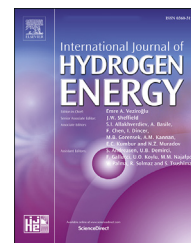


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Process analysis of hydrogen production from biomass gasification in fluidized bed reactor with different separation systems

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ABSTRACT

Gasification is one of the most effective and studied methods for producing energy and fuels from biomass as different biomass feedstock can be handled, with the generation of syngas consisting of H₂, CO, and CH₄, which can be used for several applications. In this study, the gasification of hazelnut shells (biomass) within a circulating bubbling fluidized bed gasifier was analyzed for the first time through a quasi-equilibrium approach developed in the Aspen Plus environment and used to validate and improve an existing bubbling fluidized bed gasifier model. The gasification unit was integrated with a water-gas shift (WGS) reactor to increase the hydrogen content in the outlet stream and with a pressure swing adsorption (PSA) unit for hydrogen separation. The amount of dry H₂ obtained out of the gasifier was 31.3 mol%, and this value increased to 47.5 mol% after the WGS reaction. The simulation results were compared and validated against experimental data reported in the literature. The process model was then modified by replacing the PSA unit with a palladium membrane separation module. The final results of the present work allowed comparison of the effects of the two conditioning systems, PSA and palladium membrane, indicating a comparative increase in the hydrogen recovery ratio of 28.9% with the palladium membrane relative to the PSA configuration.

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Introduction

The global energy demand continues to increase daily, and continued use of fossil fuels has already led to irreversible climate change [1,2]. Therefore, it is necessary unearth more

sustainable energy supplies. For this purpose, the use of biomass instead of fossil fuels has proved to be a valid solution for mitigating climate change and for achieving energy security [3–6]. Biomass is the world's third largest energy source after coal and oil [7] and has many advantages: it is

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inexhaustible, it can be easily stored, and its CO₂ emissions are considered climate-neutral, i.e., the CO₂ released by combustion of biofuel is approximately equal to the amount of CO₂ absorbed by biomass during its lifetime [8,9].

It is possible to convert biomass to energy (syngas, biogas, and liquid biofuels) through biological or thermochemical processes [10,11]. Combustion, pyrolysis, and gasification are the three main types of thermochemical conversion [12]. Gasification is considered the most viable alternative for the conversion of biomass into energy for achieving sustainable development as it provides energy savings and environmental protection and is becoming one of the best solutions for the valorization of solid waste [13–15]. A biomass gasification system, coupled with a gas fuelled Combined Heat and Power, can produce electricity and heat [16], and coupled with a gas cleaning and purification process, can produce pure hydrogen [17,18]. H₂ in fact represents a promising energy resource for the future: it can be used in various applications such as the production of methanol, production of ammonia, in conventional internal combustion engines, or in a more productive way, in fuel cells [19–26].

Over the last years, many studies have been carried out to predict the optimal operating conditions and system performance based on different gasification agents such as air [27], pure steam [28–30], oxygen and steam [31–33], air and steam [34–36], and in some cases, enriched air-steam mixtures [37]. Air gasification provides poor quality gas in terms of the higher heating value (HHV), compared to the case when steam is used as the gasification agent, where the latter generates fuel gas with less N₂ and more H₂ [23]. Gasification with pure oxygen gives higher quality gas, but has an additional cost for oxygen production. Indirectly heated gasification generates gas with quality similar to the case with pure oxygen/steam, as reported by Hofbauer et al. [38] for a dual fluidized-bed.

Further studies have demonstrated that the fluidized-bed reactor ensures high performance of the gasification process, providing high reaction rates and conversion efficiencies due to the very good mixing and gas-solid contact [13,39–42].

