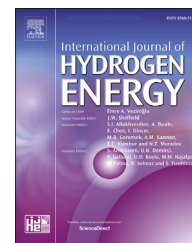




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Evaluation of sorbents for high temperature removal of tars, hydrogen sulphide, hydrogen chloride and ammonia from biomass-derived syngas by using Aspen Plus

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HIGHLIGHTS

- A simulation model for a biomass fluidized-bed gasifier was developed by Aspen Plus.
- The gasification model is the quasi-equilibrium approach based on Gibbs free energy minimisation.
- The simulation includes a gas cleaning chain simulates for several contaminants.
- The contaminants considered are toluene, benzene, naphthalene, H₂S, HCl and NH₃.
- Tars drops at 3 g/Nm³; H₂S, HCl and NH₃ drops at 3.7, 0.5 and 0.6 ppm respectively.

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ABSTRACT

Biomass gasification is a promising technology to produce secondary fuels or heat and power, offering considerable advantages over fossil fuels. An important aspect in the usage of producer gas is the removal of harmful contaminants from the raw syngas. Thus, the object of this study is the development of a simulation model for a gasifier including gas clean-up, for which a fluidized-bed gasifier for biomass-derived syngas production was considered, based on a quasi-equilibrium approach through Gibbs free energy minimisation, and including an innovative hot gas cleaning, constituted by a combination of catalyst sorbents inside the gasification reactor, catalysts in the freeboard and subsequent sorbent reactors, by using Aspen Plus software. The gas cleaning chain simulates the raw syngas clean-up for several organic and inorganic contaminants, i.e. toluene, benzene, naphthalene, hydrogen sulphide, hydrogen chloride and ammonia. The tar and inorganic contaminants final values achieved are under 1 g/Nm³ and 1 ppm respectively.

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Introduction

Among all renewable energy sources, renewable carbonaceous feedstock is one of the best candidates for heat and power generation due to its widespread availability and its potential to provide much larger load of useful energy with inferior environmental impacts respect to fossil fuels [1–3]. Biomass, which takes a large share in the available renewable energy sources, can be converted into gaseous fuels or thermal energy via biological or thermo-chemical processes. Unlike biological methods, thermo-chemical methods are more versatile, allowing an extensive range of feedstocks [4,5]. Among the different thermo-chemical processes, gasification is one of the most effective technologies because of its relatively low investment costs and its high-rate fuel gas production [6,7]. This process utilises oxidising agents (air, oxygen, steam or a mix of these) to produce a fuel gas, called syngas, rich in hydrogen, methane, carbon monoxide, carbon dioxide and steam, along with several unwanted by-products which concentrations depend on feedstock, gasifier design and process conditions [8]. These undesired by-products include organic tars and inorganic impurities (e.g. H_2S , NH_3 and HCl). Tars are typically aromatic hydrocarbons. They are also known for their toxic and carcinogenic properties and hence the aim is to remove them as much as possible during the syngas clean-up. Sulphur compounds are a well-known catalyst poison and are responsible for polluting the environment. Chlorine compounds may cause corrosion of metal equipment, health problems and environmental issues, while ammonia compounds may act as a poison for catalyst and may produce NO_x [9–12]. Thus, the raw syngas has to be cleaned for contaminants before its used in downstream applications aiming for fuel or heat and power production [13,14]. There are two main possibilities for gas cleaning [15,16]: low-temperature processes (e.g. an amine scrubber) or mid-to high-temperature cleaning processes (e.g. filter candle, sorbent reactor). Low temperature clean-up in amine scrubbers, by using chemical absorbers in the liquid state at a temperature lower than $50\text{ }^\circ\text{C}$ in counter-current with syngas with a temperature of $850\text{ }^\circ\text{C}$ (temperature of gasification), have several disadvantages: tar condensation may cause plugging and fouling of the condenser and downstream process piping, causing reduction of the efficiency of the power plant, because of inevitable consumption of water and production of a great amount of polluted water, with subsequent cost for its purification [17,18]. In order to overcome the problems encountered in low-temperature clean-up, and since the syngas has a high temperature, it is most appropriate to carry out its cleaning also at increased temperature, in order to reach an optimum cycle efficiency and protect downstream equipment and catalysts [19,20]. So, new mid- ($400\text{--}600\text{ }^\circ\text{C}$) to high-temperature ($600\text{--}850\text{ }^\circ\text{C}$) syngas cleaning methods, firstly developed for fuel cell applications, offer potential economic advantages [15,19]. Treatments inside the gasifier (so-called primary methods) for tar removal have been widely studied and can be mainly divided into two applications: in-bed gasifier sorbent and catalytic filter candles. In-bed gasifier sorbents are a viable option to reduce tar compounds at the gasification temperature [21,22]; calcined

