₂ outlet concentration, Y_{CO_2} [vol% _{dry, N2 free}]	21.2 ± 0.4	13.6 ± 0.6	15.0 ± 0.6
CH ₄ outlet concentration, Y_{CH_4} [vol% _{dry, N2 free}]	9.0 ± 0.3	0.9 ± 0.6	1.2 ± 0.2
H ₂ S [ppm _v]	30-50	30-50	30-50

reduction of catalytic activity, with a decay of tarry carbon conversion of about 60 %, i.e. a conversion to CO_x of 29-30 %. These data were used to calculate an average value for K_5 at 800 °C (Tab. II), according to Equation 3. As an example of sulfur poisoning effects on the activity of Ni-based catalytic pellets, Fig. 2 shows outlet molar flowrates of H₂, CO and CO₂ (i.e. Reaction 1 and Reaction 2 products) from Tests C and F: a relevant depletion occurred when 100 ppm_v of (equivalent) H₂S were added to the reactor (Test F), with respect to a similar test without sulfur (Test C).

4 MODELLING THE CATALYTIC PACKING INSIDE A FILTERING CANDLE

The in-situ raw syngas cleaning and conditioning device, used in the gasification tests recalled above [12], consisted of an inert Al₂O₃ ceramic candle acting as a particulate filter (supplied by PALL Filtersystems GmbH, total filtration length 440 mm, 60 mm external diameter and 40 mm internal diameter), with its inner empty space partially filled by an annular packed bed made of Johnson Matthey's catalyst pellets, the same type utilized in this study; a cylindrical, internal hollow space of 20 mm diameter was left empty, to allow the conditioned gas flowing towards the candle head (see [12] for further details).

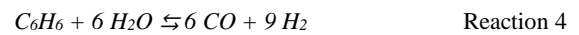
In this section, the focus is on modelling the catalytic annular packed bed inside the candle. In agreement with the experimental evidence, it was assumed that the gas particulate content had been completely removed by the external Al₂O₃ porous layer.

Tab. III summarizes averaged specifications of syngas produced during experimental tests with the pilot gasifier [12]: a gasification test with the empty Al₂O₃ candle provided typical flowrate and composition of syngas at the entrance of the annular catalytic layer; corresponding results of the catalyst performance, very close between each other, were measured by repeating test at similar operating conditions [12]. Experiments reported in Tab. III were carried out at average filter candle temperature in the range between 775-820 °C [12].

The tar molecules identified and quantified in those tests ranged between one to three aromatic rings: toluene, naphthalene, styrene, indene, phenol, biphenyl,

acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene [12]; their lumping into the pseudo-component CH_(h/c), based on quantities measured in the syngas produced in the empty-candle test [12] and assumed as the feedstock to the catalytic layer, resulted in the index $h/c = 0.9$, close to that of the toluene-naphthalene mixture used in the laboratory-scale tests ($h/c = 1.0$). In the same feedstock, the molar ratio between molecules with one aromatic ring to those with two is 2.3, less than the toluene/naphthalene molar ratio used in packed bed experiments, which is limited by low solubility of naphthalene in toluene, so to guarantee a liquid feed without solid precipitates in the laboratory tests. It is worth noticing that in a previous study about catalytic-filtering candles [4], heavier aromatics (≥ three rings) were easily reformed on a Ni-based catalytic phase, while toluene and naphthalene resulted as the most recalcitrant towards a similar reforming treatment, among lighter tar components (one or two rings); in particular, toluene was the least reformed component (in agreement with respective activation energies from literature sources and reported in Section 3 of this paper). Therefore, the higher abundance of toluene in packed bed tests discussed Section 3 results as a conservative condition, with respect to the actual toluene/naphthalene molar ratio found in real biomass gasification tests [12].

