

Article

A Technical Analysis of the H₂ Purification Trains Downstream of Alkaline Electrolyzers

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Abstract: In view of achieving decarbonization targets, green hydrogen has emerged as a promising low-emission alternative. Typically, green hydrogen is produced by splitting water using various electrolysis technologies powered by renewable energy. Among these, alkaline electrolyzers have been proven as suitable for large-scale applications, operating effectively in alkaline environments under near-atmospheric pressure levels and temperatures. Once produced, H₂ must undergo purification for use in industrial and mobility sectors, with particularly stringent purification requirements for fuel applications. Despite the relevance of H₂ purification due to its usage as an energy carrier, no comprehensive analyses of H₂ purification trains downstream of H₂ production are available in the literature. To fill this gap, the aim of this work is to perform a detailed technical assessment of purification trains downstream of alkaline water electrolyzers, considering KOH removal, oxygen removal, compression and dehydration. Different case studies are discussed, focusing on the alkaline electrolyzer operating pressure (i.e., atmospheric or higher) and considering the application of H₂ in both the industrial and mobility sectors. The design and methodology of the process were developed within the Aspen Plus[®] simulation environment, to support the electrolyzers’ integration in industrial settings.

Keywords: green H₂; alkaline electrolyzers; KOH purification; technical assessment; sustainable process design



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1. Introduction

Electrolysis offers a clean alternative to fossil fuel-based hydrogen production, reducing carbon emissions and supporting the transition to a sustainable energy economy. Electrolysis involves splitting water into hydrogen and oxygen by means of electricity produced via renewable energy sources, such as wind or solar power. A typical electrolyzer stack is composed of a number of cells in series, spacers, seals, frames and end plates, to avoid leaks and collect fluids. Each cell, in turn, is made using two electrodes in a liquid electrolyte or adjacent to a solid membrane, two porous transport layers and bipolar plates to provide support and distribute the flow. Depending on the cell structure, three main types of electrolyzers can be recognized: alkaline electrolyzers (AE), proton exchange membrane (PEM) electrolyzers and solid oxide electrolyzers (SOEC), each differing in efficiency, cost and operating conditions [1].

Alkaline electrolyzers use a liquid alkaline electrolyte (typically potassium hydroxide, KOH, or sodium hydroxide, NaOH) to facilitate the movement of hydroxide ions (OH[−]) between electrodes. Hydrogen is generated at the cathode, while oxygen forms at the anode, with typical operating conditions in the range of 60–80 °C for temperature and 1–30 bar for

pressure. Alkaline electrolysis is a mature technology, already applied industrially, with a low capital cost and long lifespan (over 60,000 h). Nevertheless, its low current density, slow response to power fluctuations (not ideal for variable renewable energy sources) and potential gas crossover issues are some of the main concerns [2].

Proton exchange membrane electrolyzers use a solid polymer electrolyte membrane (typically made of Nafion) that conducts protons (H^+) from the anode to the cathode, where hydrogen gas is produced. They typically operate at 50–80 °C and can handle higher pressure levels (up to 50–100 bar), reducing the need for additional compression. A high current density, rapid response to fluctuations in electricity supply, compact design, and high-purity hydrogen output are their main advantages, but their higher capital cost due to expensive materials (e.g., platinum and iridium catalysts), shorter lifespan (20,000–40,000 h) and membrane degradation over time still hinder their large-scale application.

Solid oxide electrolyzers use a ceramic solid oxide electrolyte that conducts oxygen ions (O^{2-}) instead of protons. They operate at high temperatures (700–1000 °C) and show the highest electrical efficiency (up to 90% when utilizing waste heat), potential for reversible operation (acting as both an electrolyzer and a fuel cell) and capability to utilize waste heat from industrial processes. Nevertheless, their high operating temperatures lead to material degradation, shorter lifetimes, complex system design and high capital costs.

Alkaline electrolyzers and PEM electrolyzers are the most consolidated technologies at the industrial scale. Once green H_2 is produced by either of these two, it has to be purified to enable downstream applications [3].

As a general remark, the design of the H_2 purification train downstream of the H_2 production section is a function of the technology used for H_2 production, together with the desired application of the hydrogen thus produced. Hydrogen obtained from PEM electrolyzers typically shows a higher purity than that produced by alkaline electrolyzers. As a result, the purification train is simplified in the former case.