One of the best ways to simulate the performance of fluidized-bed biomass gasification is the quasi-equilibrium approach [43–48], which provides a more accurate description of the syngas composition. This approach was introduced for the first time by Gumz [49]. He suggested the use of the quasi-equilibrium temperature (QET), at which the specific chemical reaction is assumed to reach equilibrium [13,50], instead of the actual operating temperature of the gasifier. The QET value can be obtained by fitting the experimental data. This approach is a compromise between equilibrium thermodynamic models and experimental models, and does not require information on the dimensions, capacity, and structure of the reactor.

Doherty et al. based the quasi-equilibrium approach on minimization the Gibb's free energy using the restricted equilibrium method for calibration of the model data against experimental data, specifying a temperature approach for the gasification reactions [51].

Following this approach, in this study, we validate a model for chemical processes analysis by improving an existing models and predicting an *ad hoc* QET. The case under investigation is the circulating bubbling fluidized bed gasifier

developed by the European Collaborative Project: UNIQUE gasifier for Hydrogen production “UNIFHY” [52], which has been evaluated in earlier studies [8,23,53].

The first aim of this study is to validate the classic UNIFHY model [52] (considering the realized UNIFHY plant of 1 MWth), with water-gas shift (WGS) and pressure swing adsorption (PSA), through a quasi-equilibrium approach based on minimization of the Gibb's free energy.

Thereafter, the original process scheme reported previously by the authors [8,23,53] is modified by replacing PSA with a separation module consisting of palladium membranes in order to evaluate the possible variation in the overall efficiency, taking into account the optimized PSA parameters that are currently utilized in industry. The WGS process requires separation of the products to obtain hydrogen with high purity. The theory and implementation of palladium membranes for hydrogen separation have long been covered by the early work of Gryaznov [54] and in a number of reviews [55–57], demonstrating the outstanding selectivity of these membranes towards hydrogen, where up to 99.99% hydrogen purity can be achieved in the permeate stream [58,59]. Pd-based membranes have been considered for use in systems for the production of hydrogen from biomass-derived processes via gasification [60] and hydrothermal gasification [61]. Furthermore, these membranes can be applied to the separation of hydrogen from hydrocarbons [62,63], methane [64] and biogas [65] reforming, and the CO₂ capture process [66,67]. For these reasons, we investigate the advantages of replacing the PSA with this kind of membrane. The results obtained by implementing this replacement are compared with the results from the classical UNIFHY system and the related model. The thermodynamic parameters of the plant are analyzed by using the process simulator Aspen Plus. The article is organized as follows: Section **Simulation methods** describes the main components of the simulation model, Section **Results and discussion** presents and discusses the main results of the work after validation of the model, and Section **Conclusion** presents the conclusions.

Simulation model

Assumptions

The following assumptions were considered in modeling the gasification process shown in Fig. 1:

- The process is in steady-state and isothermal [68].
- Drying and pyrolysis take place instantaneously and the volatile products mainly consist of H₂, CO, CO₂, CH₄, and H₂O [25,69].
- The char is 100% carbon [70].
- All gases behave ideally

Process scheme

The process scheme under investigation is shown in Fig. 1.

Hazelnut shells were used as the biomass feedstock. This is a sustainable choice because this kind of biomass is not in competition with food production, and moreover, allows the