In addition to tar compounds, CH₄ and benzene were also detected in the empty-candle test and in those with partially-filled-candle: in the latter case, these species had lower concentrations, with a simultaneous increase of H₂ (Tab. III). Therefore, besides Reaction 1 and Reaction 2, syngas conditioning through the catalytic annular packed bed involves Steam Methane Reforming (SMR, Reaction 3) and steam reforming of benzene (Reaction 4):



By virtue of these hypotheses, the catalytic annular packed bed was modelled as an isothermal, cylindrical PFR, fed radially by raw, depulverized syngas, the geometry of which was already described in the beginning of this section. For this configuration, Equation 8 describes the resulting mole balance for the generic gaseous species i , with its reaction rate defined by Equation 9.

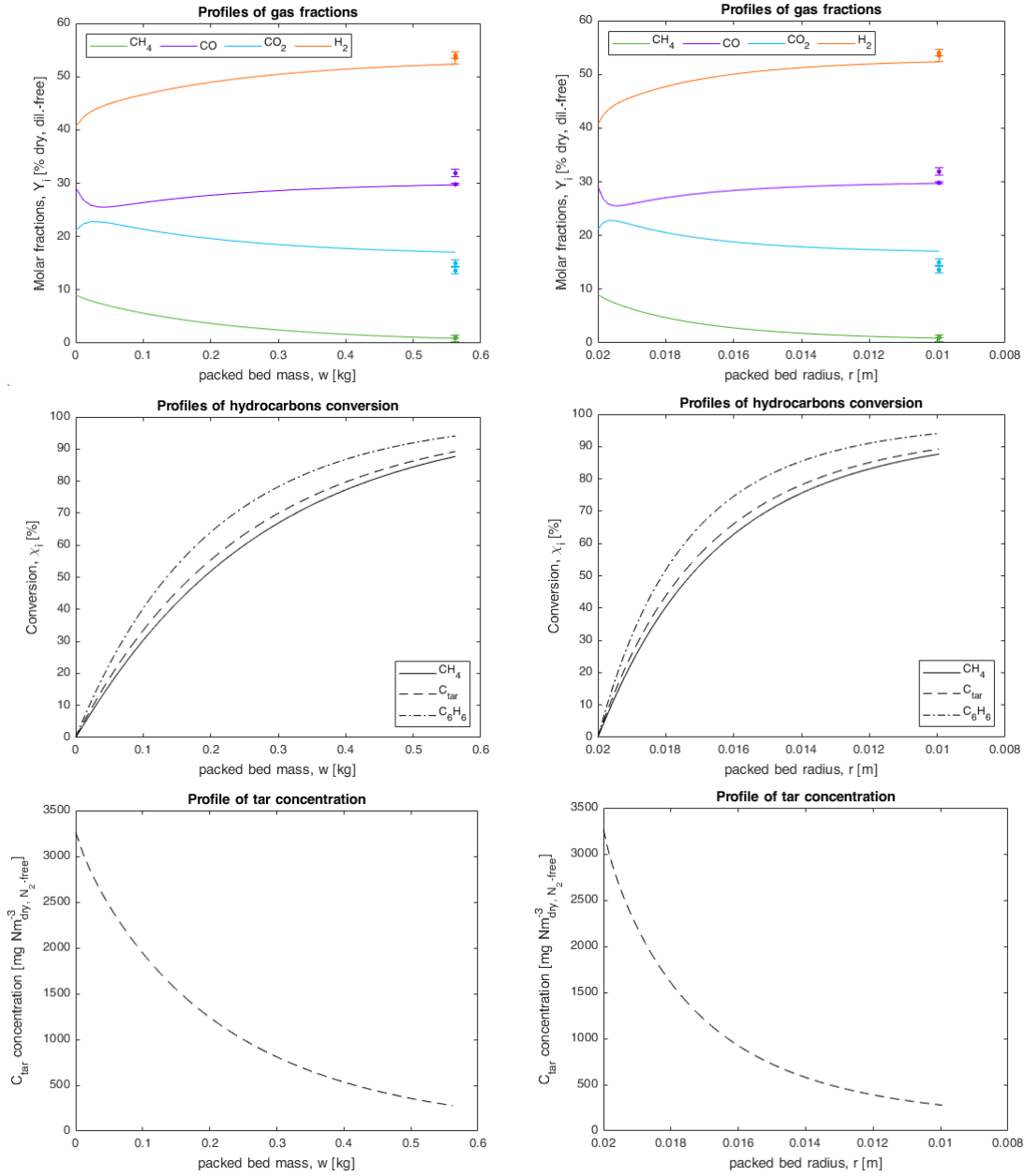


Figure 3: Simulation results: profiles of syngas composition (dry, dilution free), hydrocarbons conversion and tar fraction through the catalytic annular packed bed, predicted by the model ($T=800$ °C, $P=1$ atm, $W=562.5$ g, 40 ppm_v of H_2S); dots with error bars indicate experimental values obtained in [12] (Tab. III)

$$\frac{dF_i}{dw} = -r_i \quad \text{with } i = CH_{(h/c)}, CH_4, C_6H_6, H_2O, CO_2, CO, H_2, N_2 \quad \text{Equation 8}$$

$$r_i = \sum_j v_{i,j} r_j \quad \text{with } j = \text{Reactions 1 to 4} \quad \text{Equation 9}$$

In addition to the lumped kinetic law r_1 , defined for C_{tar} steam reforming (Reaction 1), kinetic laws were also assumed from the literature for the remaining reactions (with tuned correction factors to consider the use of a different catalyst, with respect to those in the original papers): r_2 and r_3 were expressed by Numaguchi and Kikuchi's kinetic laws [17] for WGS (Reaction 2) and SMR (Reaction 3), respectively; r_4 was described by the kinetic law proposed by Depner and Jess [16] for benzene steam reforming (Reaction 4), involving an adsorption term to take into account sulphur deactivation [16].

Table IV: Features of syngas at inlet and outlet of the catalytic annular packed bed simulated as a laterally-fed cylindrical PFR ($T=800$ °C, $P=1$ atm, $W=562.5$ g, 40 ppm_v of H_2S)

	Inlet	Outlet
N_2 , F_{N_2} [mol h ⁻¹]	48.9	48.9
