



Energy and economic analysis of alternatives for the valorization of hydrogen rich stream produced in the aqueous phase reforming of pyrolysis bio-oil aqueous fraction

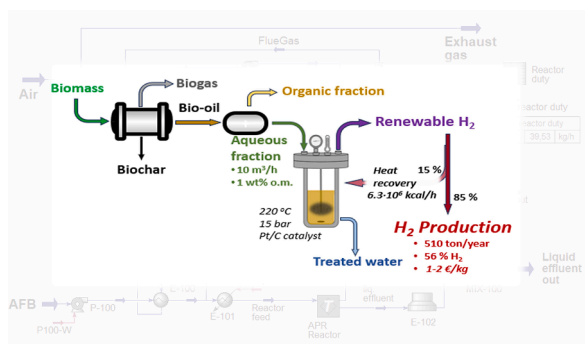
Francisco Heras^{*}, Jéssica Justicia, José A. Baeza, Miguel A. Gilarranz, Víctor R. Ferro

Department of Chemical Engineering, Universidad Autónoma de Madrid. Ciudad Universitaria de Cantoblanco, 28049 Madrid Spain

HIGHLIGHTS

- Specific thermodynamic model for aqueous fraction of bio-oil has been developed.
- Aqueous phase reforming experimental results were reproduced by process simulation.
- Different alternatives for H₂-rich product valorization were analyzed and compared.
- Unit cost optimal if H₂ is used for both energy self-covering and commercialization.
- H₂ can be produced at unit cost in competition with green one.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Aqueous-phase reforming
Bio-oil aqueous fraction
Hydrogen
Techno-economic analysis
Process alternatives

ABSTRACT

Aqueous phase reforming has been explored for renewable H₂ production from waste biomass. Promising results have been reported for pyrolysis bio-oil aqueous fractions (AFB), but economical assessments are needed to determine process feasibility, which requires both energy consumption minimization and optimal H₂ valorization. This work compares different alternatives using process simulation and economic evaluation computational tools. Experimental results and a specific thermodynamic model are used to set mass balances. An adequate heat integration allows to reduce the process energy demand, covering the 100 % of the reactor duty. Optimal H₂ unit cost is achieved if part of the produced H₂ is valorized for energy self-covering and the rest is commercialized. Renewable H₂ net production of c.a. 3.3 kgH₂/m³ of treated AFB at a preliminary 1–2 €/kg unit cost is estimated, which can be considered as competitive with green H₂, even though a case of diluted AFB is considered.

1. Introduction

Aqueous phase reforming (APR) is a catalytic process that involves the conversion of oxygenated hydrocarbons into H₂ and other valuable

products. APR shows some advantages over conventional steam reforming regarding H₂ separation and use, since water–gas shift (WGS) reaction is completely displaced whereby no CO is present in the gas product stream. APR of biomass derived hydrocarbons has gained

^{*} Corresponding author.

E-mail address: fran.heras@uam.es (F. Heras).

<https://doi.org/10.1016/j.biortech.2024.130572>

Received 10 January 2024; Received in revised form 27 February 2024; Accepted 9 March 2024

Available online 14 March 2024

0960-8524/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

attention due to its potential for sustainable and clean energy generation [Tang et al., 2023; Kim et al., 2023].

APR takes place at relatively moderate operating conditions (200–250 °C, 15–50 bar) in the presence of catalyst with activity in C-C and C-H bonds cleavage and in the WGS reaction. The most studied active phase has been Pt, and in a lesser extent Ni (mainly studied due its lower cost in comparison to Pt), because of its high activity and selectivity to H₂ [Pipitone et al., 2022]. In addition to this, the catalyst supports play an important role in the performance of catalysts for APR. Different inorganic porous materials have been used, such as alumina, zirconia and spinels, due to their high surface area and hydrothermal stability [Harju et al., 2020; Li et al., 2019]. Attention has also been paid to carbon materials as supports because of their proved chemical and thermal stability in APR hydrothermal conditions. Good results have also been reported for advanced carbon materials such as non-doped and N-doped graphene, graphitic carbon and carbon nanofibers, carbon nanotubes and graphene oxide [García-Baldoví et al., 2022; Pazos Urrea et al., 2023]. However, the most interesting results have been found for activated carbon and carbon blacks due to good balance between cost, tunable surface chemistry and texture properties [Paris et al., 2022; Justicia et al., 2022].

The APR process was initially extensively studied using as feedstocks oxygenated compounds, such as ethanol, and particularly species with C:O ratios ca. 1:1 as methanol, glucose, sugar alcohols (sorbitol, xylitol, etc.) and glycerol [Wei et al., 2015; Kirilin et al., 2012; Vikla et al., 2021]. Recent works have paid attention to the use of wastewater bearing biomass-derived pollutants as feedstock [Valenzuela et al., 2006; Oliveira et al., 2019; Chanthakett et al., 2021; Zoppi et al., 2022], and even solid biomass waste by coupling hydrothermal liquefaction/carbonization and APR [Oliveira et al., 2022; Fraia et al., 2022]. Based on the current and future significance of sustainable fuels and energy production, special interest has been given to biorefinery waste streams, such as the aqueous fraction of bio-oil (AFB). AFB is composed mainly of water (70–90 wt%) and a wide variety of organic compounds, being the most frequently found levoglucosan, hydroxyacetone (acetol), acids, furfural, methanol and others [Hernando et al., 2016; Valdez et al., 2023]. Some of these compounds have been studied individually as APR feedstocks, showing low H₂ production in the case of acetic acid and furfural [Arandia et al., 2019; Pipitone et al., 2020; Justicia et al., 2022], and a much better processability for levoglucosan and acetol [Lozano et al., 2021; Justicia et al., 2022] with H₂ production values up to 15 and 50 mmol/gTOC₀, respectively. A variety of results have been reported for APR of mixtures of AFB model compounds. Thus, lower H₂ production has been reported for mixtures of butanol, acetol and acetic acid [Lozano et al., 2021] than for the individual compounds. However, a high selectivity to H₂ has been found in the APR of acetic and lactic acids [Pipitone et al., 2020], and acetol, acetic acid, catechol and ethanol [Arandia et al., 2019] mixtures, although with lower feedstock conversion than for individual compounds. Promising results have been obtained in a previous work on the APR of complex mixtures simulating AFB [Justicia et al., 2023]. A water solution of levoglucosan, acetol, furfural, methanol and acetic and formic acids, with 1 wt% total concentration, was reformed at 220 °C using a 3 wt% Pt/CB catalyst, reaching values up to 80 % for Total Organic Carbon (TOC) conversion and a H₂ production of 40 mmol/gTOC₀.

To be implemented, APR needs to find a niche in a market where methane steam reforming (MSR) is the dominating technology, with low production costs (c.a. 0.75 €/kg) (Tian et al., 2024)], although reaches markedly higher values (4–8 €/kg in 2022) when including carbon capture (SGH2 Energy). With this framework extensive work is needed to evaluate the feasibility of APR process, through basic economic balance between cost and benefits, considering capital cost (process equipment) and energy cost as the most significant elements. In this analysis computer aided process simulation and modelling have been revealed as very useful tools, however, few studies with this approach have been reported so far. Sladkovskiy et al. (2018) concluded that the

use of a valuable raw material as sorbitol as APR feedstock has an unaffordable impact on the economic balance. Likewise, since several economic parameters indicated that APR would be a more interesting alternative to produce H₂ from glycerol in comparison to steam reforming [Khodabandehloo et al., 2020], the critical role of the feedstock in variable operating costs could be avoided using glycerol-containing waste/secondary streams from bio-diesel production process [Martin and Grossman, 2014].

The feedstock cost is a drawback for APR process that can be overcome by using waste streams (e.g. AFB) as process feedstocks. In this approach, the energy cost becomes one of the most important factors for the feasibility of the process, which can be managed through an adequate process heat integration strategy [Khodabandehloo et al., 2020]. In a previous work [Heras et al., 2022], heat balances and energy sustainability of APR process in different operating scenarios using sorbitol (1–2 wt% in water) as feedstock were calculated by means of Aspen ONE software (Aspen HYSYS V.14® and Aspen Plus V14®). It was proved that energy self-covering by energy valorization of part of the H₂-rich gas stream can be achieved.

Finally, it is necessary to point out that all the techno-economic studies reported about APR process were carried out using model compounds as feedstock, such as sorbitol and glycerol. Since the potential feasibility of APR necessarily depends on the use of waste/renewable streams with usually very complex compositions, an effort in thermodynamic modelling of feedstock streams is required prior to the development of techno-economic evaluations.

Based on previous developments [Heras et al., 2022], the APR of AFB has been studied as a realistic and more complex case. Different alternatives for the valorization of APR gas stream, based on potential commercialization or energy valorization, were evaluated to determine the more interesting process orientation from an economical perspective. A specific thermodynamic model for properties and equilibria estimation is developed to simulate APR of AFB, since inadequate estimations are obtained by usual models.