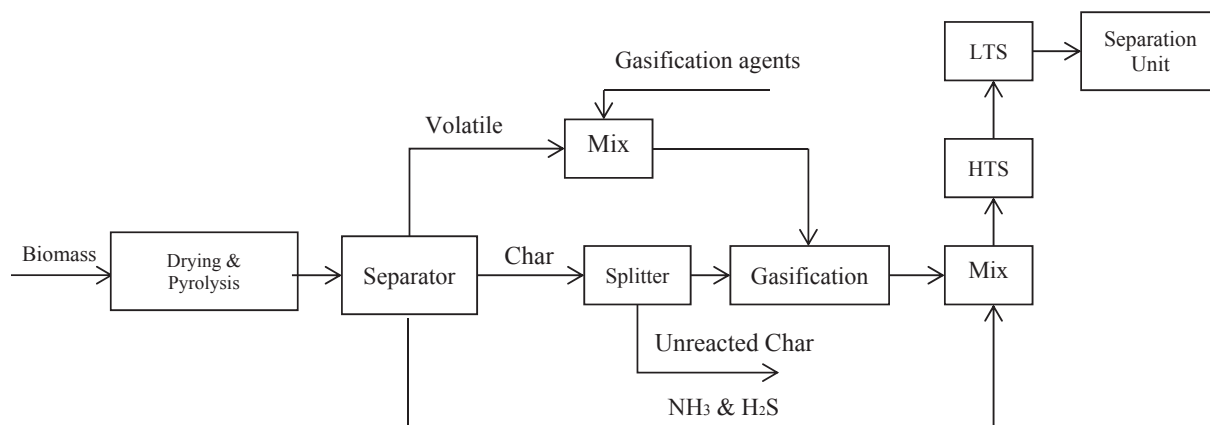


Fig. 1 – Schematic of the biomass gasification hydrogen production process.

use of waste from the agri-food industry [71]. The characteristics of hazelnut shells are presented in Table 1. The drying and pyrolysis stage simulates the first part of the gasification process and produces H_2 , CH_4 , H_2O , CO , CO_2 , and char. The separation unit block was first studied with the PSA unit and then with the palladium membrane module.

ASPEN plus flowsheet

The flowsheet developed with ASPEN Plus is shown in Fig. 2 and each unit is described in Table 2.

The BIOMASS stream, composed of hazelnut shells, with a constant flow rate set to 180 kg h^{-1} (1 MWth input size, considering HHV), enters the DECOMP block, which is a RYELD reactor, used to simulate the decomposition of the unconventional feed into its conventional components (carbon, hydrogen, oxygen, sulfur, nitrogen and ash) by specifying the yield distribution according to the biomass ultimate analysis in Table 1.

Because DECOMP generates N and S as elemental components that are well known to produce mainly NH_3 and H_2S , and the results of the experimental fractional conversion model are more similar to the experimental data than that of the restricted chemical equilibrium, the off product from

DECOMP is moved to the RSTOIC block to simulate the production of NH_3 and H_2S through the following reactions:



where the fractional conversion of H_2S is equal to 1 and that for NH_3 is equal to 0.5 [73].

The resulting stream S2 moves into the separator SEP, which divides the stream into three sub-streams: the volatile part VOLATILE, char part CHAR, and a stream composed of NH_3 and H_2S , termed H_2SNH_3 . The VOLATILE stream, after mixing with the oxidizing fluid, enters the gasifier GASIF.

The CHAR stream is split in two sub-streams: S3, which represents the unreacted char, and S4 which represents the char reacted in the gasifier.

The stream GASRAW out of the gasifier is mixed with the H_2SNH_3 stream. This is done because the contaminants do not follow a temperature approach equilibrium.

Stream S6 from the gasifier undergoes the water-gas shift reaction:



which occurs in two reactors: high temperature shift (HTS) and low temperature shift (LTS) [53]. The gas from the HTS and LTS is mainly composed of H_2 , CO_2 , residual steam, and traces of CH_4 and CO ; thus, in order to produce pure hydrogen, these gases must be separated. Therefore, the flow after the WGS is fed into the PSA system to obtain pure hydrogen.

Gasifier

The reactions considered in the gasification process are listed in Table 3.

The Boudouard reaction is not considered in this simulation as it does not achieve kinetic equilibrium and causes destabilization of the reactor performance [30].

To simulate the gasification process in Aspen Plus, we used the Gibb's reactor with a quasi-equilibrium approach, which allows more accurate description of the syngas composition than equilibrium models, as explained in the Introduction.

Table 1 – Physical and chemical properties of hazelnut shells [72].