Steam, F_{H_2O} [mol h ⁻¹]	15.2	12.1
Tar [g Nm ⁻³ _{dry, N2 free}]	3276	278
Tar conversion [%]	/	89.2
Benzene [g Nm ⁻³ _{dry, N2 free}]	2439	114
Benzene conversion [%]	/	94.1
H_2 [vol% dry, N2 free]	40.6	52.3
CO [vol% dry, N2 free]	29.2	29.7
CO ₂ [vol% dry, N2 free]	21.2	17.1
CH ₄ [vol% dry, N2 free]	9.0	0.9

A catalytic annular packed bed of 562.5 g was simulated, at representative process conditions of 800 °C, 1 atm, 40 ppm of H₂S in the syngas: mole balances (as expressed by Equation 8) were implemented in MATLAB® and numerically integrated by “ode45” routine; molar flowrates obtained in the empty-candle test and reported in [12] were used as inlet conditions. Tab. IV summarizes results of this simulation, in fair agreement with gasification experiments, as can be seen by the comparison with syngas conditioning data shown in Tab. III.

It is worth noticing that the lumped kinetic model for reforming of tar species, together with kinetic constant values obtained from micro-reactor tests of C_{tar} catalytic conversion to CO_x (Tab. II, Equation 2, Equation 3, Equation 4) allowed a reliable prediction of tar decomposition in the partially-filled-candle. On the other hand, SMR and benzene steam reforming rates from literature had to be tuned, in order to fit the experimental results: it was needed to multiply their kinetic constant by a factor of $1.8 \cdot 10^{-2}$ and 6, respectively, to match CH₄ and benzene measurements from gasification tests (Tab. III). In the case of SMR catalysed by pellets, it is well known that an effectiveness factor of the order 10^{-2} is reasonable [18]. As far as WGS is concerned, no tuning of rate law was carried out, as the outlet composition of cleaned syngas resulted close to thermodynamic equilibrium. With these assumptions, the integration of the PFR model allowed to describe the evolution of reforming phenomena through the mass of catalytic annular packed bed (w), and the corresponding annular packed bed radius ($r=r(\sqrt{w})$) (Fig. 3). The trend of concentration profiles as functions of catalytic bed thickness could be influenced by tuning the WGS rate law, as done for SMR and benzene reforming; however, within reasonable adjustment limits, the outlet gas composition would result always close to WGS equilibrium.