2. Materials & methods

The modeling of the APR of AFB was developed based on the experimental results previously obtained [Justicia et al., 2023]. The AFB was simulated by a water solution with 1 wt% total organic matter content (c.a. 4,500 mgTOC/L) and the composition showed in Table 1.

The best experimental results (Table 2) were obtained operating at 220 °C, 15 bar and 4 h using a 3 wt% Pt catalyst supported on carbon black ENSACO250 [Justicia et al., 2023]. Substrate conversion was evaluated by organic matter removal from solution in terms of TOC conversion (X_{TOC}), carbon-to-gas conversion (CC_{gas}), i.e., carbon in gas products with respect to total carbon fed to the reactor, and gas product stream composition.

APR is a complex process which involves several chemical reactions. Main reactions include reforming, which takes place through C-C bonds cleavage to generate H₂ and CO, WGS, and reactions resulting in CH₄ formation as major process by-product. Other reactions, such as Fisher-Tropsch, dehydration and hydrogenation, occur to a much less extent and their contribution to reaction enthalpy is significantly lower than that of main reactions [Smith et al., 2010; Sladkovskiy et al., 2018], whereby their significance in the material and energy balance is much lower, and therefore they have not been taken into account in the process modelling. Table 3 compiles the reactions considered.

Table 1
Composition of synthetic AFB used as APR feedstock (wt%).

Levoglucosan	Acetic acid	Hydroxyacetone	Furfural	Formic acid	Methanol
0.50	0.20	0.20	0.04	0.04	0.02

Table 2

Experimental results of TOC conversion, CCgas and gas product stream composition (mol%) in the APR of synthetic AFB.

Feed conversion (%)		Gas product stream composition (mol%)					
X _{TOC}	CC _{gas}	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₃ H ₈
77	52	49	37	0	9	2	3

Table 3

Reactions considered for APR modelling.

Reforming	Levogluconan	$C_6H_{10}O_5 + H_2O \rightarrow 6H_2 + 6CO$
	Acetic acid	$C_2H_4O_2 + 2H_2O \rightarrow 4H_2 + 2CO$
	Hydroxyacetone	$C_3H_6O_2 + H_2O \rightarrow 4H_2 + 3CO$
	Furfural	$C_5H_4O_2 + 3H_2O \rightarrow 5H_2 + 5CO$
	Formic acid	$CH_2O_2 \rightarrow H_2 + CO_2$
	Methanol	$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$
Water Gas Shift		$CO + H_2O \rightleftharpoons CO_2 + H_2$
Methanation	Carbon dioxide	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$
	Carbon monoxide	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$

2.1. Thermodynamic properties and equilibria estimation

The process simulation was carried out by means of Aspen HYSYS V.14® software, for which the selection of the components involved in the process (Component List) and the definition of an adequate model (Fluid Package) is needed as a preliminary step. In this software a large database of components and a wide variety of thermodynamic models of different types including equations of state, activity coefficient, electrolyte, among others, is implemented. However, in the current work, a model mixture composed by six oxygenated hydrocarbons, namely acetol, levoglucosan, furfural, acetic and formic acids and methanol, water and five gases (CO₂, H₂, CH₄, N₂ and O₂) was considered. These components are strongly different in their properties and exhibit different interaction patterns in aqueous solutions and, correspondingly, equilibrium phase behaviors. Furthermore, some of the selected components, such as formic and acetic acids and CO₂, can be dissociated in water yielding ionic species, and water itself can participate in dissociation equilibria. On the other hand, it can be accepted that acetol, levoglucosan, furfural and methanol remain undissociated in dilute water solutions. Finally, the gases produced, including the undissociated CO₂, take part in gas–liquid equilibria. This entails severe difficulty for selecting the thermodynamic model to predict the fluid properties, even when the water excess in the liquid phase is relevant.

Successfully description of all these thermodynamic features is essential to reproduce different aspects of process simulation. In particular, the correct description of vapor phase composition has a relevant importance for mass and energy balances in the reactor and the operations related to the energy integration in the overall process. Another relevant aspect to be properly described is the aqueous phase in

the APR reaction medium, which has a moderately low pH value (c.a. 4.0) according to experimental data. It is important to underline that the chemical reaction and the phase equilibria are strongly coupled in the reactor, which represents a challenge for the correctness of the mass and heat balances. Thus, the energy balance at the reactor depends not only on the reaction heats but also, in an important extension, on the water vaporization for the selected operating conditions. This challenge was tackled in current work using the simplified model of APR reactor (see [Supplementary Material, S1](#)).

2.2. Proposal and description of the APR process

[Fig. 1](#) shows the block diagram of the APR process with indication of heat consumption and potential generation/recovery in the different units. The feedstock (AFB) is initially conditioned and fed to the reactor at operating conditions (220 °C and 15 bar). After heat recovery, the liquid reaction effluent can be considered as a treated wastewater that can be sent to discharge or managed by conventional wastewater treatment if needed. On the other hand, the H₂-rich gas constitutes, after water removal, the main process product stream. For heat and mass balances, and economic estimations, a basis of 10 m³AFB/h was used.

2.3. Alternatives for the valorization of APR gas product stream

To determine the optimal strategy towards APR process feasibility through H₂-rich stream benefit, three different alternatives, i.e., technical solutions, were proposed: commercialization, energy valorization and a combination of both. The commercialization of the produced H₂ has the advantage of simplicity, since process equipment for energy valorization is not needed and the related investment, maintenance and utilities costs are lower. This alternative also benefits from the expanding renewable H₂ market, but the need for an external energy source to compensate process consumption and for H₂ purification as demanded by some consumers can be considered as the main handicaps. On the other hand, the energy valorization of the APR gas product can provide with self-covering of the process heat demand but has some drawbacks, including the related costs commented above and integration with other process to export the excess of energy generated. The alternative combining commercialization and energy valorization is proposed to assess the balance between the advantages and disadvantages of both options and to achieve the cost-benefit optimum ratio. All cases are based in heat recovery optimization with the aim to minimize the net energy consumption in the process. The Aspen Energy Analyzer (AEA) tool was used to determine the potential energy savings as a measurement of the process energy integration. The Available Energy Savings obtained by means of the tool is an indicator of the maximum possible savings opportunities as dictated by thermodynamics as energy flow and percentage of the actual current utility usage (kcal/h and %, respectively), and allows to estimate the potential reduction in utilities usage [[Aspen Tech, 2022](#)]. In all cases, three main utilities have been used: electricity, cooling water (cw@1bar, 30–40 °C) and high-pressure steam (hps@40 bar, 250 °C). The conditions of cw and hps were properly

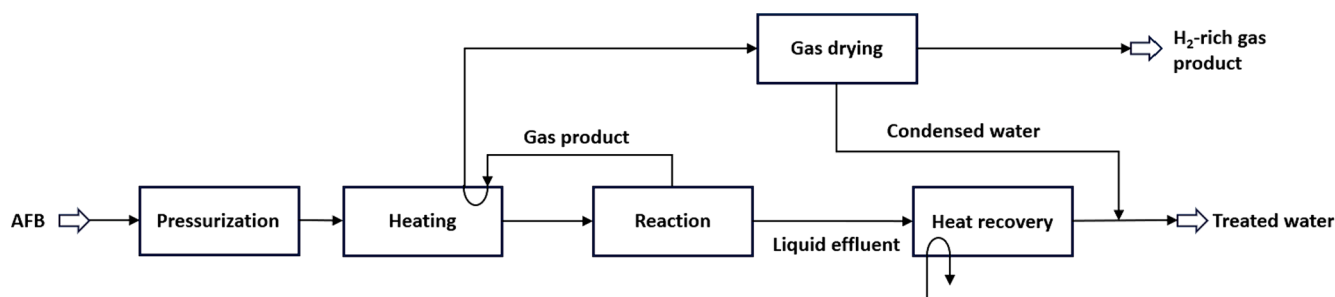


Fig. 1. Conceptual APR process block diagram.

modified in the Utility Manager of the simulation software to achieve correct mass/energy balances and economic estimations.

Case 1. Gas product commercialization

Since the gas product of APR is composed of H_2 and CO_2 , with low concentration of CH_4 , C_2H_6 and C_3H_8 , it can be assimilated to a crude H_2 stream obtained after water gas shift units in the H_2 production plants from syngas. Therefore, potential users can be identified within syngas consumers, such as methanol plants, ammonia and derivatives production, H_2 demanding refining units (HDS, hydrocrackers, hydrofinishers, etc.), with the added value that APR gas could be considered as renewable fuel-gas, whose market is expanding. It must be taken into account that this is a conservative consideration because syngas sell-price is conditioned by the cost of high and low temperature WGS as part of the purification process for H_2 production. Any case, the impact of H_2 separation is considered later, for final unit production cost estimation.