dolomite is one of the best catalysts thanks to its low cost and wide availability and there are a lot of publications [23–25] that demonstrate its efficiency. Another primary method for hot gas cleaning and conditioning is represented by catalytic filter candles [26,27] that are inserted directly in the freeboard of the gasifier and have the advantage of operating at a temperature close to the gasification temperature. By means of the catalytic filter candle, tars can be converted by reforming reactions into syngas. Sorbent reactor for removing inorganic impurities can be considered the final step of the hot gas cleaning chain [28]. Several types of sorbents based on zinc, iron, copper, cerium, manganese, calcium, titanium have been developed over the last years and they are able to remove inorganic contaminants from syngas at mid-to high-temperature ranges [29–33]. The main criteria that these sorbents must satisfy are: high adsorption capacity for inorganic impurities in order to reduce both sorbent quantity and process equipment size, fast adsorption kinetics, high equilibrium constant, ability to tolerate high temperature, capacity of regeneration maintaining efficient sorption and multifunctional removal [15]. The Aspen Plus simulator has been demonstrated as a very powerful tool for chemical plant investigation. Up to now, most simulations using Aspen Plus have been focused on the gasification process with different biomass feedstocks, temperatures, oxidising agents, and steam to biomass (S/B) ratios in order to improve syngas composition and system efficiency. There are a few studies that have also considered the formation of tars and inorganic contaminants and, thus, the integration of gas cleaning steps. Detchusananard et al. [34] studied the integration and the optimization of a sorption enhanced gasification (SEG) of biomass combined with a solid oxide fuel cell (SOFC) and gas turbine for the production of power and heat from eucalyptus wood chips. For this purpose, they investigated the hot gas cleaning units, developing a CaO chemical looping that reduces the tar concentration (they have considered toluene, naphthalene, phenol and pyrene) increasing hydrogen, and introducing a ZnO sorbent reactor for the adsorption of H_2S . Puig-Gamero et al. [35] developed an Aspen Plus simulation for biomass gasification coupled with hot gas cleaning based on dolomite to reduce tar (the only tar considered was benzene), and Cu/ZnO catalyst to remove H_2S . The aim of this work is to improve a reliable biomass gasification simulation, already validated by authors in Marcantonio et al. [36], using Aspen Plus, that considers the removal of tars (toluene, naphthalene and benzene) and inorganic contaminants (H_2S , NH_3 and HCl) and to evaluate different configurations of hot gas cleaning chains for the raw syngas in order to obtain the maximum level of hydrogen, while respecting limits for contaminants after the raw syngas clean-up. Thus, this study presents the novelty of simulating biomass gasification process including a variety of contaminants and an innovative hot gas cleaning and conditioning, constituted by a combination of catalyst sorbent inside the gasifier reactor and catalysts in the freeboard for tar removal and a subsequent sorbent reactor for H_2S and HCl removal. With this aim, a model has been constructed by means of Aspen Plus that considers a system made of three reactors, a sorbent reactor feeding by catalyst material that simulates the in-bed gasifier sorbent at the gasifier temperature, a stoichiometric reactor that simulates

the bundle of ceramic filter candles at the gasifier temperature and two lower temperature (with respect to the gasification temperature) sorbent reactors. The main purpose of this study is to evaluate the performance of this innovative system configuration, able to remove contaminants such as tars, H₂S, NH₃ and HCl from syngas through catalytic methods, varying operative conditions, such as temperature and S/B ratio in the gasification process to find the best combination.

Materials and methods

Biomass characteristics

In the present work, hazelnut shells are used as biomass feeding material for the gasification process. Using agricultural waste allows to have zero costs for the feedstock and avoid fuel vs food biomass competition. The properties of hazelnut shells are shown in Table 1.

Aspen Plus modelling

The simulation of the biomass gasification process and hot gas cleaning by means of Aspen Plus is based on mass-energy preservation and chemical equilibrium among all processes. The following assumptions have been considered for the simulation:

- Gasification process is steady-state and isothermal [38];
- drying and pyrolysis are instantaneous and volatile products principally consist of H₂, CO, CO₂, CH₄ and H₂O [39];
- char is 100% carbon [40];
- all gases behave ideally;
- catalyst is defined as conventional solid (since it has already defined in the Aspen Plus databank by its physic and chemical properties);
- the organic contaminants considered are toluene (1-ring), naphthalene (2-ring) and benzene;
- the inorganic contaminants considered are H₂S, NH₃ and HCl.

The Aspen Plus flow sheet of the developed model is shown in Fig. 1 and all the unit operations are described in Table 2.

In this simulation, the biomass is defined as nonconventional component, by its ultimate and proximate analysis. For the calculation of the enthalpy and the density of nonconventional components, the model selected are HCOALGEN and DCOALGEN, respectively. The chosen thermodynamic methods are based on Peng-Robinson equation of state, with Boston-Mathias (PR-MB) modification, since it's suitable for high temperature gasification processes [41].

Description of Aspen Plus flow-sheet

The power plant is mainly composed of a gasifier producing syngas from hazelnut shells that feeds a hot gas cleaning chain. Firstly, the stream BIOMASS, made by hazelnut shells, with constant flow rate (m_{bio}) set to 180 kg/h (1 MWth input size, considering HHV), is fed to the DECOMP block (a RYELD reactor), utilised to simulate the decomposition of the unconventional feed into its conventional components (C, H₂, O₂, S, N₂ and ash, by declaring the yield distribution following the biomass ultimate analysis in Table 1). Since DECOMP creates N, Cl and S as elemental components that are known to produce mainly HCl, NH₃ and H₂S, and the results of the real fractional conversion model are closer to the experimental data than that of the restricted chemical equilibrium, the product comes from DECOMP goes to the Rstoic block to simulate the production of H₂S, NH₃ and HCl by the following reactions:



The fractional conversion considered for S, Cl₂ and N₂ is equal to 1 [42]. Resulting stream S2 goes into a separator SEP, that separates the stream into three sub-streams: volatile part VOLATILE, char part CHAR and a stream composed by HCl, NH₃ and H₂S, called INORG. Next, VOLATILE stream is still split in two sub-streams: VOL and H2, the first one after mixing with oxidising fluid goes into the gasifier GASIF and the second one is used to simulate tar production in the RYield block TARPROD. The block TARPROD is necessary since the

Table 1 – Physical and chemical properties of hazelnut shells [37].