Bulk density (kg/m^3)		Moisture content (wt%)			
319.14		12.45			
Proximate analysis (%wt wet basis)					
Ash		Volatile matter		Fixed carbon	
0.77		62.70		24.08	
Ultimate analysis (%wt, dry basis)					
C	H	N	O	Cl	S
46.76	5.76	0.22	45.83	0.76	0.67
Heating values (MJ/kg_{dry})					
HHV				LHV	
20.20				18.85	

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

ASPEN Plus name	Block ID	Description
RYIELD	DECOMP	Yield reactor – converts the non-conventional stream “BIOMASS” into its conventional components
RSTOIC	RSTOIC	Rstoic reactor – simulates the production of NH ₃ and H ₂ S
SEP	SEP	Separator – separates the biomass into three streams: volatile, char, and a stream of NH ₃ and H ₂ S
MIXER	PSA	Separator – extracts pure hydrogen with 70% efficiency
	MIX	Mixer – mixes oxidizing fluid with VOLATILE stream, which represents combustible fluid
FSPLIT	MIX2	Mixer – mixes the gas from gasifier with NH ₃ and H ₂ S
	SPLIT	Splitter – splits unreacted char (S3) from combustible char (S4)
RGIBBS	GASIF	Gibb's free energy reactor – simulates drying, pyrolysis, partial oxidation, and gasification and restricts chemical equilibrium of the specified reactions to set the syngas composition by specifying a temperature approach for individual reactions
REQUIL	HTS	Requil reactor – simulates the water gas shift reaction at high temperature
HEATER	LTS	Requil reactor – simulates the water gas shift reaction at low temperature
	HEATER	Heater – lowers the temperature between HTS and LTS
COMPR	COMPR	Compressor – raises gas pressure upstream of PSA

β is the hydrogen permeability and is calculated by applying Shu's experimental equation [84,85] and set to $4.58 \cdot 10^{-7} \frac{\text{kmol}}{\text{m h Pa}^{0.5}}$

δ is the thickness of the membrane, set to 20 μm [85].

n is the pressure exponent, and according to Sievert's law, was set to 0.5 [86,87].

P_h^n and P_l^n are the partial pressure of hydrogen on the high pressure side and the low pressure side, respectively

P_l^n is set to $7 \cdot 10^4$ Pa

The area of one membrane module was fixed to 0.1 m² and 8 modules were applied for a total membrane area of 0.8 m² [88].

Assuming a hydrogen separation efficiency of 90%, $P_h^n = 2.7 \cdot 10^5$ Pa.

As predicted by Sievert's law, by increasing the difference ($P_h^n - P_l^n$), the permeate hydrogen increased.

Chen et al. [89] demonstrated that the minimum difference ($P_h^n - P_l^n$) to ensure hydrogen transport against the membrane resistance has to be 30 kPa: in the present study, the driving force ($P_h^n - P_l^n$) = 200 kPa was imposed.

The temperature of the membrane was set to 420 °C [90,91]; this is the optimum temperature because a lower temperature could cause hydrogen embrittlement of the membrane and a higher temperature could cause thermal stress and loss of selectivity.

Table 3 – Gasification reactions.

Reaction	Reaction name	Reaction number
Heterogeneous reaction		
$\text{C} + 0.5 \text{O}_2 \rightarrow \text{CO}$	Char partial combustion	(4)
$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	Water-gas	(5)
Homogeneous reactions		
$\text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O}$	H ₂ partial combustion	(6)
$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	CO shift	(7)
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Steam-methane reforming	(8)

Results and discussion

Gas composition

The Data Fit conducted with the data reported in Table 4 allowed determination of the minimum of the objective

Table 4 – Data for Data Fit analysis.