Case 1 corresponds to the process described in Fig. 1 and was simulated by Aspen HYSYS V.14® according to the process flow diagram (PFD) showed in Fig. 2 (simulation diagram is included as [Supplementary Material, S1](#)). *Heater/Cooler* and *Pump* simulation models were used for heat exchanges and feed stream pressurization, respectively. The APR reactor was simulated by a sequence of three Aspen HYSYS reactor models to each of them a different *Reaction Set* was associated, including the corresponding reactions of those listed in Table 3. All the reforming reactions were included in a first *Conversion Reactor* model, followed by an *Equilibrium Reactor* for the WGS reaction and another *Conversion Reactor* to which a *Reaction Set* containing methanation reactions was associated. The conversion values input for each *Conversion Reaction* considered were properly adjusted through stoichiometric calculations to achieve the same gas product composition as in the experiments taken as a reference (Table 2). The APR gas stream heat content is recovered for reactor feed stream preheating up to 210 °C (E-100), keeping a minimum approach of 10 °C in this exchanger. After preheating, the reactor feed needs to be conditioned up to reactor operating temperature (E-101) using high pressure steam as utility to assure the isothermal operation regime at the reactor; this second heating step could be avoided at the cost of increasing the reactor duty. Finally, the APR gas

stream temperature does not allow further heat recovery in the process, therefore it is dried by water condensation and sent to commercialization. On the other hand, the reaction liquid effluent is air-cooled and mixed with the water condensed from gas stream and sent out of process battery limit to proper final treatment if required.

Case 2. Energy valorization

In this alternative, the gas stream produced in APR is used as fuel-gas for self-covering of the process heat demand. Previous results [Heras et al., 2022] suggest a potential heat excess in the case of energy valorization of whole stream, which could be recovered elsewhere in the plant where the APR is installed or exported to nearby plants. This solution is commonly adopted in some chemical processes to improve their economic performance, as in the case of methanol production by liquid-phase process.

Fig. 3 shows the PFD for Case 2. In addition to the process previously calculated for Case 1, the dry APR gas stream is used as fuel-gas in a fire-tube boiler for energy valorization by high pressure steam production to supply the energy demand in the reactor. This steam boiler is simulated by means of a *Fired Heater* model operating with a 10 % air excess and 75 % of efficiency, which are the usual values found in heuristics literature for these parameters [Ulrich and Vasudevan, 2004]. The boiler feed water (bfw) stream for hps generation is produced from a water stream which is pressurized to 40 bar. The flue gas from boiler is used to preheat the combustion air up to 140 °C and finally vented to atmosphere. Simulation diagram for this alternative is given as [supplementary material \(Fig. S3\)](#).

Case 3. Combined alternative.

In this case combination of the two previous ones was proposed, whereby only the fraction of APR gas strictly necessary for the process to be energetically self-sustainable is combusted in the furnace, while the rest is sold as crude H_2 . Therefore, the PFD (Fig. 4) results also as a combination of the two previously presented. The split ratio in TEE-100 was adjusted in order to use the minimum dry gas flowrate to cover the heat demand according to the proposed PFD (see simulation diagram, Fig. S4).

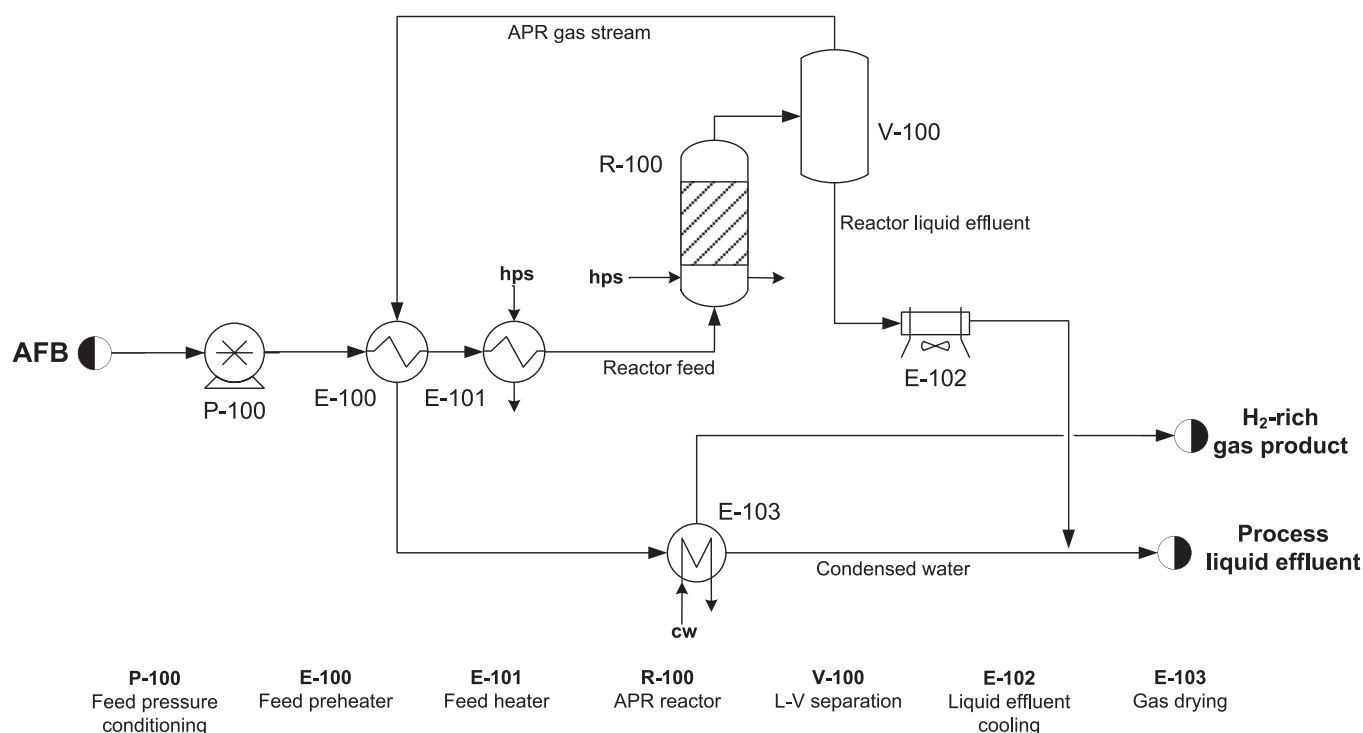


Fig. 2. Process Flow Diagram for gas product commercialization alternative (Case 1).

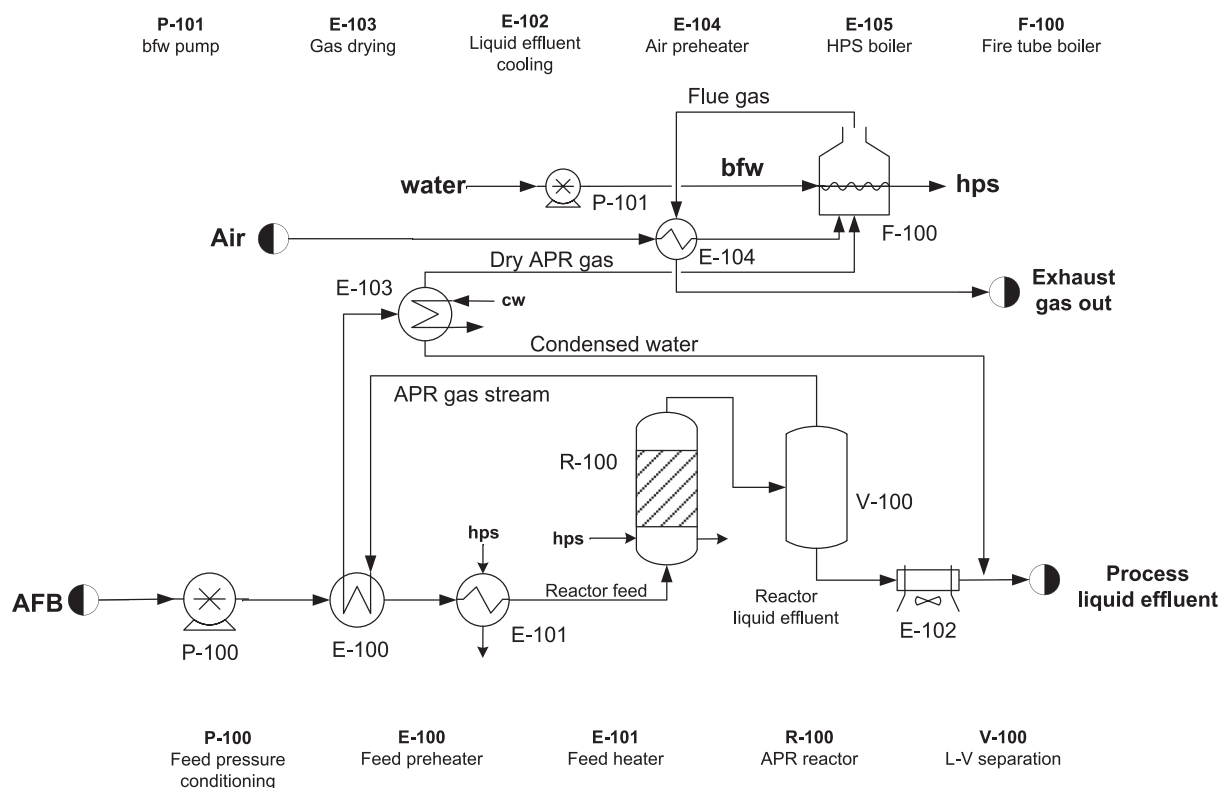


Fig. 3. Process Flow Diagram for gas product energy valorization alternative (Case 2).