Moreover, hydrogen intended for the mobility sector has more stringent purity requirements than that used in the industrial sector. Du et al. (2021) specified H_2 purity requirements for fuel cell application, both in China and abroad [4], while Dawood et al. (2020) and Bensmann et al. (2016) provide H_2 purity requirements for different applications [5,6].

Figure 1 shows a typical block flow diagram (BFD) of the purification trains downstream of both alkaline electrolyzers and PEM electrolyzers.

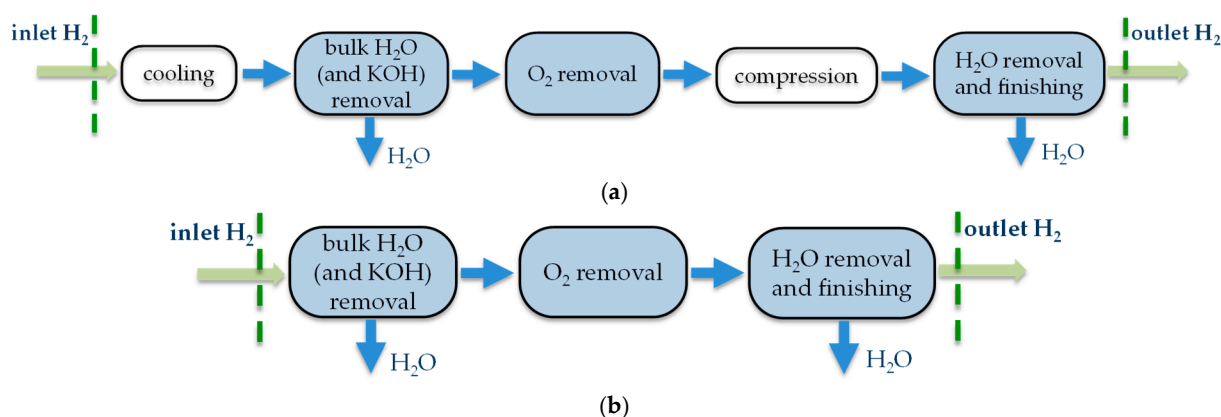


Figure 1. Block flow diagram (BFD) of hydrogen purification downstream: (a) alkaline electrolyzers and (b) PEM electrolyzers.

As regards alkaline electrolysis, the produced hydrogen is cooled and routed to a scrubber (usually a gas–liquid separator equipped with a demister) for water and KOH abatement. For this purpose, some papers also show the implementation of a vessel in

which the hydrogen to be purified is bubbled in water [7], or the use of specific patented devices [8]. No information is reported in the literature regarding the maximum allowable content of KOH in the produced hydrogen. Only Ligen et al. (2020) report that, considering the use of hydrogen in fuel cells, the concentration of K^+ and Na^+ ions must be reduced to 0.05 ppm, to avoid possible poisoning of the polymeric membrane [7].

The KOH^- and humidity-free hydrogen stream undergoes oxygen removal in the DeOxo unit, a reactor in which O_2 is converted into water. The product coming from the DeOxo unit is then compressed and routed to the water removal section, which is typically performed by temperature swing adsorption or pressure swing adsorption, with some sources indicating a preference for one technology or the other [7,9]. Typically, the removal of the residual water is required to take place downstream of the oxygen removal, as H_2O is produced in the DeOxo unit. Heat exchange as well as hydrogen compression can be arranged in a different fashion within the purification train, depending on the specific case study.

Table 1 provides an overview of the available literature discussing hydrogen purification using both alkaline and PEM electrolysis. None of the references in Table 1 detail the purification train from a process engineering perspective, instead just providing a qualitative analysis of the sequence of unit operations. Sánchez and co-authors [10] performed a process simulation of alkaline electrolysis in Aspen Plus® V11, with the stack operating at 7 bar and 75 °C. Downstream of the electrolyzer, on the hydrogen side, only a gas–liquid separator equipped with a demister was considered. From a thermodynamic point of view, the system was modeled with a γ - ϕ approach, in which the NRTL method was used to estimate the γ activity coefficients of each molecular component in the liquid phase. Therefore, the presence of electrolytes was neglected. The behavior of the gas phase is assumed to be ideal.

In addition, Qiao et al. [11] performed an Aspen Plus simulation to determine the effects of different separation temperatures and separation pressure levels on the final hydrogen outlet, together with the system energy consumption. The focus was to perform a system sensitivity analysis based on operating conditions, rather than defining a systematic process design methodology.

Table 1. Literature references concerning hydrogen purification through alkaline electrolyzers and PEM electrolyzers.