Bulk density (kg/m ³)		Moisture content (wt%)			
319.14		7.9			
Proximate analysis (% _{wt} , dry basis)					
Ash		Volatile matter		Fixed carbon	
0.77		62.70		24.04	
Ultimate analysis (% _{wt} , dry basis)					
C	H	N	O	Cl	S
49.00	6.03	0.22	42.06	0.76	0.67
Heating values (MJ/kg _{dry})					
HHV		LHV			
20.20		18.85			

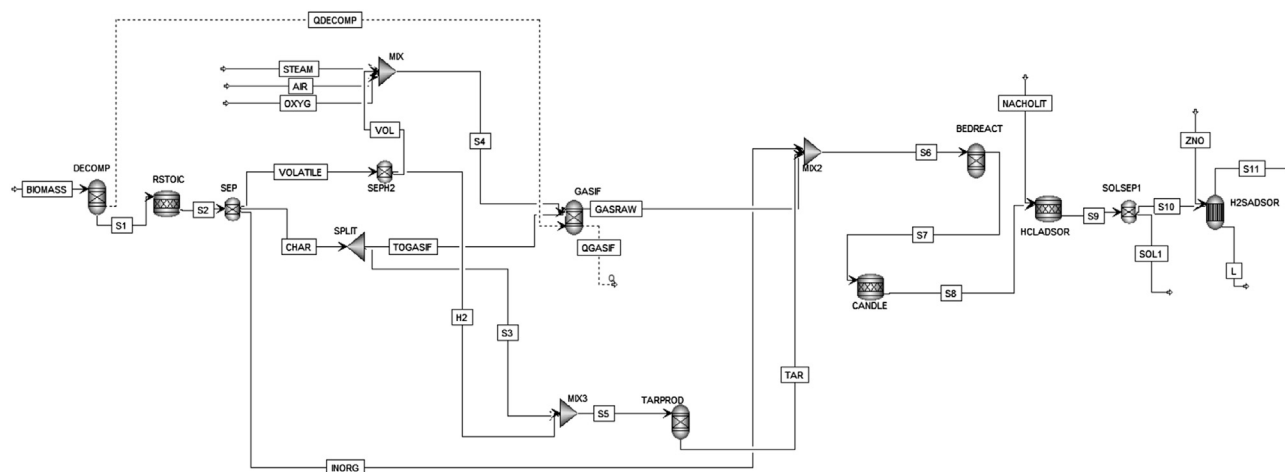


Fig. 1 – Flowsheet of the plant evaluated in this study (the dashed streams are heat streams, representing thermal recovery; the continuous streams are material streams).

simulation is at equilibrium and it's not possible to simulate tar formation inside the gasifier GASIF. CHAR stream is divided in two sub-streams: S4 that represents the char reacted in the gasifier and S3 that represents the unreacted char, the last one is fed to TARPROD where it reacts with hydrogen from the H2 stream. The quantities of tars are set in accordance with literature reference [43] and maintaining the proportion of about 60%, 20% and 20% for benzene (C_6H_6), toluene (C_7H_8) and naphthalene ($C_{10}H_8$), respectively [44]. The stream S6 is the stream that represents the real output of the gasifier, i.e. the sum of the GASRAW, INORG and TAR streams. Raw syngas S6 needs to be clean, for this reason the following blocks have been added: a RGibbs reactor BEDREACT that simulates in-bed gasifier sorbent at high temperature to

reduce tar and inorganic contaminants, a RStoic reactor CANDLE that simulates the catalytic filter reaction and a RStoic and a REquil reactor, DECLOR and DESULPH respectively, that simulates hydrogen chloride and hydrogen sulphide removal.

Gasification process

The gasifier represents a very important part in a gasification process, determining the quality of syngas that affects directly the efficiency of the system. Among the various types of gasifiers, the fluidized-bed reactor demonstrates a better gasification performance, allowing high reaction rates and conversion efficiencies thanks to the very good mixing and

Table 2 – Description of ASPEN Plus flowsheet unit operation presented in Fig. 1.

ASPEN Plus name	Block ID	Description
RYIELD	DECOMP	RYield reactor - converts the non-conventional stream "BIOMASS" into its conventional components
	TARPROD	RYield reactor – simulates the production of toluene, naphthalene and benzene
RSTOIC	RSTOIC	RStoic reactor – simulates the production of HCl, NH_3 and H_2S
	CANDLE	RStoic reactor – simulates the catalyst filter reaction
	DECLOR	RStoic reactor – simulates the reaction between HCl and nahcolite
SEP	SEP	Separator – separates the biomass in three streams: VOLATILE, CHAR and INORG
	SEPH2	Separator – separates an amount of hydrogen used to produce tar
	SOLSEP1	Separator- separates the solid components
	SEPSORB	Separator – separates the sorbent solid fraction reacted
MIXER	MIX1	Mixer – mixes oxidising fluid with VOL stream, that represents combustible fluid
	MIX2	Mixer – mixes the gas from gasifier with INORG and TAR
	MIX3	Mixer – mixes the stream S3 and H2
FSPLIT	SPLIT	Splitter – splits char unreacted (S3) from char to burn (S4)
RGBBS	GASIF	Gibbs free energy reactor – simulates drying, pyrolysis, partial oxidation and gasification and restricts chemical equilibrium of the defined reactions to set the syngas composition by specifying a temperature approach for individual reactions
	BEDREACT	Gibbs free energy reactor – simulates the high temperature reaction of dolomite with tar
	DESULPH	REquil reactor – simulates the reaction of sorbent with H_2S

Table 3 – Gasification reactions [49].