Test	1 [74]	2 [74]	3 [74]	4 [74]	5 [75]	6 [75]	7 [76]	8 [76]	9 [76]
Operational conditions									
Biomass flow rate (kg/h)	122	140	150	170	137	177	1400	1400	1400
Air flow rate (kg/h)	0	0	0	0	0	0	87	174	348
Oxygen flow rate (kg/h)	44	46	58	61	40	51	0	0	0
Steam flow rate (kg/h)	48.8	56	75	85	55	70	0	0	0
Gasifier temperature (°C)	850	850	850	850	825	870	785	785	785
Main variable for analysis									
SB (steam to biomass ratio)	0.4	0.4	0.5	0.5	0.4	0.4	0	0	0
Gas composition and yield (mole fraction)									
CO (%dry)	0.217	0.2420	0.2545	0.267	0.30	0.31	0.14	0.1511	0.1706
H ₂ (%dry)	0.289	0.2975	0.306	0.323	0.31	0.25	0.1323	0.1547	0.1668
CO ₂ (%dry)	0.318	0.31875	0.3195	0.321	0.25	0.26	0.1337	0.1415	0.1322
CH ₄ (%dry)	0.095	0.09725	0.095	0.104	0.11	0.13	0.0182	0.0149	0.0140

Table 5 – Composition of stream GASRAW out of the gasifier and model validation.

	Simulation results	Literature data [92]	Discrepancy
H ₂ (%dry mole fraction)	31.3	44.0	28%
CO (%dry mole fraction)	20.6	28.0	26%
CO ₂ (%dry mole fraction)	14.7	18.0	18%
H ₂ O (%dry mole fraction)	19.1	16.0	19%
CH ₄ (%dry mole fraction)	9.7	10.0	3%

function, and thus the QET at which each reaction occurs. In this way, it was possible to determine the composition of the gas stream out of each unit, as reported in the Tables below.

Model validation

In Table 5, the simulation results for the gasifier outlet stream are compared with the results reported in Ref. [92], achieved with a steam biomass gasifier.

In Ref. [92] the biomass considered was almond shell, and given the almost identical features of hazelnut shells, the comparison can be considered valid. The characteristics of the almond shells are reported in Table 8. The data in this table show that based on the almost identical composition from ultimate analysis (regarding the main elemental components), the comparison is valid.

Table 6 – Composition of stream S8 out of the HTS reactor (at 400 °C).

H ₂ (%dry mole fraction)	41.1
CO (%dry mole fraction)	10.6
CO ₂ (%dry mole fraction)	24.0
H ₂ O (%dry mole fraction)	10.0
CH ₄ (%dry mole fraction)	9.6

Table 7 – Composition of stream S11 out of the LTS reactor (at 200 °C).

H ₂ (%dry mole fraction)	47.5
CO (%dry mole fraction)	4.2
CO ₂ (%dry mole fraction)	30.0
H ₂ O (%dry mole fraction)	3.6
CH ₄ (%dry mole fraction)	9.6

Table 8 – Physical and chemical properties of almond shells [72].

Bulk density (kg/m ³)		Moisture content (wt%)			
450		12			
Proximate analysis (%wt, dry basis)					
Ash		Volatile matter		Fixed carbon	
components1.2		80.6		18.2	
Ultimate analysis (%wt, dry basis)					
C	H	N	O	Cl	S
47.9	6.3	0.32	44.27	0.012	0.015

As shown in Table 5, the model provided more conservative values, maybe this is due to the fitting of our gasifier model with experimental air and low steam to biomass ratio gasification data.

However, the under or over-prediction of CH₄ is a common problem in this kind of modeling as the tar is not considered in the equilibrium models [93].

Effect of gasification temperature

The model was used to perform sensitivity analysis for the gasifier temperature in the range of 700–1000 °C. Fig. 3 shows the variation of the syngas composition as a function of the temperature.

The H₂ and CO concentration increased remarkably as the temperature increased. The increase in the H₂ concentration is due to endothermic reactions (5) and (8), while reaction (5) at higher temperature is responsible for the increase in CO. The endothermic reaction (8) can generate CO₂, but reaction (5) is favored and increases the CO and decreases CO₂. The endothermic reaction (8) results in a decrease in CH₄.

Effect of increased steam

Like the temperature, the steam rate has a marked influence on the composition of the product gas. Fig. 4 presents the results of the sensitivity analysis with variation of the steam flow while keeping the biomass flow and the oxygen flow constant.