2.4. Costs-based alternative evaluation

The evaluation and selection of the proposed alternatives has been carried out by means of the Aspen Process Economic Analysis (APEA) tool integrated in Aspen HYSYS V.14® through the interface Aspen Economics (AE), including capital costs (purchase and installed equipment costs, CAPEX) and main utilities costs (OPEX). Although this is a very preliminary estimate, the results are valid at a comparative level, thus allowing us to determine the most promising alternative in the search for process feasibility.

Economic Analysis with Aspen Technology tools requires, firstly, the selection of the type of physical equipment (process apparatus) that corresponds to each simulation model (*Mapping*). For each available equipment option, a model Piping and Instrumentation Diagram (P&ID) and a set of correlations included in the APEA data base allow for a basic sizing of process apparatus (*Sizing*) based on the material and heat balances data obtained by the simulation. In addition to this, the APEA data bases include utilities and other operating costs, compiled in an estimation *Scenario*. After *Mapping* and *Sizing* stages, the different process costs can be finally estimated by APEA (*Evaluate*) using different correlations as a function of the weight and other equipment design specification. Table 4 shows the used *Mapping*. A continuous full-scale APR process should be carried out using a multi-tubular fixed-bed plug flow reactor (PFR), the most adequate alternative when isothermal regime is required for reactor operation. This reactor alternative is not included among the Mapping options in APEA since it is usually cost-estimated as a fixed-tubes & shell heat exchanger due to the similar geometry and the availability of well-defined correlations for exchangers cost estimation. Although the APR reaction was simulated using three consecutive reactor models, only one reactor would be necessary in a real process, therefore, for cost estimation purposes only the first reactor simulation model was considered and mapped. Other alternatives for process equipment mapping were considered and tested but not significant differences on cost estimation were obtained.

In addition, cooling water (cw@1bar,30–40 °C) and high-pressure steam (hps@40 bar) were selected as cooling and heating process utilities, for which APEA estimates c.a. 0.02 and 4 €/ton as unit costs, respectively.

On the other hand, although the catalyst initial cost is commonly included as part of CAPEX, it was not considered in current study due to the price variability and the neutral impact on a comparative economic evaluation since the cost would be similar in the three proposals.

Finally, to allow an adequate evaluation of operating and investment costs, CAPEX were temporized considering an amortization factor of 10 %; therefore, the annual cost of tied-up capital is 0.1·CAPEX.

3. Results

3.1. Thermodynamic properties and equilibria estimation

Although Aspen HYSYS V.14® software was used for process simulation, because of some limitations found in properties estimation using its own data bases, the thermodynamic model used in this work was previously developed using Aspen Plus V14® and then exported to Aspen HYSYS V.14®.

3.1.1. Preliminary evaluation of thermodynamic properties estimation

To obtain a general overview of the problem to be solved, the model shown in Fig. S1 was calculated in a first stage using different thermodynamic models and combinations of them available in Aspen Plus (Ideal, RK, PRSK, NRTL, e-NRTL and UNIQUAC). All the components involved in the process except levoglucosan are accessible in the Aspen Properties databases and, correspondingly, taken from them. When possible or required, CO₂, H₂, CH₄, N₂ and O₂ were declared as Henry components in the Properties Environment of Aspen Plus, thus making possible the use of the Henry law for describing the corresponding liquid–gas equilibrium. Moreover, in this preliminary calculation, all the required parameters of the thermodynamic equations were taken from

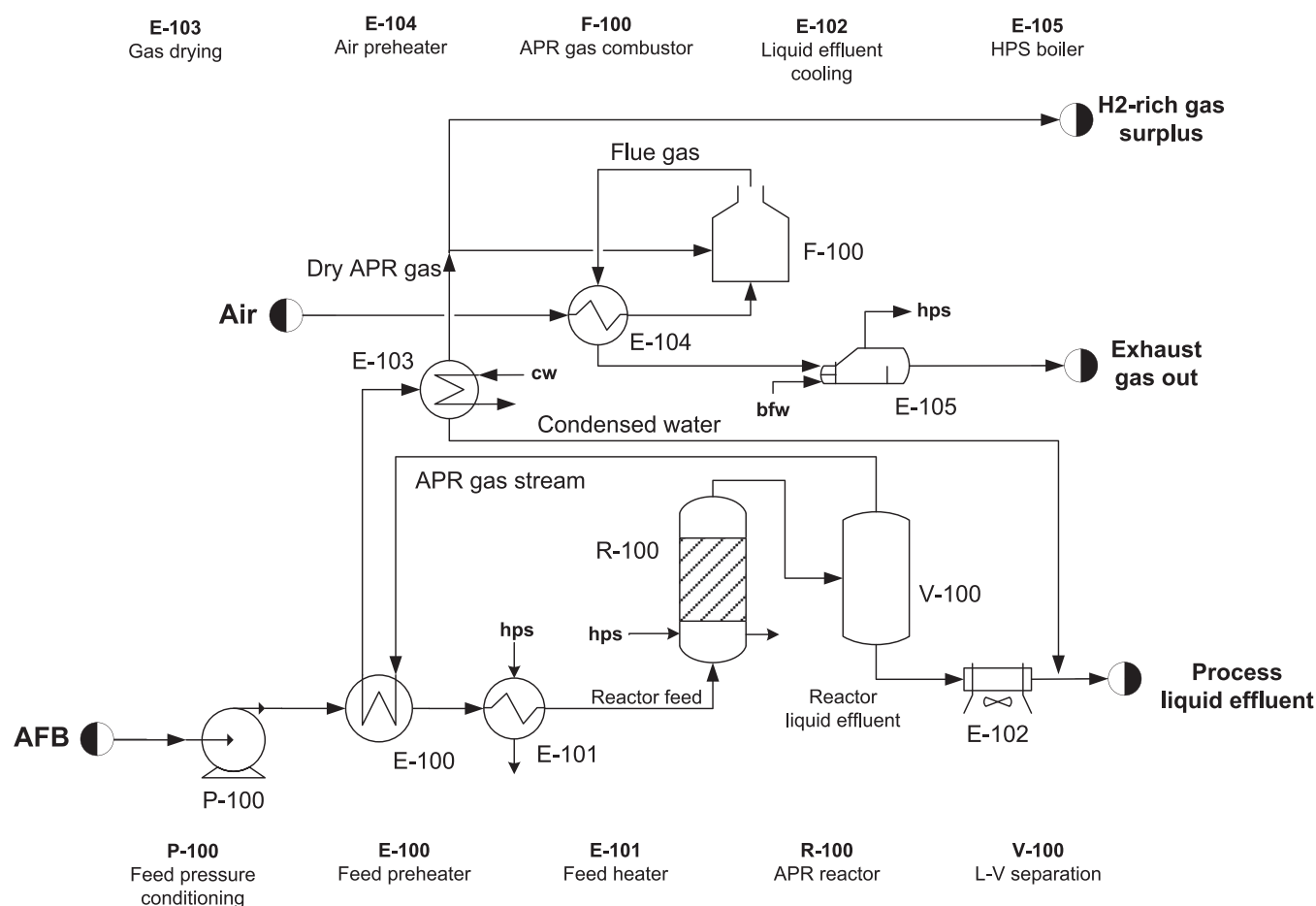


Fig. 4. Process Flow Diagram for gas product combined energy valorization and commercialization alternative (Case 3).

Table 4
Selected Mapping for alternative cost estimation.

Unit operation	Equipment Type in Mapping
Heat exchangers	TEMA shell & tube exchanger
Air cooler	Air cooler, free-standing or rack-mounted
Pumps	Positive displacement - Diaphragm
APR reactor	Fixed tube sheet shell & tube exchanger
Condenser	Fixed tube sheet shell & tube exchanger
Fire-tube steam boiler	Packaged boiler unit

the Aspen Properties databases or estimated implicitly by the program using the corresponding relationships integrated in the properties system (based on group contribution models). This way, no missing parameters were found when the executing program of the Aspen Plus performed the analysis of the input specifications and the initial flow-sheet analysis, which ensures a minimum of confidence on the results. As indicated above, the only exception in this regard was the NRTL and UNIQUAC binary interaction parameters for the pair levoglucosan-water because the software was not able to recognize the component structure throughout the UNIFAC groups available in Aspen Properties. This was ignored in the initial calculations, but preserving the total organic concentration of 1 %wt.