General		
Reference	H ₂ destination (purity)	Topic
Pyle (1998) [8]	-	Informative magazine article on H ₂ purification
Smolinka et al. (2015) [12]	-	Analysis of electrolysis technologies
Taibi et al. (2020) [1]	-	Report on the scale-up of electrolysis technologies
Alkaline electrolyzers		
Ramsden et al. (2009) [13]	Mobility (99.9998 mol%)	Analysis of levelized cost of centralized and distributed hydrogen production Cost estimation also available in Morgan et al. (2013) [14]
Yao et al. (2017) [15]	(99.9 mol%)	Techno-economic assessment of H ₂ production via gasification, reforming and alkaline electrolysis
Ligen et al. (2020) [7]	Mobility (ISO 14687:2019) [16]	H ₂ drying and purification for fuel cell vehicles
Sanchez et al. (2020) [10]	(98.89 mol%)	Aspen Plus® model of alkaline electrolysis

Table 1. Cont.

General		
Reference	H ₂ destination (purity)	Topic
Acevedo et al. (2023) [17]	(99.99 mol%)	H ₂ production cost via alkaline electrolysis
Nejadian et al. (2023) [18]	Mobility	Optimization of integrated H ₂ production via SOEC, PEM and alkaline electrolyzer
Sakas et al. (2022) [19]	(99.999 mol%)	Based on industrial scale alkaline electrolyzer
Hu et al. (2024) [20]	n.a.	Strategy for regulation of pressure and lye flow rate during high load periods
Qiao et al. (2024) [11]	n.a.	Aspen Plus® simulation of alkaline water electrolysis
Shangguan et al. (2024) [21]	>99.8 mol%	Optimization of performance to establish dynamic thermal balance model
Zhang et al. (2024) [22]	n.a.	Model of O ₂ purity based on 50 Nm ³ H ₂ /h industrial scale system
Wang et al. (2025) [23]	99.8 mol%	Comparative experimental study of alkaline and PEM electrolysis
PEM electrolyzers		
Cohen et al. (2009) [9]		
Kwon et al. (2023) [24]	Fuel cell (99.9998 mol%)	Effects of operating conditions in DeOxo reactor
Nejadian et al. (2023) [18]	Mobility	Optimization of integrated H ₂ production via SOEC, PEM and alkaline electrolyzer
Crespi et al. (2023) [25]	Fuel cell (99.9995 mol%)	Experimental and theoretical evaluation of PEM electrolysis for dynamic operation
Wang et al. (2025) [23]	99.99 mol%	Comparative experimental study of alkaline and PEM electrolysis
Molina et al. (2025) [26]	n.a.	Study of parameters affecting efficiency, focusing on temperature control

n.a. stands for “not available” in the selected reference.

In the case of proton exchange membrane electrolyzers, the purification section is simplified (see Figure 1b)—this is only required for hydrogen that will be applied in the mobility sector. For industrial applications, H₂ exiting from PEM can be used as is.

Despite the relevance of H₂ purification due to its usage as an energy carrier [27], no comprehensive analyses of H₂ purification trains downstream of H₂ production are available in the literature. To fill this gap, the aim of this work is to detail the sequence of purification steps from a process design point of view. Alkaline electrolyzers are considered as a reference, since the purification train is much more complex in this case. Different case studies are discussed, focusing on the alkaline electrolyzer operating pressure (i.e., atmospheric or 30 bar-a) used to produce a H₂ stream with a purity suitable for both industrial and mobility sectors. The process design and methodology are developed within Aspen Plus® simulation environment, to support the electrolyzers’ integration in industrial settings.

2. Tuning of the Thermodynamic Package

Before the process simulation step, the thermodynamic package has to be properly calibrated to accurately predict the system’s behavior under the operating conditions of interest ($0 < P < 35$ bar-a, $10 < T < 100$ °C). The species involved in the system are H₂, O₂, H₂O, KOH, K⁺, OH[−] and H₃O⁺. Both ionic and molecular components have to be included due to the electrolytes’ presence in aqueous solution. As a consequence, the thermodynamic package has to account for the following:

- Physical equilibrium, to describe the vapor–liquid equilibrium in the separation equipment;
- Chemical equilibrium, to describe the electrolytes' dissociation in water.