Reaction	Reaction name	Heat of reaction	Reaction number
Heterogeneous reaction			
$C + 0.5 O_2 \rightarrow CO$	Char partial combustion	$(-111 \text{ MJ kmol}^{-1})$	(R4)
$C + H_2O \leftrightarrow CO + H_2$	Water-gas	$(+172 \text{ MJ kmol}^{-1})$	(R5)
Homogeneous reactions			
$H_2 + 0.5 O_2 \rightarrow H_2O$	H_2 partial combustion	$(-283 \text{ MJ kmol}^{-1})$	(R6)
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water gas-shift	$(-41 \text{ MJ kmol}^{-1})$	(R7)
$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam-methane reforming	$(+206 \text{ MJ kmol}^{-1})$	(R8)

operate conditions [45,46]. A very good way to simulate the performance of fluidized-bed biomass gasification is the quasi-equilibrium temperature (QET) method [42,47], that gives a more precise characterization of syngas composition. In this article, the gasification process is simulated by mean of a RGibbs reactor, called GASIF in the flow sheet of Fig. 1, modelled with the quasi-equilibrium approach. So, the reactions within the reactor (listed in Table 3) are conducted at their QET, rather than at the actual temperature of the gasification reactor. In order to be more rigorous, a Data Fit of experimental data (about hazelnut or almond shells, using steam and/or oxygen as gasification media with a gasification temperature around 800 °C and S/B around 0.5) has been executed on Aspen Plus, similar to the approach in Marcantonio et al. [36]. In this way RGibbs determinates the chemical equilibrium constant for every reaction at gasifier temperature, by that giving equilibrium syngas composition [41,48]. The operative conditions of the gasification system are 800 °C and 1 bar; the only oxidising agent considered is steam and the S/B ratio is set to 0.5. The gasification model has been validated by authors in Marcantonio et al. [36].

In-bed gas cleaning

The performance of the biomass gasifier is improved by in-bed use of calcined dolomite, simulated in Aspen Plus with a RGibbs reactor BEDREACT, settled at 800 °C and 1 bar. The effect of calcined dolomite (CaO–MgO) in the gasifier bed under stationary conditions is to increase the gas yield by the decrease of tar and inorganic impurities. In the present work, under the assumption of non-considering by-products formed by the reaction of components with calcined dolomite, the conversion rates considered for the tar and inorganic impurities (the dolomite acts as a primary sorbent for ammonia, hydrogen sulphide and hydrogen chloride) are shown in Table 4.

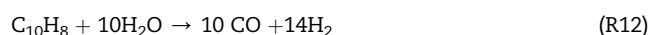
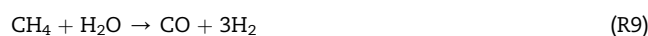
Catalytic filter candles

The catalytic filter candles were simulated by using an isothermal RStoic reactor (called CANDLE). The only

Table 4 – Conversion rate (X) of components that react with dolomite [12,15,50–54].

$X_{C_6H_6}$ (%)	50
$X_{C_{10}H_8}$ (%)	82
$X_{C_7H_8}$ (%)	80
X_{H_2S} (%)	85
X_{HCl} (%)	85
X_{NH_3} (%)	95

compounds considered for the simulation are toluene, benzene and naphthalene. So, the reactions considered in the CANDLE block are:



As regard reaction conversions, data from Savuto et al. [26], experimentally validated for S/B = 0.5, were used. Data come from lab-scale gasification tests, thus the behaviour can be replicated in pilot and commercial size gasifiers if the temperature can be maintained constant (as in the case of heat supply or burn of a little portion of gas) and if it is in agreement with the isothermal model chosen. The conversion rate (X) of components that react in the stoichiometric reactor CANDLE is reported in Table 5.

The limits for tar content in the syngas for the main end users are reported in Table 6.

Sorbent reactor

Since H_2S , NH_3 and HCl are responsible for corrosion and environmental problems, as explained in the Introduction, it's important to take into account, in the gas cleaning chain, a block dedicated to their removal below the desired limits, different for each consequent application. Table 7 reports some values of contaminant limits for different commercialized applications.

A multifunctional reactor, able to remove at the same time all the contaminants, is preferable, but it's not practical that a sorbent remove simultaneously multiple contaminants in hot gas cleaning [52] since some contaminants may interfere in the adsorption of others (e.g. HCl inhibit the adsorption of H_2S in many metal oxides). For this reason, different steps have been developed in order to achieve the desired ppm level for the inorganic impurities considered in the simulation.

Table 5 – Conversion rate (X) of components that react in the catalytic candle [26].

	S/B = 0.5
X_{CH_4} (%)	90
$X_{C_6H_6}$ (%)	95
$X_{C_7H_8}$ (%)	92
$X_{C_{10}H_8}$ (%)	90

Table 6 – Tar levels in biomass gasification and syngas users limits [20,55].

	Biomass waste gasification	Ammonia production	Gas turbine	SOFC	Methanol synthesis
Tars (mg/Nm ³)	3000–20000	<0.1	<30	<100 ^a	<0.1

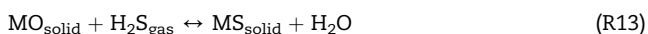
^a Following Aravind et al. [20], for the admissible level of tars in the SOFC three cases could be considered: optimistic case, that assumes tars can be reformed at SOFC anodes and so the inlet concentration of tar could be not taking into account; intermediate case, that assumes a few hundred mg/Nm³ of tars can be tolerated but not full tar loads from biomass gasifier and then conservative case, in which it can be assumed that the tar must be removed to low mg/Nm³ levels for safe SOFC operations. In this work a value between intermediate and conservative case has been selected.