The molar fraction of CO decreases with increasing steam. The molar fraction of CO₂ increases with an increase in the steam rate, and after a maximum, shows a decrease with increasing steam. Initially, the amount of H₂ increases due to the interaction between CO and H₂O, but after a maximum, decreases. The increase in the amount of H₂ with increasing steam rate indicates that the gas-shift reaction has a strong effect on steam gasification [94].

Analysis of separation process

Table 9 shows the operating and process conditions of the PSA unit and the palladium membrane module. The classic configuration of the UNIfHY scheme ensures a hydrogen yield of 3.76 kmol h⁻¹, i.e. recovery ratio (produced hydrogen/input biomass) equal to $\frac{H_2}{B} = 38\%$. After replacement with the palladium membrane, the hydrogen yield reached 4.83 kmol h⁻¹ and the recovery ratio was equal to $\frac{H_2}{B} = 49\%$.

This result is due to the greater hydrogen permeability and high selectivity of the palladium membrane. For industrial applications, the hydrogen purification level is based on both economic and technical considerations as the amount of hydrogen recovered increases the economic impact on large-scale applications. For this reason, palladium membranes are more suitable for use in small to medium applications, while PSA is best suited to large-scale applications.

Moreover, with membranes, it is possible to achieve a higher level of recovery, but it should be noted that greater recovery means a larger membrane area and therefore higher investment and operating costs. However, the high costs of

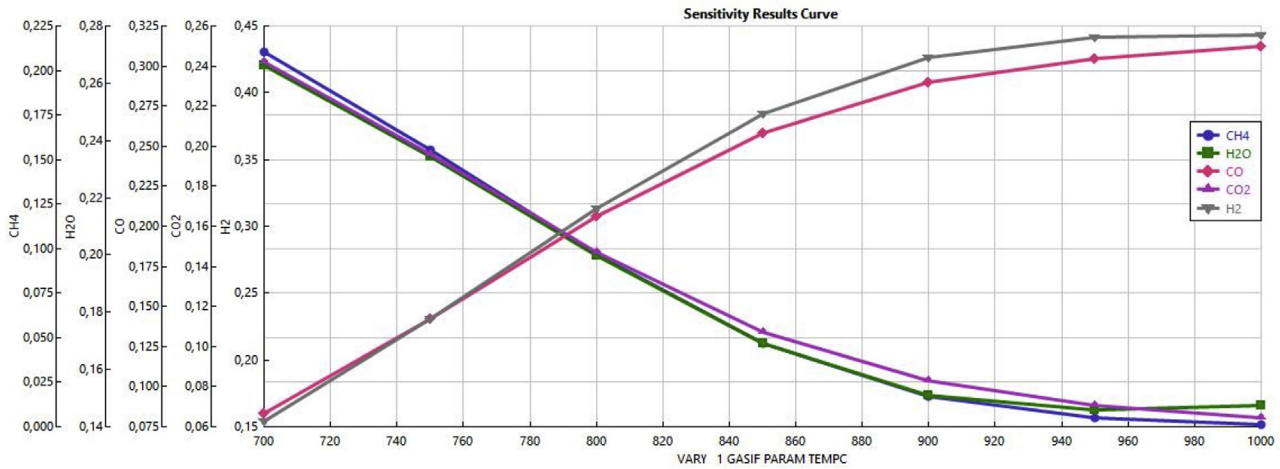


Fig. 3 – Effect of gasification temperature on syngas composition out of gasifier.