2.1. Physical Equilibrium: Vapor–Liquid Equilibrium Model

The most appropriate choice for modeling the vapor–liquid equilibrium (VLE) of the mixture of interest is to use a γ - ϕ approach. This approach involves explicating the equality between the fugacities of each component i (Equation (1), the necessary condition to impose equilibrium on mass transfer), as shown in Equation (2), where the i -th fugacity in the vapor phase is a function of the fugacity coefficient $\hat{\phi}_i^V$, while the i -th fugacity in the liquid phase is a function of the activity coefficient γ_i . Unless Poynting's correction is used to take into account the variation of the liquid molar volume with pressure (not available below but considered in process simulation), Equation (2) can be rewritten as in (3) for subcritical compounds or as in (4) for supercritical compounds, with x_i being the molar fraction of component i in the liquid phase; y_i being the molar fraction of component i in the liquid phase; $P_i^0(T)$ as the vapor pressure of component i at temperature T ; γ_i^∞ as the activity coefficient of component i in the liquid phase at infinite dilution; and $H_i(T)$ as the Henry constant of component i at temperature T .

$$\hat{f}_i^V(T, P, \underline{y}) = \hat{f}_i^L(T, P, \underline{x}) \quad (1)$$

$$\hat{\phi}_i^V y_i P = x_i \gamma_i f_i^0 \quad (2)$$

$$\hat{\phi}_i^V y_i P = x_i \gamma_i P_i^0(T) \quad (3)$$

$$\hat{\phi}_i^V y_i P = x_i \frac{\gamma_i}{\gamma_i^\infty} H_i(T) \quad (4)$$

The Henry's components for the present system are H_2 and O_2 .

For the activity coefficient calculation of each component in the liquid phase, the ENRTL-RK model was selected, as it is capable of satisfactorily predicting the phase equilibrium for systems with electrolytes in aqueous solution. On the other hand, as regards the most suitable equation of state for the calculation of the fugacity coefficients in the vapor phase $\hat{\phi}_i^V$, considering the available components in the mixture, different types of models can be chosen:

1. PC-SAFT (perturbed chain SAFT), based on perturbation theory. A generated function is used, which can be distinguished in different terms, representing the repulsive interactions (hard chain, expressed by ψ^{hc}) and attractive interactions (dispersion, expressed by ψ^{disp} , polar, expressed by ψ^{polar} and association, expressed by ψ^{assoc}) [28]. The generated function is related to the residual Helmholtz energy, which, in turn, depends on the compressibility coefficient. Knowing Ψ , it is possible to determine all the thermodynamic functions of interest. In particular, the fugacity coefficient can be calculated.
2. Redlich-Kwong [29] (RK—i.e., the default choice for modeling the vapor phase when ENRTL is selected in Aspen Plus®) or Peng–Robinson (PR) [30], a cubic equation of state.

Each of the two options has been tested by comparing the model predictions with the experimental data available in the literature. Specifically, considering the liquid–vapor equilibrium and the components in the mixture, only isothermal series ($T = 366.459$ K; $T = 422.004$ K; $T = 477.554$ K; $T = 588.667$ K) are available for the binary mixture H_2 – H_2O . On the other hand, no equilibrium data are available for the ternary mixture H_2 – H_2O – O_2 nor for the binary mixture O_2 – H_2O in the temperature and pressure ranges of interest ($T < 373$ K, $P < 30$ bar-a).

Therefore, for each of the temperatures of the isothermal experimental series, the bubble and dew point curves of the binary $\text{H}_2\text{-H}_2\text{O}$ mixture were obtained by the PC-SAFT and PR models, as representatives of cubic equations of state. The obtained results are summarized in Figures 2–5.