Table 7 – Typical H₂S, NH₃ and HCl concentration in biomass waste derived syngas and target level associated syngas applications [12,32,56–59].

Contaminants (ppm)	Biomass waste gasification	Ammonia production	Gas turbine	SOFC	Methanol synthesis
H ₂ S	20–500	<0.1	<20	<1	<0.5
HCl	30–1000	<1.5	<1.5	<1	<1
NH ₃	20–1000	–	<50	<5000	<10

Cleaning of hydrogen sulphide

The high temperature sorbents for syngas applications involve a solid-gas reaction between a metal oxide and the contaminant, as follow:



The reaction R13 concerns H₂S. The equilibrium constant for the reaction R13 is

$$K_{\text{eq,H}_2\text{S}} = \frac{[\text{H}_2\text{O}][\text{MS}]}{[\text{H}_2\text{S}][\text{MO}]} = \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{S}]} \quad (\text{R14})$$

since that the activity of a pure solid is, by definition, equal to one. In order to simulate the sorbent reactor, the Aspen Plus model includes a REquil block DESULPH for desulphurization. Equation R13 and R14 point out the effect of a great amount of water concentration on the level of sulfidation of a metal oxide resulting in the possibility for the reaction to go on only if the sorbent has a very great equilibrium constant for the reaction [60]. In consequence, the amount of steam in the syngas represents an interesting challenge in the material advancement and in the present work a sensitivity analysis on the S/B ratio has been carried out and shown in the Results and Discussion section, paragraph [Effect of steam on sulfidation of a metal oxide](#), in order to investigate the impact of steam on the sorbent performance. Another limit of metal oxide sorbents, linked to chemical and mechanical degradation in hot gas cleaning, is their thermal instability at the higher end of the temperature range [61], an aspect that until now has been rarely mentioned in the literature and taken into account in the paragraph [Effect of temperature on sulfidation of a metal oxide](#). The metal oxide sorbent must satisfy some criteria: affordability, high equilibrium constant, high adsorption capacity, fast adsorption kinetics, fast and cheapness regeneration capability [15]. According to the previous criteria, zinc-based sorbents are nowadays the leading sorbent competitor for H₂S removal [11,31,62], showing a quasi-total removal of hydrogen sulphide at the operative mid-temperature of 400 °C. Besides zinc-based sorbents, the

other only sorbents that are capable of cleaning H₂S below 1 ppm are the ones based on cerium or copper [20]. In general, the H₂S cleaning capability of different oxides in the mid- and high-temperature range is the following: Sn < Ni < Fe < Mn < Mo < Co < Zn < Cu and Ce [20] and is shown in Fig. 2.

The properties of the metal oxides considered as sorbent in the present work are shown in Table 8.

Cleaning of hydrogen chloride

The most promising method for HCl removal at mid- and high-temperature involves alkali-based sorbents, mostly sodium and potassium compounds [56]. Dou et al. [52] shew nahcolite (NaHCO₃) as one of the best alkali-based sorbents, since it can remove HCl to concentrations lower than 1 ppm in the temperature range of 526–650 °C. Using nahcolite, the following reaction will take place:

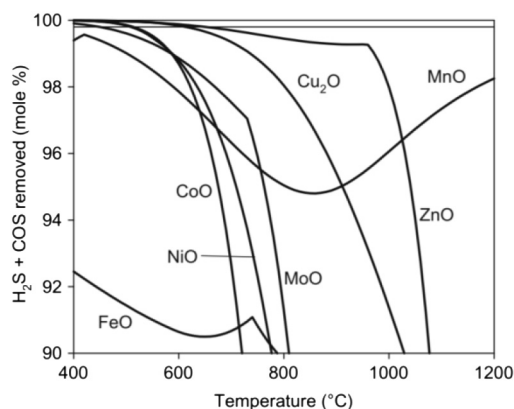
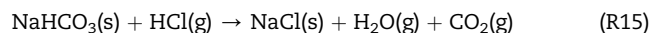
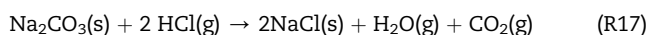
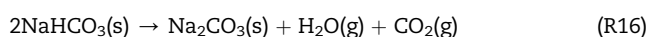


Fig. 2 – Thermodynamic equilibrium adsorption of metal oxide [63].

Table 8 – Characteristics of metal oxides for hydrogen sulphide removal [51,64,65].

Sorbent type	Chemical formula	Theoretical sorption capacity (g S/g sorbent)	Temperature range (°C)	Price (USD/kg)
Cerium oxide	Ce ₂ O ₃	0.093	500–700	5.9
Copper oxide	Cu ₂ O	0.224	540–700	5.8
Zinc oxide	ZnO	0.395	450–650	2.6
Manganese oxide	MnO	0.400	400–900	4.2
Iron oxide	FeO	0.445	450–700	1.4

However, it has to be taken into account that, when the temperature of nahcolite is raised up 550 °C (reaction R16), water molecules are separated. Then, nahcolite disintegrates to sodium carbonate and HCl will react with Na₂CO₃ to form sodium chloride (reaction R17).



Experimental results show that in order to reduce HCl ppm levels until 1 ppm the nahcolite temperature has to be approximately of 550 °C. In the Aspen Plus simulation, the removal of HCl is simulated by means of an RGibbs reactor DECLOR, settled at 550 °C and 1 bar with the restricted chemical equilibrium option, using the reactions R15–R17.

Results and discussion

The composition of the syngas produced by the gasifier, the bed gas cleaning reactor and the candle filter is shown in Table 9.