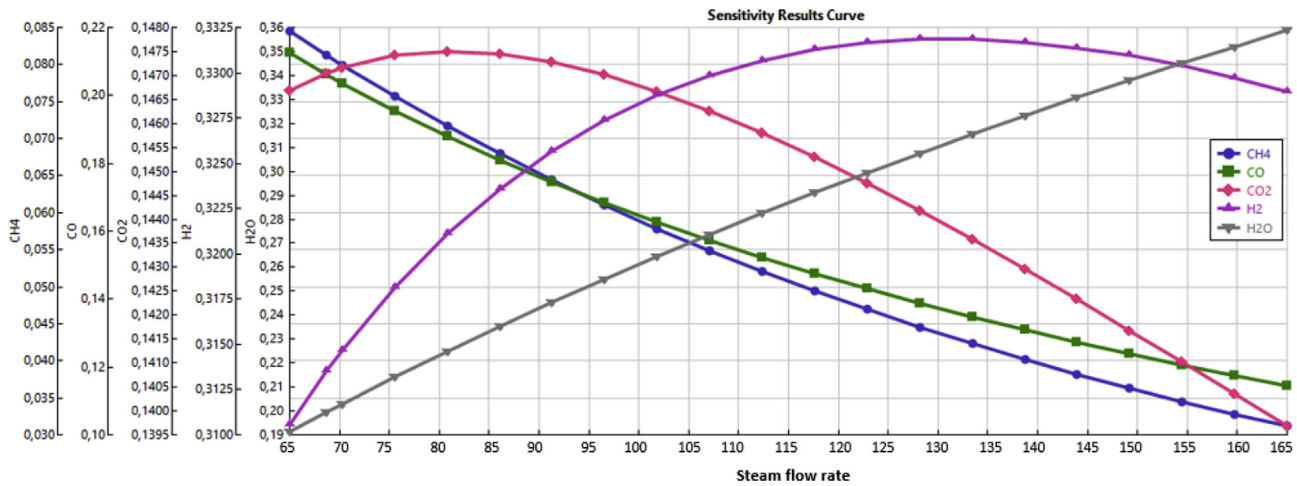


Fig. 4 – Effect of steam variation on syngas composition out of gasifier.

palladium membranes can be offset by combining palladium or replacing it with less pure metals [95,96].

If the costs and reliability of membrane processes are improved in the future, an effective replacement of the PSA unit can be achieved. Considering that the energy consumption of PSA is much higher than that of membranes, the replacement (if economically viable from the point of view of installation and maintenance costs) would lead to lower energy consumption for the plant.

Given the current cost of membrane installation and the good results provided by the simulation for the use of the

palladium membrane, a possible solution could be the combined use of PSA and palladium membranes, with a lower number of modules and therefore lower costs, in order to increase product recovery during hydrogen production.

Conclusion

Simulation and validation of a bubbling fluidized bed gasifier with WGS reactors and a PSA unit were performed using ASPEN Plus. The simulation was carried out with the quasi-equilibrium model by the creation of a Data Fit from the experimental results. To date, no other study has been conducted on the gasification of hazelnut shells using the quasi-equilibrium approach, and the results out of the gasifier are in good agreement with the experimental data, confirming the validity of the quasi-equilibrium model. The final and interesting outcomes of the present study are: the hydrogen recovery ratio of the process, expressed as the ratio of hydrogen produced to the input biomass, was 38%; after replacement of the PSA unit with the palladium membrane, the hydrogen recovery of the process increased to 49%; finally a comparative

Table 9 – PSA vs. Palladium membrane.

	PSA	Palladium membrane
Inlet temperature [°C]	610	420
Pressure [bar]	7 (inlet)	2.7 (low-pressure side) 9 (high-pressure side)
H ₂ separation efficiency [%]	70	90
Hydrogen yield [kmol/h]	3.76	4.83
Hydrogen recovery ratio [%]	38	49

increase of 28.9% was achieved relative to that with the classic PSA configuration. However, the economic impact of the membrane should be taken into account. At present, PSA is more economically viable. Obviously, the model is valid within the range of the data used for fitting, i.e., SB from 0.4 to 0.5 and temperature from 785 to 870 °C. Future studies will focus on extension of the validation range, improvement of the simulation results, increasing the dataset for fitting, and consideration of the bed material.

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