As expected, the reactor duty correlates linearly with the flow of water transferred from the liquid to the vapor phase when the chemical and phase equilibria were satisfied simultaneously. However, it is relevant that, as can be seen in Fig. 5, the thermodynamic models considered gave rather different results. The variation coefficient values calculated for the overall set of estimations using different models were 17.7 % for the amount of water vaporized in the reactor, 29.8 % for the reactor duty

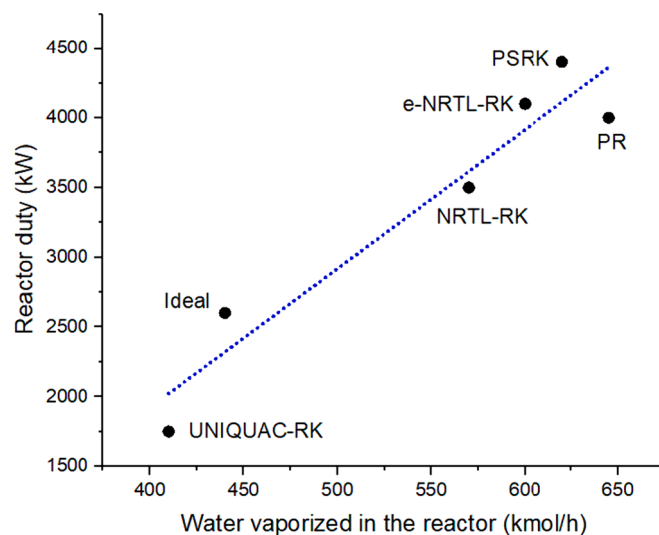


Fig. 5. Mass and energy balances at the APR reactor using different thermodynamic models in Aspen Plus V14®.

and 21.5, 8.3 and 0.6 % for CO₂, CH₄ and H₂ flows transferred from the liquid to the vapor phase under the equilibrium conditions, respectively. These results confirm the need for ad-hoc thermodynamic model optimization for this system to obtain reliable results. On the other hand, the e-NRTL model predicted a pH value of 4.4 for the liquid phase, being the unique model capable of predicting the acidic character of the APR

liquid phase in correspondence with the experimental determination.

3.1.2. Specific thermodynamic model development

Taking in consideration all the previously mentioned factors and results, the electrolyte-NRTL model, as implemented in Aspen Properties [Chen and Evans, 1986], was selected for predicting the thermodynamic properties of the mixture, including the phase equilibria. e-NRTL model consists of a generalized equation for describing the thermodynamic of mixtures containing both ionic and molecular species where the activity coefficient (γ) for any component (i) in the aqueous phase is calculated by the contribution of two types of interactions (Eq. (1)).

$$\ln(\gamma_i) = \ln(\gamma_i^{NRTL}) + \ln(\gamma_i^{DHP}) \quad (1)$$

The so-called short-range interactions are those arising among molecular species (intermolecular interactions) and are described by the classical NRTL model, $\ln(\gamma_i^{NRTL})$. Meanwhile, the long-range interactions, involving ionic species, are evaluated by the Debey-Huckel-Pitzer equation, $\ln(\gamma_i^{DHP})$. Significantly, the long-range term in Eq. (1) for e-NRTL model are negligible when non-dissociation occurs, and, consequently, the e-NRTL equation is reduced to the classical NRTL formulation. This fact ensures the flexibility required for the thermodynamic calculations in the current work.

For improving the description of the liquid–gas equilibria the e-NRTL model was coupled, additionally, to the Henry law in the formulation adopted by the Aspen Properties. To support this type of calculations, the components CO₂, CH₄, H₂, N₂ and O₂ were selected as Henry components in the property's environment of Aspen Plus as already mentioned.

All the gas–water/water–gas binary parameters required by the Henry equation for the current system are available in the Aspen Properties databases and, correspondingly were taken from there, namely CO₂–H₂O, CH₄–H₂O and H₂–H₂O parameters from the databases APV140 e-NRTL-RK, APV140 Henry and APV140 Binary, respectively. Gas-organic/organic-gas binary Henry parameters were ignored taking into consideration the composition of the mixture fed to the reactor. A similar solution was given to the e-NRTL electrolyte-water/water-electrolyte binary parameters being formic and acetic acids and CO₂ considered the ion-forming species. These parameters were taken from the APV140 e-NRTL-RK database. The ion concentrations in the aqueous phase were determined taking into consideration the dissociation, salt formation and hydrolysis reactions of the electrolytes and their derivatives. These reactions were taken from the reactions databases in the Aspen Properties (APV140-REACTIONS).

The circumstances were not the same for the NRTL binary interaction parameters of some of the components selected in this work. When they were not available, two different strategies were used to obtain them: i) if experimental data for the liquid–vapor/gas equilibria were accessible through the link to the NIST databases existing in the Aspen Plus property environment, the binary parameters were obtained by the function regression available in the simulator and ii) for those components not falling into the previous group, the parameters were evaluated by the UNIFAC group contribution method in the formulation existing in Aspen Plus.

In the case of the levoglucosan, as explained previously, none of the two solutions displayed in the previous paragraph were feasible, as no experimental data on the liquid–vapor equilibrium of the mixture levoglucosan–water were found and the parameters could not be evaluated by the UNIFAC group contribution method. The solution applied in this case comprised the following approaches [Cadoret et al., 2009; Tian et al., 2010]: i) the molecular geometry was optimized using quantum chemical methods, ii) the liquid–vapor equilibrium for the binary mixture with water was predicted by the COSMO-RS [Klamt, 2005] theory and, iii) the NRTL binary levoglucosan–water/water–levoglucosan NRTL interaction parameters were regressed using the equilibrium data previously obtained. Molecular geometry

optimizations were carried out considering the molecule in the gas phase and not interacting with any other molecule or media, and, alternatively, immersed in a continuous solvent media having $\epsilon \rightarrow \infty$ (COSMO theory). Calculations were performed at the Density Functional Theory (DFT) in the program package Turbomole 7.3. The density functional used was the BP86 and the atomic basic sets selected were the TZVPD. The algorithm FINE was used to improve the COSMO calculations i.e., BP/TZVPD-FINE computational level. The resulting “.energy” and “.cosmo” files obtained from the COSMO calculations were employed as input data for the liquid–vapor predictions of the binary mixture levoglucosan–water by means of the COSMO-RS theory as implemented in the COSMOtherm program. The resulting liquid–vapor equilibrium was specified in Aspen Plus for regressing the NRTL parameters. The same procedure was employed to obtain the NRTL parameters for the binary mixtures levoglucosan–acetic acid and levoglucosan–furfural.

The source of the NRTL parameters used in the final version of e-NRTL-RK thermodynamic model employed in the current work are summarized in Table 5. The NRTL interaction parameters gas–organics and gas–gas were neglected taking into consideration the physical nature of the system investigated. The regressed NRTL interaction parameters ensured good predictions of the liquid–gas equilibria of the binary mixtures, as suggested by the RRMSE value lower than 300 in both cases respect to the experimental data.

Finally, the pH calculated by the revisited e-NRTL-RK model for the liquid at the APR reactor was 3.9, in better agreement with the experimental results than the preliminary prediction, which indicates the improvement of the prediction capacity of the model.

3.2. Alternatives for the valorization of APR gas product stream

Case 1. Gas product commercialization

Mass balances and conditions for main process streams are compiled in Table SM1 (Supplementary Material). The composition of APR gas stream obtained by the proposed simulation of Case 1 (55.97 H₂, 0.00 CO, 35.12 CO₂ and 9.91 CH₄, mol% dry basis), matches reasonably well the experimental composition. Calculated errors between these results obtained by simulation model and those experimental (compiled in Table 2) are 14, 0, 5 and 10 % for H₂, CO, CO₂ and CH₄ compositions, respectively. Mass flow of water evaporated in APR reactor, which incorporated to the gas stream, reached 985.1 kg/m³AFB, resulting in a high energy consumption in the reactor and in the need to separate the water for further valorization of APR gas product.

The high temperature and flow of wet gas stream allow the reactor feed preheating up to 210 °C as proposed, resulting in a gas stream outlet temperature of 213 °C, but no additional further energy recovery is possible. This point was corroborated attending the results of AEA tool. The obtained value of Available Energy Savings was 6,000 kcal/h (50/50 in heating and cooling utilities), equivalent to only 0.07 % of total utilities usage, indicating that the process is properly heat-integrated. Finally, the gas stream is dried by water condensation at 45 °C, to decrease the moisture up to 0.5 %, resulting in c.a. 72.5 kg/h per feed stream basis (580.2 ton per year) of H₂-rich gas product which can be commercialized as crude H₂.