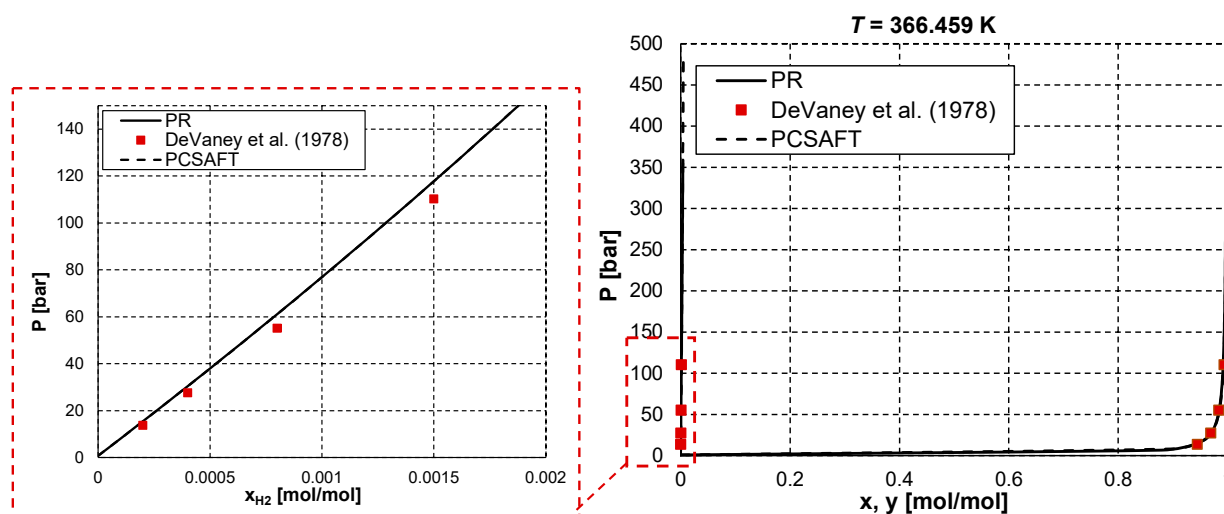


Figure 2. P - x - y diagram of $\text{H}_2\text{-H}_2\text{O}$ mixture at $T = 366.459$ K. Comparison between experimental data (squares) and predictions of PC-SAFT (dashed line) and PR-EoS (solid line) models [31].

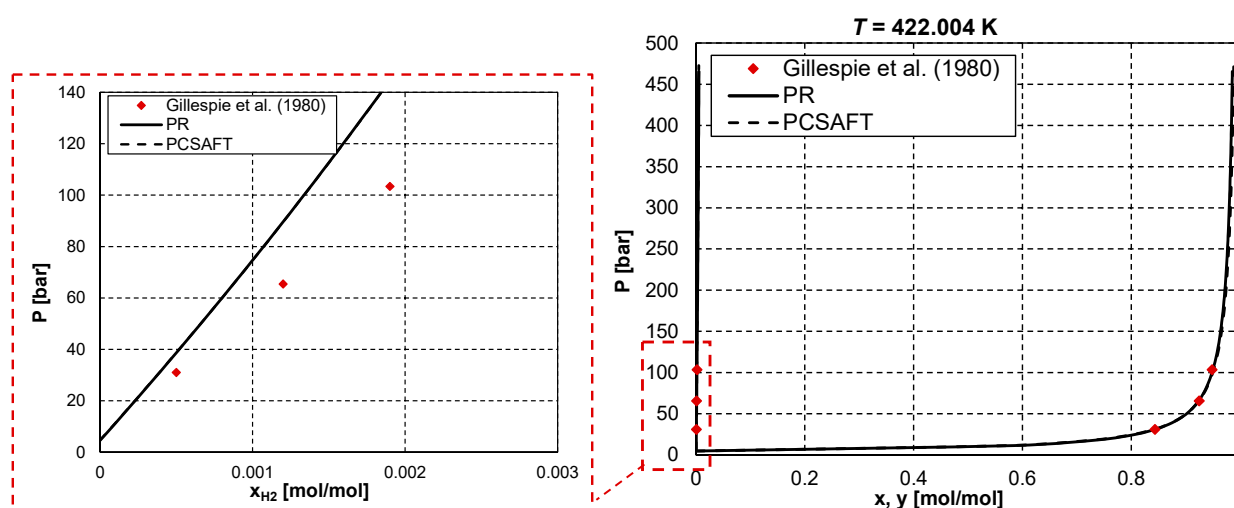


Figure 3. P - x - y diagram of $\text{H}_2\text{-H}_2\text{O}$ mixture at $T = 422.004$ K. Comparison between experimental data (diamonds) and predictions of PC-SAFT (dashed line) and PR-EoS (solid line) models [32].

Both for the bubble curves and the dew point curves, the predictions of the two models overlap. Qualitatively, slight differences can be appreciated at a temperature of 588.667 K; however, this is outside the operating range of interest for the present case studies. A deviation between the model predictions and the experimental data is evident for the liquid phase (bubble curves) starting from $T = 422.004$ K, corresponding to pressure levels greater than 30 bar—see Figure 3. This discrepancy could be due to the use of the NRTL model at relatively high-pressure levels, as it is more suitable for describing the behavior of non-ideal liquid phases at low pressure levels (indicatively less than 10 bar).