As shown in the last column of Table 9, the only contaminant up to the limit value reported in Table 7 for the most common syngas applications is the H₂S. In fact, toluene, benzene, naphthalene and NH₃ have been reduced to the desired levels in the primary catalyst (block BEDREACT) by means of dolomite, while HCl has been reduced in the alkali-sorbent based reactor DECLOR. The reduction of the hydrogen

Table 10 – Effect of H₂S adsorption by different sorbents.

Sorbent type	Sorbent flow rate (kg/h)	Sorbent temperature (°C)	H ₂ S level (ppm) in the stream S11
Cerium oxide	1.300	600	0.8
Copper oxide	0.530	600	0.8
Manganese oxide	0.299	600	0.8
Zinc oxide	0.289	450	0.8
Iron oxide	0.265	600	0.8

sulphide, using the sorbents shown in Table 8 by means of the DESULPH reactor, is reported in Table 10 (in which each sorbent is considered at its higher stability temperature). All the values of the other components remain unaltered.

As shown in Table 10, it has been evaluated, from sorption capacity shown in Table 8, the flow rate of each sorbent needed for lower the amount of H₂S under 1 ppm at the reference temperature chose within the temperature range showed in Table 9. In this way, out of the DESULPH block all the contaminants are under the limits.

Sensitivity analysis

The effect of the main operating conditions such as steam to biomass ratio, temperature and humidity on syngas composition and H₂S conversion are discussed in this section. In

Table 9 – Composition of the syngas.

Component	Out of the gasifier (stream S6)	Out of the bed gas cleaning BEDREACT (stream S7)	Out of the candle filter CANDLE (stream S8)	Out of the dechloration DECLOR (stream S9)
H ₂ (%wet mole fraction)	31.3	31	38	42
CO (%wet mole fraction)	15	14	17	18
CO ₂ (%wet mole fraction)	18.5	16.5	15	17
H ₂ O (%wet mole fraction)	30	28	20	22
CH ₄ (%wet mole fraction)	4.6	4.3	0.4	0.4
NH ₃ (ppm)	1200	50	48	48
H ₂ S (ppm)	2134	290	280	280
HCl (ppm)	976	120	110	0.25
C ₆ H ₆ (g/Nm ³)	13	5.9	0.065	0.065
C ₇ H ₈ (g/Nm ³)	4.5	0.8	0.039	0.039
C ₁₀ H ₈ (g/Nm ³)	6.3	1.2	0.09	0.09

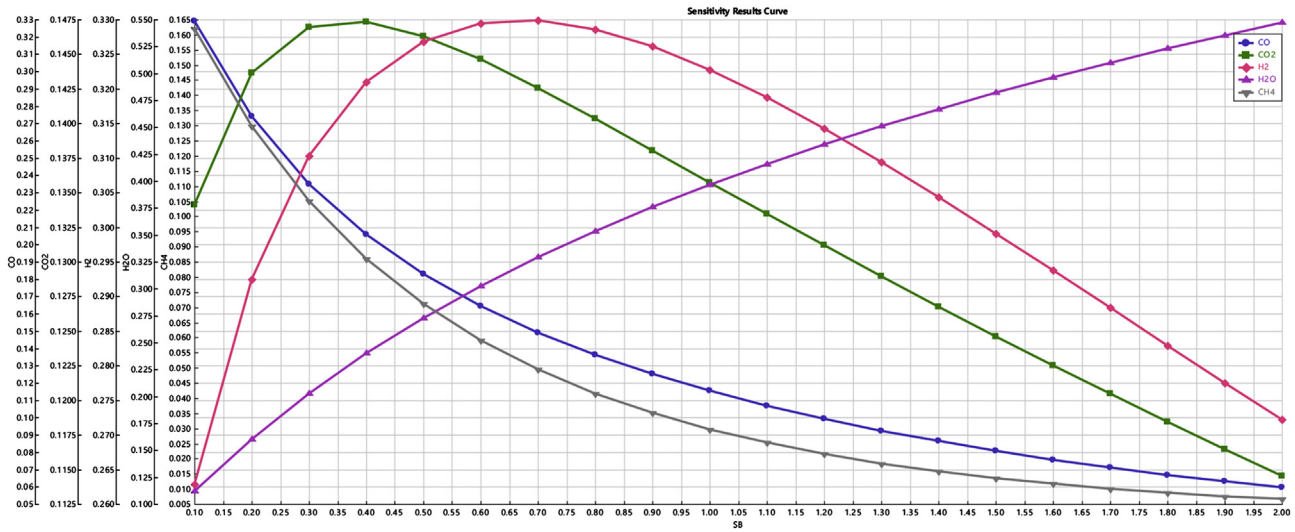


Fig. 3 – Effect of S/B ratio on syngas composition.

order to investigate these processes, simple assumptions have been developed over the simulation. Just one of the parameters is varied while the rest of them are kept constant. So, the gasification temperature is varied between 700 °C and 1050 °C, the S/B ratio between 0.10 and 2, the steam concentration between 0.5% and 21.5% and the temperature at which the sorbent works is varied within its operative temperature range. In addition, the biomass feed rate is fixed at 180 kg/h for all cases.

Effect of steam to biomass (S/B) ratio on syngas composition
 Fig. 3 shows the effect of the S/B ratio on the product syngas composition out of the gasifier at a gasification temperature of 800 °C for hazelnut shells. The concentration of H₂ and CO₂ rises with the rise of S/B ratio and the concentrations of CO and CH₄ decrease with S/B ratio. The increase of steam favours the water gas (R5), water gas shift (R7) and steam methane reforming (R8) reactions, which determine an increase of H₂ and CO₂ concentrations. The decrease of CO with the increase of S/B ratio is due to the reaction between CO and

steam in R10 and the decrease of CH₄ is because of the reaction of methane with steam in R11. Similar trends were reported in literature references [66,67].