Case 2. Energy valorization

Unlike Case 1, in this case the final dry gas product stream is used as fuel-gas for energy valorization (see mass balance and conditions for main streams in Supplementary Material, Table SM2). The exhaust gas generated at the combustor is used firstly to preheat the combustion air (fed at 10 % in excess) up to 140 °C and later as heat source for the generation of 53.6 kg of high-pressure steam (@250 °C, 40 bar) per m³ fed AFB, which can be further used in two different alternatives:

- Cover the reactor heating demand. Since the global heating demand in APR reactor reached 1.61·10⁶ kcal/h, only 39.5 kg/h of the generated hps are consumed, resulting in a net steam excess of 496

Table 5

Source of the NRTL binary interaction parameters used in the final e-NRTL-RK model used in the current work for estimating the thermodynamic properties of the fluids.

	Levog.	Acetic ac.	Furfural	H ₂ O	CO ₂	H ₂	CH ₄
Acetol	Estimat.	Estimat.	Estimat.	Estimat.	n.r.	n.r.	n.r.
Levog.		Regress.*	Regress.*	Regress.*	n.r.	n.r.	n.r.
Acetic ac.			NISTV140	APV140	n.r.	n.r.	n.r.
			NIST-HOC	VLE-HOC			
Furfural				APV140	n.r.	n.r.	n.r.
				VLE-HOC			
H ₂ O					APV140	Regress.	Regress.
					VLE-HOC		
CO ₂						n.r.	n.r.
H ₂							n.r.

n.r.: interaction not relevant.

Regression: experimental liquid–gas equilibrium data were employed as input in the regression calculations (Yokoyama et al., 1988; Wang et al., 1995; Kiepe et al., 2003; Yarrison et al., 2006; Awan et al., 2010; Li et al., 2010; Frost et al., 2014; Bottger et al., 2016; Maslennikova et al., 1976; DeVaney et al., 1978; Kling and Maurer, 1991).

Regression*: the liquid–vapor equilibrium data used for regressing the interaction parameters were obtained from COSMO-RS calculations.

kg/h (c.a. 4,000 ton per year) which can be used in other heating demands, either in the plant itself or in other nearby ones. The sale of this steam excess as an income result in a net income of 15.9 k€/year for 10 m³AFB/h of treatment capacity.

- ii) Cover the feed heater (E-101) duty. The hps generated in the recovery boiler allows to achieve similar target temperature in this exchanger in comparison to that considered in the initial proposal (217 °C vs 220 °C). In this case, no net hps surplus is produced in the recovery boiler but the heating cost in E-101 is saved in exchange.

In this Case 2, the potential energy savings calculated by AEA reached 2.14·10⁵ kcal/h, 1.10·10⁵ kcal/h in heating utilities and 1.04·10⁵ kcal/h in cooling utilities, which represents 2.29 % and 2.58 % of current heating and cooling needs, respectively, and 2.42 % of total utilities demand. The decrease in energy efficiency for Case 2 in comparison to Case 1 is caused by the high-pressure steams net production excess, which is not used in the same APR process.

Case 3. Combined alternative.

Due to the high energy content of generated APR dry gas, with a Higher Heating Value of 5,165 kcal/kg, the stream fraction that needs to be burned is only 12 %, while the 88 % remaining is sent out battery limit as crude hydrogen surplus for commercialization (6.4 kg/m³AFB, 510.4 ton per year for the used basis of 10 m³AFB/h). This partial self-consumption of APR gas stream allows to cover the reactor energy demand, which is one of the main drawbacks pointed for APR technology. Likewise, a significant amount of a valuable H₂-rich gas is produced for recovery or valorization. The mass balance and conditions of main process streams for this alternative are shown in Table SM3 (Supplementary Material).

Finally, by adjusting the fraction of APR gas product used as fuel-gas to the minimum needed to cover the reactor duty a significant increase in the process energy efficiency is achieved. The AEA calculated an available energy saving of 21,000 kcal/h (11,000 and 10,000 kcal/h in heating and cooling, respectively) that corresponds to 0.25 % of total

used utilities (0.23 and 0.26 % in heating and cooling, respectively).

3.3. Costs-based alternative evaluation

The Aspen Process Economic Analyzer results for the three cases proposed above are summarized and compared in Fig. 6. Detailed results are compiled in Tables SM4 to SM6). As can be observed, CAPEX for Case 1 is noticeably low in comparison to other alternatives because of the markedly higher cost of the fire-tube boiler used for energy valorization of APR gas in comparison to the rest of process equipment. After the boiler, heat exchangers are the most expensive equipment for unit operations. On the other hand, Case 2 is the only alternative in which process heat demand is fully self-covered by means of energy valorization of APR gas product stream, resulting in dramatically lower CAPEX costs due to the minimization of heating steam consumption. It can be seen that there is a crossover effect that results in similar overall yearly cost for Cases 1 and 3 while much lower value is obtained for Case 2. At this point, the results suggest that maximum energy recovery is the key factor for the potential feasibility of APR process, more than complete or partial H₂-rich gas commercialization. In any case, it should be taken into account that AFB is a difficult-to-treat wastewater stream due to its content of several compounds known to be refractory to anaerobic digestion and other conventional processes. Thus, if proper treatment for the removal of contaminants is achieved, even at neutral economic balance, can be considered itself as an interesting goal.

As showed in Table 6, a production cost of 1.1 € per kg of crude H₂ is obtained for Case 1. It was expected this value to increase for Case 3 because of the investment in the boiler and other needed process equipment penalizes the economic results. However, since the heat consumption of the process is partially covered through energy valorization of a fraction of H₂-rich gas, similar production cost was calculated for Case 3 (c.a. 1.2 €/kg). In addition to this, after covering CAPEX depreciation (investment amortization), the calculated production cost decreases to 0.93–0.95 €/kg of crude H₂ for Cases 1 and 3, respectively.

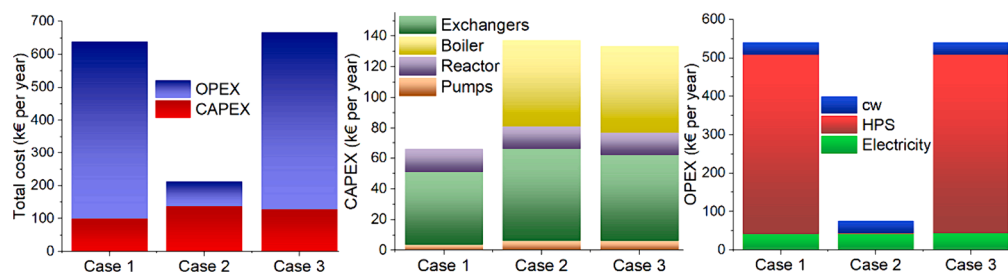


Fig. 6. Total, CAPEX and OPEX yearly costs for different process alternatives.

Table 6

H₂ production costs and economic balances (considering green H₂ sell price) for the process alternatives including net H₂ production (Cases 1 and 3).

	Case 1	Case 3
	Hydrogen production cost (€/kg)	
Including CAPEX depreciation	1.10	1.31
Not including CAPEX depreciation	0.93	1.06
Economic balance (k€/year @ 2€/kgH ₂)		
PSA separation not included	519.9	352.5
PSA separation included	400.7	332.6

The results should be corrected considering the additional cost of H₂-CO₂ separation. Based on the obtained crude H₂ flowrates and composition, the most adequate separation method is pressure swing adsorption (PSA). Attending to previously reported estimations [Khodabandehloo et al., 2020], the cost of PSA with this purpose could be estimated at 20 % of total CAPEX, resulting in about 201.9 k€ for the process proposed (20.2 k€, yearly depreciation cost) in the current work. With this, the H₂ production cost would increase up to 1.14 and 1.35 €/kgH₂ for Case 1 and Case 3, respectively, suggesting that renewable H₂ at competitive cost can be produced by APR process.

A different approach can be considered attending to the production cost of generated H₂, and the consequent economic balance for Cases 1 and 3. Since H₂ produced by APR from biomass or waste biomass is considered as renewable, economic assessment should not be made only in the context of H₂ global market. More than 95 % of global production corresponds to grey hydrogen obtained by MSR at about 0.75 €/kg [Tian et al., 2024]. However, H₂ from biomass is in competition with production from other renewable sources, such as green hydrogen, for which an estimated sell-price range of 1.95–3.00 €/kg [Burchardt, 2023] for 2030 can be considered [Tian et al., 2024]. In this context, H₂ production costs and potential economic balance can be estimated for Cases 1 and 3 since a net H₂ production is considered in these two alternatives (not in Case 2). For Cases 1 and 3 a negative balance in 350 to 450 k€/year interval would be obtained for grey H₂ market price but as can be seen in Table 6, considering an average price of 2 €/kg for renewable H₂, a net income of 520 and 353 k€ per year can be calculated, including 400 and 333 k€/year PSA cost, respectively.