In order to quantify the deviation between the two models and the experimental data, the Absolute Average Deviations % (AAD%) were calculated and are reported in Table 2. It can be observed that the AAD% increases with increases in temperature and, consequently, in operating pressure. Although the AAD% is relatively high under high pressure, the

predicted impact of the deviation on the KOH residue under the actual operating pressure (<30 bar) can be ignored (<0.1 ppm). The PC-SAFT model performs better than the PR model at high pressure levels. However, for the operating conditions of interest (pressure lower than 30 bar), no significant differences are evident. For this reason, due to the simpler approach, the Peng-Robinson (PR) equation of state was selected to model the behavior of the vapor phase. PC-SAFT may be more accurate in the supercritical region (such as $T > 500$ K), but the PR model focusing on the low temperature and pressure ranges of this study is sufficient.

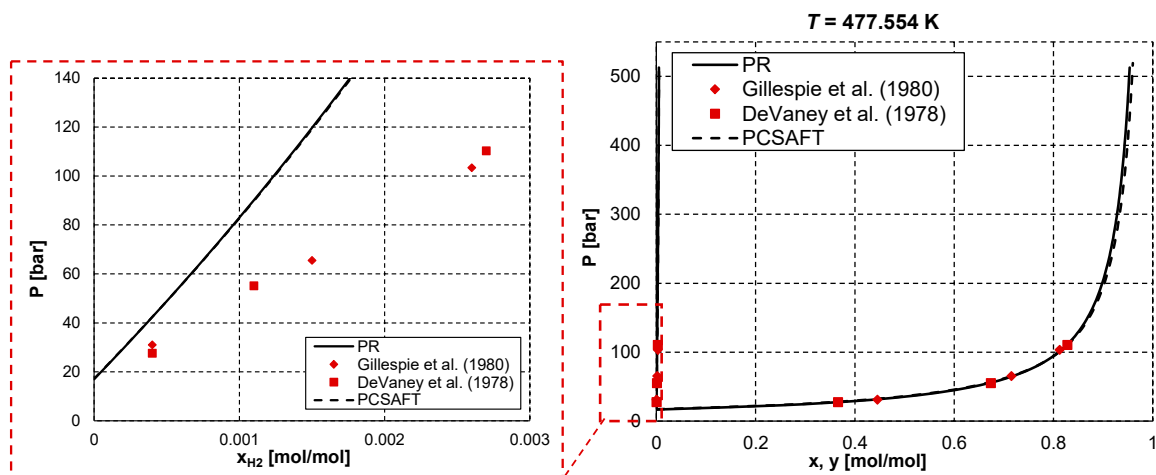


Figure 4. P - x - y diagram of H_2 - H_2O mixture at $T = 477.554$ K. Comparison between experimental data (squares and diamonds) and predictions of PC-SAFT (dashed line) and PR-EoS (solid line) models [31,32].

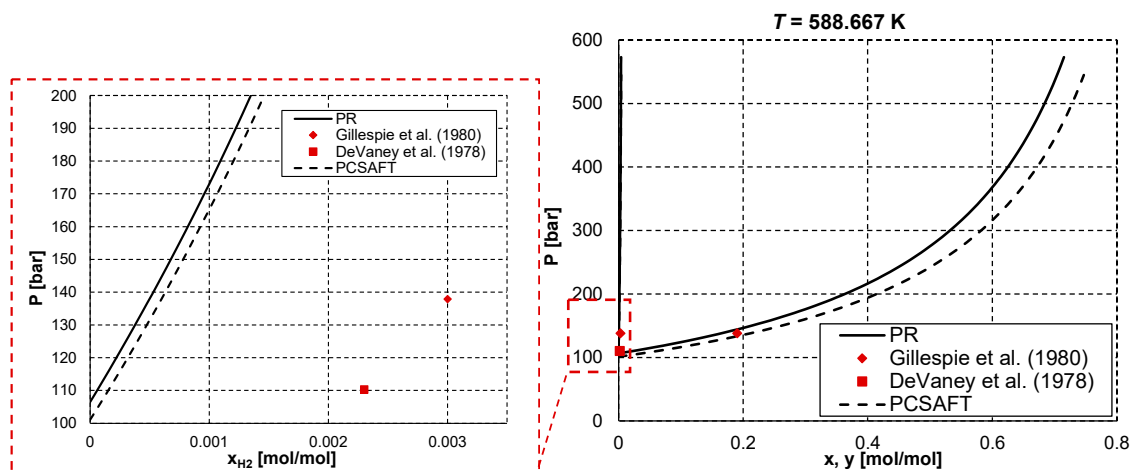


Figure 5. P - x - y diagram of H_2 - H_2O mixture at $T = 588.667$ K. Comparison between experimental data (squares and diamonds) and predictions of PC-SAFT (dashed line) and PR-EoS (solid line) models [31,32].