Effect of gasification temperature on syngas composition
 The trend of the syngas composition respect to the temperature in the range 700–1000 °C is shown in Fig. 4. It can be observed that H₂ and CO concentrations increase with the increase of temperature, due to the endothermic reactions R5 (Water gas) and R8 (Steam methane reforming). Otherwise, the increase of temperature determines the decrease of CO₂, CH₄ and H₂O. The decrease of CO₂ production depends on reaction R7 (Water gas shift) that is exothermic, being advantaged at low temperatures, and consequently the higher temperature means the higher CO and the lower CO₂ production. Similar trends were observed by Refs. [35,47].

Effect of steam on sulfidation of a metal oxide
 According to equation R13, a higher steam concentration reduces the extent of sulfidation of a metal oxide. This issue, in

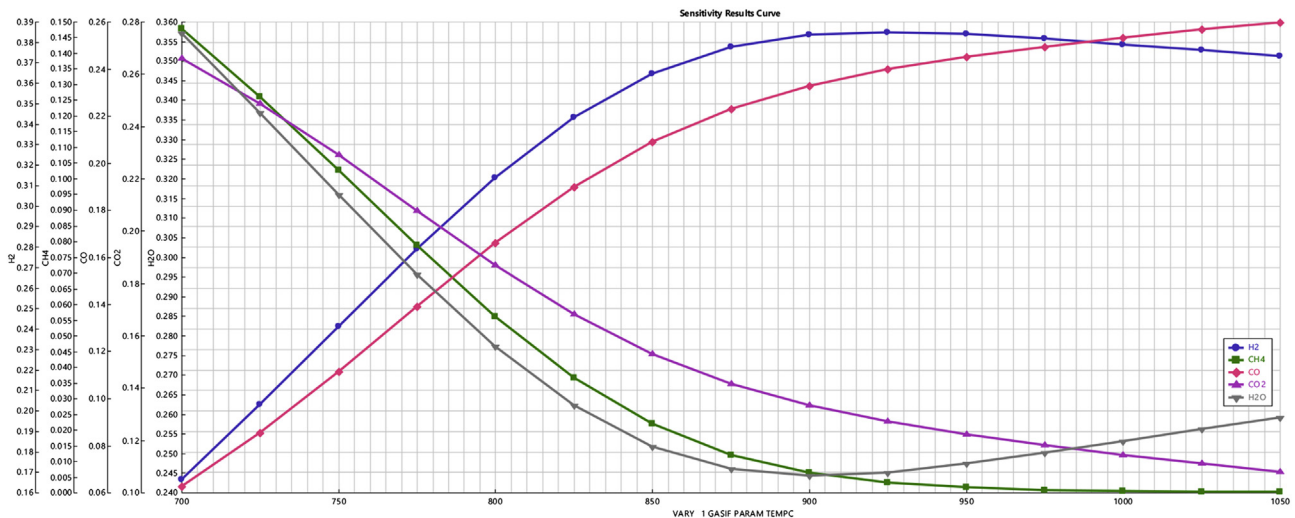


Fig. 4 – Effect of temperature on syngas composition.

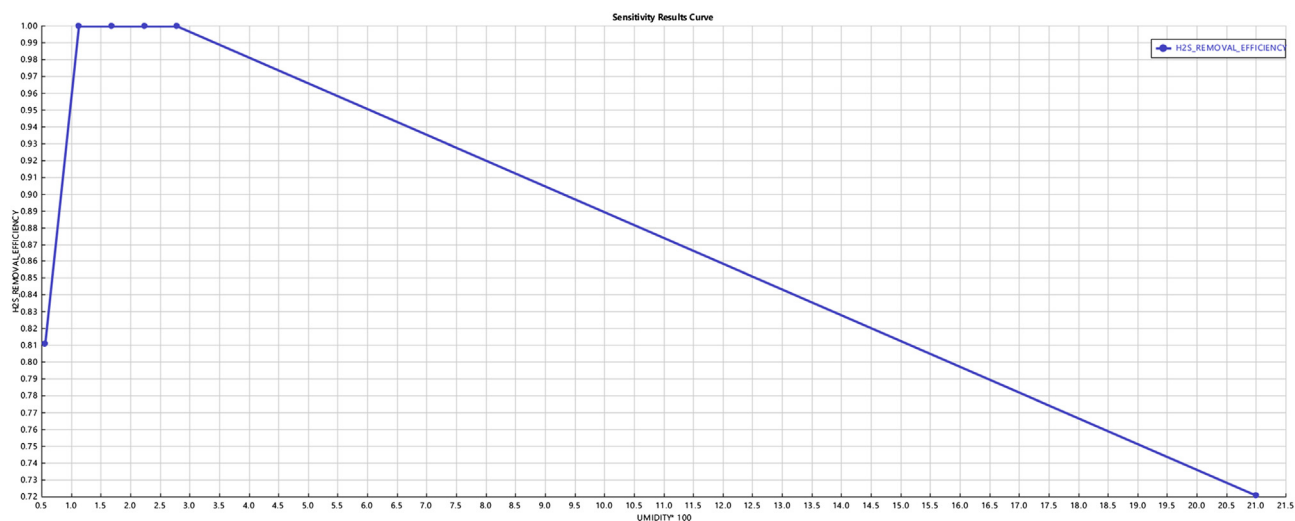


Fig. 5 – Result of sensitivity analysis of H₂S concentrations respect to steam content in syngas.

literature, is rarely studied; there are a lot of publications that focus on sulphur sorbents for dry syngas cleaning, but not so many that involve sorbents for cleaning syngas at high steam concentration. In the present study this aspect has been taken into account and in Fig. 4 the sensitivity analysis is shown that is carried out on zinc oxide (similar trends have been obtained for the other metal oxides under investigation) while varying the steam concentration. The H₂S removal efficiency, reported in the y-axis of Fig. 5 and Fig. 6, has been evaluated as:

$$H_2S_{\text{removal efficiency}} = \frac{H_2S_{\text{in the stream S10}} - H_2S_{\text{in the stream S11}}}{H_2S_{\text{in the stream S10}}} \quad (R18)$$

The study demonstrates that the conversion of H₂S lowers with the increase of moisture content and confirm the high steam content of syngas as a compelling challenge in sorbent material advancement.