4. Conclusions

The use of a waste stream as process feedstock combined with an adequate heat integration could overcome the main APR process drawbacks, resulting in a potentially feasible technology. The energy valorization of less than 15 % of the APR gas product allows to cover the reactor heat consumption plus c.a. 30 % of the feedstock preheating duty, while additional 6 kg H₂/m³ AFB treated could be commercialized at a price in competition with green H₂ (1–2 €/kg). APR was revealed as an interesting solution for the combined treatment and valorization of the AFB in conventional biorefineries.

CRedit authorship contribution statement

Francisco Heras: Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jéssica Justicia:** Writing – review & editing, Writing – original draft, Investigation, Data curation. **José A. Baeza:** Writing – review & editing, Validation. **Miguel A. Gilarranz:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition. **Víctor R. Ferro:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Francisco Heras reports equipment, drugs, or supplies and travel were provided by Government of Spain. Ministry of Science and Innovation. Jessica Justicia reports financial support, equipment, drugs, or supplies, and travel were provided by Government of Spain. Ministry of Science and Innovation. Jose A Baeza reports equipment, drugs, or supplies and travel were provided by Government of Spain. Ministry of Science and Innovation. Miguel A Gilarranz reports equipment, drugs, or supplies and travel were provided by Government of Spain. Ministry of Science and Innovation. Víctor Ferro reports equipment, drugs, or supplies and travel were provided by Government of Spain. Ministry of Science and Innovation.

Data availability

No data was used for the research described in the article.

Acknowledgment

This work was supported by Community of Madrid (research network BIO3, P2018/EMT- 4344) and Ministry of Science and Innovation (Recovery, Transformation and Resilience Plan, project HYDROCIRCLE, TED2021-130054B-I00). Jessica Justicia thanks supporting from Ministry of Science, Innovation and University through the project WASTEVALOR (PID2019-108445RB-I00).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2024.130572>.

References

- Arandia, A., Coronado, I., Remiro, A., Gayubo, A.G., Reinikainen, M., 2019. Aqueous-phase reforming of bio-oil aqueous fraction over nickel-based catalysts. *Int. J. Hydrogen Energy* 44, 13157–13168. <https://doi.org/10.1016/j.ijhydene.2019.04.007>.
- Aspen HYSYS V14 Help 2022. Aspen Tech Inc., MA (USA).
- Awan, J.A., Thomsen, K., Coquelet, C., Fosbol, P.L., Richon, D.J., 2010. Vapor-liquid equilibrium measurements and modeling of the propyl mercaptan + methane + water system. *Chem. Eng. Data* 55, 842–846. <https://doi.org/10.1021/jc900441f>.
- Botter, A., Kamps, A.-P.-S., Maurer, G., 2016. An experimental investigation on the solubility of methane in 1-octanol and n-dodecane at ambient temperatures. *Fluid Phase Equilib.* 407, 209–216. <https://doi.org/10.1016/j.fluid.2016.08.009>.
- Burchardt, J., Hegnsholt, E., Holm, M., Klose, F., Ritter, D., Schönberger, S., 2023. Turning the European green hydrogen dream into reality: a call to action. Boston consultingGroup. <https://media-publications.bcg.com/Turning-the-European-Green-H2-Dream-into-Reality.pdf>. Last access 2024, Jan 2nd.
- Cadore, L., Yu, C.-C., Huang, H.-P., Lee, M.-J., 2009. Effects of physical properties estimation on process design: a case study using AspenPlus. *Asia-Pac. J. Chem. Eng.* 4 (5), 729–734. <https://doi.org/10.1002/apj.328>.
- Chanthakett, A., Arif, M.T., Khan, M.M.K., Oo, M.M.K., 2021. Hydrogen production from municipal solid waste (MSW) for cleaner environment. *Bioenerg. Resour. Technol.* 219–247. <https://doi.org/10.1016/B978-0-12-822525-7.00017-2>.
- Chen, C.C., Evans, L.B., 1986. A local composition model for the excess gibbs energy of aqueous-electrolyte systems. *AIChE J.* 32 (3), 444–454. <https://doi.org/10.1002/aic.690320311>.
- DeVaney W., Berryman J.M., Kao P.L., Eakin B., 1978. High temperature V-L-E measurements for substitute gas components. GPA Research Report RR-30, Gas Processing Association. Tulsa, OK.
- Fraia, A.D., Milliotti, E., Rizzo, A.M., Zoppi, G., Pipitone, G., Pirone, R., Rosi, L., Chiaramonti, D., Bensaid, S., 2023. Coupling hydrothermal liquefaction and aqueous phase reforming for integrated production of biocrude and renewable H₂. *AIChE J.* 69 (1), e17652.
- Frost, M., Karakatsani, E., Solms, N.V., Richon, D., Kontogeorgis, G.M.J., 2014. Vapor liquid equilibrium of methane with water and methanol. Measurements and Modeling. *Chem. Eng. Data* 59, 961–967. <https://doi.org/10.1021/je400684k>.
- García-Baldoví, A., Peng, L., Santiago-Portillo, A., Asiri, A.M., Primo, A., García, H., 2022. Aqueous phase methanol reforming catalyzed by Fe–Cu alloy nanoparticles wrapped on nitrogen-doped graphene. *ACS Appl. Energy Mater.* 5 (7), 9173–9180. <https://doi.org/10.1021/acsaem.2c01806>.