To achieve higher accuracy in hydrogen compression modeling, where the operating pressure reaches values as high as 30 bar-a, the PR model was selected for compression and finishing sections within the purification train.

Ultimately, the process simulation considers two different sections to model the separation train:

- A main section using the ENRTL-RK model, which is suitable to describe the behavior of electrolytes in aqueous solution at low pressure levels (i.e., the default choice

for modeling the vapor phase when ENRTL as a property package is selected in Aspen Plus®);

- A subsection (subflowsheet) using the PR model, which is suitable to describe the behavior of the gas phase at high pressure levels.

Table 2. Absolute Average Deviations % (AAD%) of PR and PC-SAFT models compared to experimental data at variable temperatures.

Ref.	T [K]	x _{H2}	P _{exp} [bar]	P _{calc,PR} [bar]	P _{calc,SAFT} [bar]	AAD _{PR} [%]	AAD _{SAFT} [%]
DeVaney et al. (1978) [31]	366.459	0.0004	27.58	30.45	30.43	10%	10%
	366.459	0.0008	55.16	61.18	61.14	11%	11%
Gillespie et al. (1980) [32]	422.004	0.0005	31.03	38.76	38.74	25%	25%
	422.004	0.0012	65.50	89.66	89.52	37%	37%
	422.004	0.0019	103.42	119.67	144.56	40%	40%
DeVaney et al. (1978) [31]	477.554	0.0011	55.16	90.13	89.81	63%	63%
	477.554	0.0004	27.579	42.35	42.40	54%	54%
	477.554	0.0027	110.32	220.88	220.05	100%	99%
Gillespie et al. (1980) [32]	477.554	0.0015	65.50	119.67	119.16	83%	82%
	477.554	0.0004	31.03	42.35	42.40	37%	37%
	477.554	0.0026	103.42	211.58	210.75	105%	104%
DeVaney et al. (1978) [31]	588.667	0.0023	110.32	289.93	277.32	163%	151%
Gillespie et al. (1980) [32]	588.667	0.003	137.90	379.19	362.38	175%	163%

2.2. Chemical Equilibrium: Electrolyte Dissociation in Water

The dissolution of KOH in water involves its dissociation into corresponding ions. The correct prediction of ionic dissociation is of paramount importance in process simulation. Only molecular species take part in the liquid–vapor equilibrium and, therefore, in the mass transfer involved in unit operations. A reliable estimation of electrolyte dissociation in water allows for a correct estimate of the separation process performance.

Two different approaches can be used to model ionic dissociation reactions:

- Dissociation approach: This describes the complete dissociation of strong electrolytes in the liquid phase (see (5)). In this case, an equilibrium constant is not required, as the molecular species dissociates completely into the corresponding ions.



- Equilibrium approach: This describes the dissociation equilibrium of electrolytes in the liquid phase (see (6)). In this case, an equilibrium constant is necessary for determining the amount of molecular species dissociated into the corresponding ions.



As KOH is a strong electrolyte, its almost complete dissociation in water is expected. However, the residual KOH content in the outlet gases should be reduced to very low levels: this requires adopting a conservative approach in the simulation phase, to ensure that the product meets the required purity. For this reason, the equilibrium approach was chosen to estimate the ionic dissociation of KOH. As a consequence, the corresponding equilibrium constant is required. Again, two different approaches can be adopted: calculating the K_{eq}

as a function of the thermodynamic properties of the species involved (Equation (7)) or, alternatively, determining it via built-in correlations (as in Equation (8)).

$$\ln K_{eq} = -\frac{\Delta G_{r(aq)}^0}{RT} \quad (7)$$

$$\ln K_{eq} = A - \frac{B}{T} \quad (8)$$

Therefore, for the equilibrium constant estimate to be reliable, it is necessary that the values of the thermodynamic properties of the species involved are correct. Table 3 reports a comparison of the thermodynamic properties of K^+ , OH^- and KOH between the NIST databank (i.e., the physical properties databank of Aspen Plus®) and the literature data, showing a certain discrepancy (about 30%) between the gas phase thermodynamic properties of KOH. For this reason, the enthalpy and Gibbs free energy of formation of KOH in the gas phase were set as those from Barin (1995) [33].