5 CONCLUSIONS

This work dealt with investigation of the tar reforming process that takes place in the freeboard of a fluidized bed biomass steam gasifier by means of ceramic filtering candles integrated with an annular packed bed of commercial catalyst pellets partially filling their empty inner space. Experimental tests for in-situ tar removal according to this methodology were recently performed in a gasification and syngas conditioning pilot reactor, with satisfactory results [12]. The present study aimed at a better characterization of high temperature syngas purification from condensable tars by means of steam reforming tests of high molecular weight hydrocarbons (naphthalene and toluene) carried out at laboratory scale in a fully controlled packed bed reactor (3.9 g of catalyst in total).

This experimental campaign allowed inferring a lumped kinetic law (pseudo-first order) for the steam reforming of a mixture of tar key-compounds, with activation energy of the same order of magnitude of those referred in literature for benzene, toluene, naphthalene. The lumping process consisted in reducing the tar mixture into a representative pseudo-component by means of a general procedure and considering conversion with steam into hydrogen and carbon oxides of tar

constitutive group CH_(h/c) simultaneously to water gas shift.

This lumped reaction rate was then implemented in a mathematical model of the annular catalytic packed bed inside a filtering candle, radially fed with the raw syngas produced in the fluidized bed of the biomass steam gasifier. Additional reforming processes converting methane and benzene, also present in syngas, were included in the model by means of the respective kinetic laws, taken from the literature. Simulations provided numerical results in fair agreement with experimental findings from the actual pilot gasifier equipped with a catalyst-filled candle.

As a result, an effective and quite simple procedure was proposed, carried out and validated, useful to investigate optimum conditions for tar reforming by means of hot syngas cleaning and conditioning, strictly integrated with a gasification process.

6 NOMENCLATURE

4.1 Abbreviations

PFR	Plug Flow Reactor
SMR	Steam Methane Reforming
WGS	Water Gas Shift

4.2 Symbols

c	index in molecular formula of C _{tar}
C_i	molar concentration of gaseous species i , mol m ⁻³
$E_{a,j}$	activation energy of Reaction j , kJ mol ⁻¹
F_i	molar flowrate of species i , mol h ⁻¹
h	index in molecular formula of C _{tar}
k_j	specific reaction rate of Reaction j , m ³ kg _{cat} ⁻¹ h ⁻¹
K_S	H ₂ S adsorption equilibrium constant, atm ⁻¹
m_i	number of H atoms in the formula of hydrocarbon i
N	number of hydrocarbons in tars mixture
n_i	number of C atoms in the formula of hydrocarbon i
P	pressure, atm
R	universal gas constant, $8.314 \cdot 10^{-3}$ kJ mol ⁻¹ K ⁻¹
r_i	overall reaction rate of species i , mol kg _{cat} ⁻¹ min ⁻¹
r_j	reaction rate of Reaction j based on its reference species, mol kg _{cat} ⁻¹ min ⁻¹
T	temperature, K
t	time, h
w	packed bed mass (variable), kg
W	total packed bed mass, kg
$x_{tar,i}$	molar fraction of hydrocarbon i in tars mixture, mol mol ⁻¹
y_j	molar fraction of species i , mol mol ⁻¹
Y_i	molar percentage dry, dilution-free of gaseous species i , vol% dry,dil.-free

4.3 Greek symbols

α	molar steam to carbon ratio, mol mol ⁻¹
β	molar N ₂ to steam ration, mol mol ⁻¹
$\nu_{i,j}$	stoichiometric coefficient of species i in Reaction (<0 for reactants, >0 for products)
χ_i	conversion of species i

4.3 Subscripts and superscripts

app	apparent
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fin final
in inlet
out outlet
start initial

7 REFERENCES

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