- Harju, H., Pipitone, G., Lefferts, L., 2020. Influence of the catalyst particle size on the aqueous phase reforming of n-butanol over Rh/ZrO₂. *Front. Chem.* 8, 17. <https://doi.org/10.3389/fchem.2020.00017>.
- Heras, F., de Oliveira, A.S., Baeza, J.A., Calvo, L., Ferro, V.R., Gilarranz, M.A., 2022. Toward sustainability of the aqueous phase reforming of wastewater: heat recovery and integration. *App. Sci.* 12, 10424. <https://doi.org/10.3390/app122010424>.
- Hernando, H., Jiménez-Sánchez, S., Feroso, J., Pizarro, P., Coronado, J.M., Serrano, D. P., 2016. Assessing biomass catalytic pyrolysis in terms of deoxygenation pathways and energy yields for the efficient production of advanced biofuels. *Catal. Sci. Technol.* 6, 2829. <https://doi.org/10.1039/C6CY00522E>.
- Justicia, J., Baeza, J.A., de Oliveira, A.S., Calvo, L., Heras, F., Gilarranz, M.A., 2022. Aqueous-phase reforming of water-soluble compounds from pyrolysis bio-oils. *Renew. Energ.* 199, 895–907. <https://doi.org/10.1016/j.renene.2022.09.021>.
- Justicia, J., Baeza, J.A., Calvo, L., Heras, F., Gilarranz, M.A., 2023. Valorization to hydrogen of bio-oil aqueous fractions from lignocellulosic biomass pyrolysis by aqueous phase reforming over Pt/C catalyst. *Chem. Eng. J.* 477, 146860 <https://doi.org/10.1016/j.cej.2023.146860>.
- Khodabandehloo, M., Larimi, A., Khorasheh, F., 2020. Comparative process modeling and techno-economic evaluation of renewable hydrogen production by glycerol reforming in aqueous and gaseous phases. *Energ. Convers. Manag.* 225, 113483 <https://doi.org/10.1016/j.enconman.2020.113483>.
- Kiepe, J., Horstmann, S., Fischer, K., Gmehling, J., 2003. Experimental determination and prediction of gas solubility data for methane + water solutions containing different monovalent electrolytes. *Ind. Eng. Chem. Res.* 42, 5392–5398. <https://doi.org/10.1021/ie030386x>.
- Kim, M., Badakhsh, A., Akpe, S.G., Kim, Y., Nam, K.-J., Kim, Y., Jeong, H., Nam, S.W., Ham, H.C., Choi, S.H., Sohn, H., 2023. Highly selective PtCo bimetallic nanoparticles on silica for continuous production of hydrogen from aqueous phase reforming of xylose. *Int. J. Hydrogen Energy* 48 (75), 29162–29177. <https://doi.org/10.1016/j.ijhydene.2023.03.458>.
- Kirilin, A.V., Tokarev, A.V., Kustov, L.M., Salmi, T., Mikkola, J.-P., Murzin, J.-P., 2012. Aqueous phase reforming of xylitol and sorbitol: Comparison and influence of substrate structure. *App. Catal. A* 435–436, 172–180. <https://doi.org/10.1016/j.apcata.2012.05.050>.
- Klamt, A., 2005. COSMO-RS: from quantum chemistry to fluid phase thermodynamics and drug design, first ed. Elsevier, Amsterdam.
- Kling, G., Maurer, G.J., 1991. The solubility of hydrogen in water and in 2-aminoethanol at temperatures between 323 K and 423 K and pressures up to 16 MPa. *Chem. Thermodyn.* 23, 531–541. [https://doi.org/10.1016/S0021-9614\(92\)80095-3](https://doi.org/10.1016/S0021-9614(92)80095-3).
- Li, Z., Guo, X.-Q., Tian, H., Xuebao, H., 2010. Calculation for solubility of methane and carbon dioxide in water in presence of hydrate. *Huagong Xuebao/CIESC J.* 61, 1341–1348.
- Li, D., Li, Y., Liu, X., Guo, Y., Pao, C.-W., Chen, J.-L., Hu, Y., Wang, Y., 2019. NiAl₂O₄ spinel supported Pt catalyst: high performance and origin in aqueous-phase reforming of methanol. *ACS Catal.* 9 (10), 9671–9682. <https://doi.org/10.1021/acscatal.9b02243>.
- Lozano, P., Simon, A.I., García, L., Ruiz, J., Oliva, M., Arauzo, J., 2021. Influence of the Ni-Co/Al-mg catalyst loading in the continuous aqueous phase reforming of the bio-oil aqueous fraction. *Processes* 9, 81. <https://doi.org/10.3390/pr9010081>.
- Martin, M., Grossmann, I.E., 2014. Optimal simultaneous production of hydrogen and liquid fuels from glycerol: integrating the use of biodiesel byproducts. *Ind. Eng. Chem. Res.* 53, 7730–7745. <https://doi.org/10.1021/ie500067d>.
- Maslennikova, V.Y., Goryunova, N.P., Subbotina, L.A., Tsiklis, D.S., 1976. The solubility of water in compressed hydrogen. *Russ. J. Phys. Chem.* 50 (2), 411–414.
- Oliveira, A.S., Baeza, J.A., Calvo, L., Alonso-Morales, N., Heras, F., Rodríguez, J.A., Gilarranz, M.A., 2019. Production of hydrogen from brewery wastewater by aqueous phase reforming with Pt/C catalysts. *App. Catal. B* 245, 365–375. <https://doi.org/10.1016/j.apcatb.2018.12.061>.
- Oliveira, A.S., Sarrión, A., Baeza, J.A., Diaz, E., Calvo, L., Mohedano, A.F., Gilarranz, M. A., 2022. Integration of hydrothermal carbonization and aqueous phase reforming for energy recovery from sewage sludge. *Chem. Eng. J.* 442 (1), 136301 <https://doi.org/10.1016/j.cej.2022.136301>.
- Paris, C.B., Howe, A.G., Lewis, R.J., Hewes, D., Morgan, D.J., He, Q., Edwards, J.K., 2022. Impact of the experimental parameters on catalytic activity when preparing polymer protected bimetallic nanoparticle catalysts on activated carbon. *ACS Catal.* 12 (8), 4440–4454. <https://doi.org/10.1021/acscatal.1c05904>.
- Pazos Urra, M., Herold, F., Chen, D., Rønning, M., 2023. Nitrogen-containing carbon nanofibers as supports for bimetallic Pt-mn catalysts in aqueous phase reforming of ethylene glycol. *Catal. Today* 418, 114066. <https://doi.org/10.1016/j.cattod.2023.114066>.
- Pipitone, G., Zoppi, G., Bocchini, S., Chiaramonti, A.M., Pirone, R., Bensaid, S., 2020. Aqueous phase reforming of the residual waters derived from lignin-rich hydrothermal liquefaction: investigation of representative organic compounds and actual biorefinery streams. *Catal. Today* 345, 237–250. <https://doi.org/10.1016/j.cattod.2019.09.040>.
- Pipitone, G., Zoppi, G., Pirone, R., Bensaid, S., 2022. A critical review on catalyst design for aqueous phase reforming. *Int. J. Hydrogen Energy* 47 (1), 151–180. <https://doi.org/10.1016/j.ijhydene.2021.09.206>.
- SGH2 Energy. H₂ cost comparison. <https://www.sgh2energy.com/economics/#econheader>. Last access 2024, Jan 2nd.
- Sladkovskiy, D.A., Godina, L.I., Semikin, K.V., Sladkovskaya, E.V., Smirnova, D.A., Murzin, D.Y., 2018. Process design and techno-economical analysis of hydrogen production by aqueous phase reforming of sorbitol. *Chem. Eng. Res. Des.* 134, 104–116. <https://doi.org/10.1016/j.cherd.2018.03.041>.
- Smith, B., Loganathan, M., Samanta, M.S., 2010. A review of the water gas shift reaction kinetics. *Int. J. Chem. React. Eng.* 8 (1), 32. <https://doi.org/10.2202/1542-6580.2238>.
- Tang, W., Chen, Z., Millan, M., Zuo, X., Yuan, G., Cui, Z., Dong, Z., Cong, Y., Li, X., 2023. Facile fabrication of porous carbon nanofibers encapsulated with nanoscale exposed Ni for producing high-purity hydrogen from cheap glycerol. *Int. J. Hydrogen Energy* 48 (97), 38172–38187. <https://doi.org/10.1016/j.ijhydene.2023.06.190>.
- Tian, Z., Lu, Y., Wang, J., Shu, R., Wang, C., Chen, Y., 2024. Advances in hydrogen production by aqueous phase reforming of biomass oxygenated derivatives. *Fuel* 357 A, 129691. <https://doi.org/10.1016/j.fuel.2023.129691>.
- Tian, X., Zhang, X., Wei, L., Zeng, S., Huang, L., Zhang, S., 2010. Multi-scale simulation of the 1,3-butadiene extraction separation process with an ionic liquid additive. *Green Chem.* 12 (7), 1263–1273. <https://doi.org/10.1016/j.seppur.2021.118656>.
- Ulrich, G.D., Vasudevan, P.T., 2004. Chemical engineering. process design and economics. a Practical guide, 2nd ed. Process Publishing, Durham, New Hampshire.
- Valdez, G.D., Valois, F.P., Bremer, S.J., Bezerra, K.C.A., Hamoy Guerreiro, L.H., Santos, M.C., Bernar, L.P., Feio, W.P., Moreira, L.G.S., Mendonça, N.M., Rocha de Castro, D.A., Sergio Duvoisin, J., Pizarro Borges, L.E., Teixeira Machado, N., 2023. Improving the bio-oil quality of residual biomass pyrolysis by chemical activation: effect of alkalis and acid pre-treatment. *Energies* 16, 3162. <https://doi.org/10.3390/en16073162>.
- Valenzuela, M.B., Jones, C.W., Agrawal, P.K., 2006. Batch aqueous-phase reforming of woody biomass. *Energy Fuels* 20 (4), 1744–1752. <https://doi.org/10.1021/ef060113p>.
- Vikla, A.K.K., Simakova, I., Demidova, Y., Keim, E.G., Calvo, L., Gilarranz, M.A., He, S., Seshan, K., 2021. Tuning Pt characteristics on Pt/C catalyst for aqueous-phase reforming of biomass-derived oxygenates to bio-H₂. *Appl. Catal. A* 610, 117963. <https://doi.org/10.1016/j.apcata.2020.117963>.
- Wang, Y., Han, B., Yan, H., Liu, R., 1995. Solubility of CH₄ in the mixed solvent t-butyl alcohol and water. *Thermochim. Acta* 253, 327–334. [https://doi.org/10.1016/0040-6031\(94\)02011-C](https://doi.org/10.1016/0040-6031(94)02011-C).
- Wei, Z., Karim, A., Li, Y., Wang, Y., 2015. Elucidation of the roles of re in aqueous-phase reforming of glycerol over Pt-Re/C catalysts. *ACS Catal.* 5 (12), 7312–7320. <https://doi.org/10.1021/acscatal.5b01770>.
- Yarrison, M., Cox, K.R., Chapman, W.G., 2006. Measurement and modeling of the solubility of water in supercritical methane and ethane from 310 to 477 K and pressures from 3.4 to 110 MPa. *Ind. Eng. Chem. Res.* 45, 6770–6777. <https://doi.org/10.1021/ie0513752>.
- Yokoyama, C., Wakana, S., Kaminishi, G.-I., Takahashi, S.J., 1988. Vapor-liquid equilibria in the methane-diethylene glycol-water system at 298.15 and 323.15 K. *Chem. Eng. Data* 33, 274–276. <https://doi.org/10.1021/je00053a015>.
- Zoppi, G., Pipitone, G., Pirone, R., Bensaid, S., 2022. Aqueous phase reforming process for the valorization of wastewater streams: application to different industrial scenarios. *Catal. Today* 38 (1), 224–236. <https://doi.org/10.1016/j.cattod.2021.06.002>.