In the case of zinc oxide, it has been shown that it is able to reach close to 100% H₂S removal for syngas containing steam between 1.5% and 3%.

Effect of temperature on sulfidation of a metal oxide

A sensitivity analysis, on the influence of temperature on the sorbent capacity to adsorb hydrogen sulphide, has been carried out. The analysis reveals similar trends for each sorbent considered in this paper and it has been chosen to report only the behaviour of zinc oxide (in its temperature range) as representative. The result is shown in Fig. 6 and demonstrates that the temperature has a negative impact on the H₂S conversion.

In the case of zinc oxide, the maximum conversion of H₂S is achieved at temperatures between 450° and 470 °C. The trend is in line with the expected results, since K_{eq,H_2S}

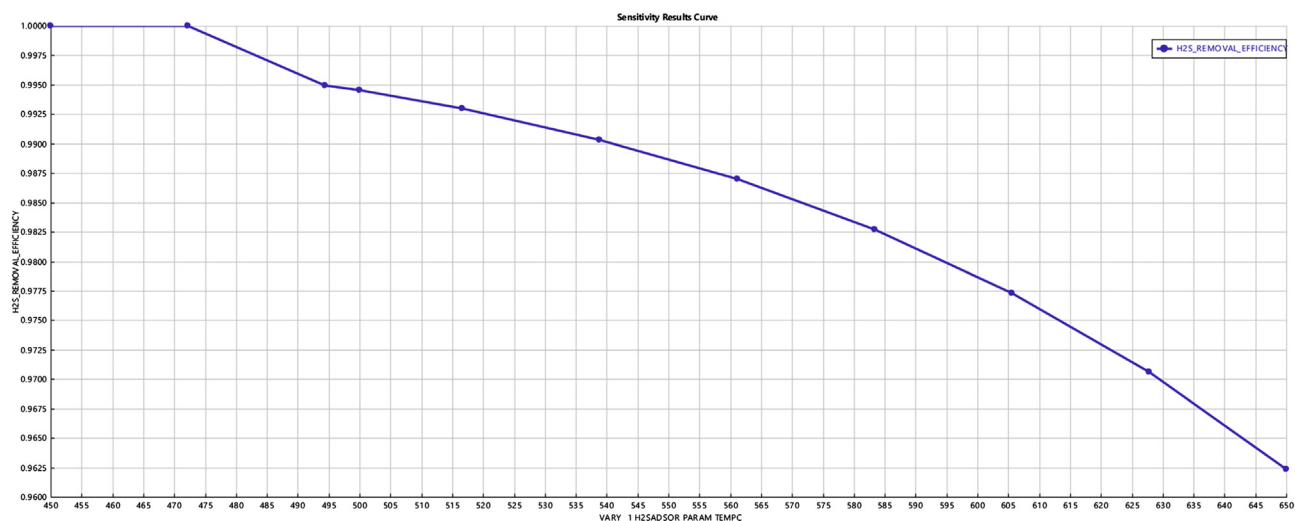


Fig. 6 – Result of sensitivity analysis of H₂S concentrations respect to temperature.

decreases with the increase of temperature and both chemical and mechanical degradation disrupt the thermal stability of metal oxides at the higher end of the temperature ranges [52].

Conclusions

In this work a simulation of hot gas cleaning of syngas obtained through hazelnut shells gasification in a bubbled fluidized-bed gasifier, using Aspen Plus software, was developed. The quasi-equilibrium method based on Gibbs free energy minimisation has been selected for the modelling of the gasification process. Both the influence of the steam to biomass ratio and the temperature on the syngas composition was investigated. The operational condition of the gasification process chosen, for its best performance, was 800 °C and S/B ratio of 0.5. Among the main technical restrictions for the syngas production there are the undesired by-products coming from the gasification, so the production of organic and inorganic contaminants (toluene, benzene, naphthalene, hydrogen sulphide, hydrogen chloride and ammonia) were simulated according to literature yields and a process scheme for syngas purification was developed. The innovative hot gas cleaning proposed in this work was constituted by a combination of catalyst sorbent inside the gasifier reactor and catalysts in the freeboard for tar removal and a subsequent sorbent reactor for H₂S and HCl removal. The main purpose was to study the performance of this innovative configurations, able to remove contaminants such as tars, H₂S, NH₃ and HCl from syngas through catalytic methods, varying operative conditions, such as temperature and steam content to find the best combination. The developed simulation model allows for obtaining, for each contaminant, values below the limit for the main commercialized applications. More attention had been paid to hydrogen sulphide removal, the most utilizing metal oxide sorbents had been introduced and their amount for the removal of the H₂S and trend respect to steam content and temperature was studied. For the zinc oxide, the best configuration calculated, that allows to removal near the 100% of H₂S, is around 2% of humidity and 460 °C.

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