Table 3. Thermodynamic properties of K^+ , OH^- and KOH. Comparison between NIST databank and available literature.

Ref.	Species	Gas Phase		Aqueous Phase		Solid Phase	
		ΔG_f @ 25 °C [J/mol]	ΔH_f @ 25 °C [J/mol]	ΔG_f @ 25 °C [J/mol]	ΔH_f @ 25 °C [J/mol]	ΔG_f @ 25 °C [J/mol]	ΔH_f @ 25 °C [J/mol]
NIST	KOH	−299,999.24	−304,396.46	0	0	−378,678.78	−424,391.49
	K^+	480,879.67	513,916.54	−283,080.56	−252,211.1	0	0
	OH^-	0	−143,414.13	−157,138.91	−229,840.09	0	0
Barin (1995) [33]	KOH	−233,762	−232,630	-	-	−378,858	−424,676
	K^+	-	-	-	-	-	-
	OH^-	-	-	-	-	-	-
Wagman et al. (1982) [34]	KOH	−231,000	−232,600	−440,500	−482,370	−379,080	−424,764
	K^+	-	514,260	−283,270	−252,380	-	-
	OH^-	0	−143,500	−157,244	−229,994	-	-
Pokrovskii and Helgeson (1997) [35]	KOH	-	-	−434,621.37	−469,043.14	-	-
	K^+	-	-	−282,461.84	−252,169.68	-	-
	OH^-	-	-	−157,297.48	−230,023.77	-	-
Hausmann et al. (2021) [36]	KOH	-	-	−437,107	-	-	-
	K^+	-	-	−282,462	-	-	-
	OH^-	-	-	−157,270	-	-	-

To complete the analysis, the K_{eq} needed for KOH dissociation in water has been examined.

Figure 6 shows a comparison between the equilibrium constants proposed in the literature by Hausmann et al. (2021) [36] and Pokrovskii and Helgeson (1997) [35] as a function of temperature. The estimation by Hausmann et al. (2021) [36] (red curve in Figure 6) is the most conservative, being the lowest K_{eq} estimation available.

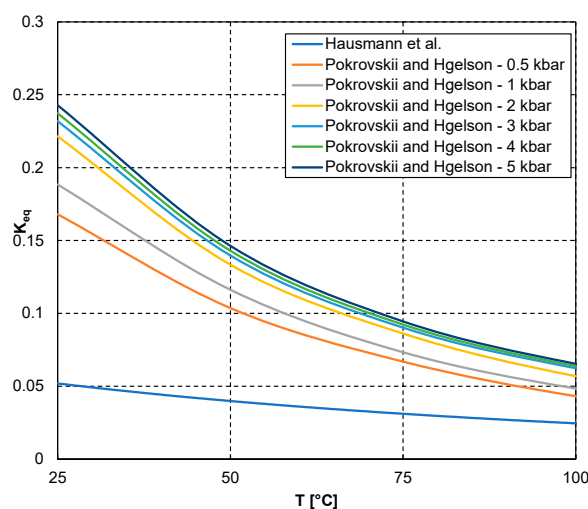


Figure 6. Literature values of equilibrium constant (K_{eq}) as function of temperature (T) [35,36].

As a result, starting from the values of the equilibrium constant as a function of temperature, provided by Hausmann et al. (2021) [36], the parameters of Equation (8), to be implemented in Aspen Plus[®], were regressed and are reported in Equation (9).

$$\ln K_{eq} = 0.0884 - 0.0102T \quad (9)$$

3. Simulation of the H₂ Purification Train

After tuning the thermodynamic package, simulation of the complete purification process was performed in Aspen Plus[®] V11, considering two case studies: an atmospheric pressure alkaline electrolyzer and a high-pressure alkaline electrolyzer, each one described in the following sections. In both cases, the impurity content of H₂ exiting the battery limits was assumed to be as shown in Table 4, making it suitable for use in both the industrial and mobility sectors. These maximum allowable values were fixed considering what is reported in the literature and discussed in Section 1.

Table 4. H₂ impurity content.

Component	Value
O ₂	<5 ppm
H ₂ O	<5 ppm
KOH	<2 ppm

3.1. Atmospheric Pressure Alkaline Electrolyzer

For the atmospheric pressure electrolyzer, two different sections were included in the process simulation: a main section, shown in Figure 7, using the ENRTL-RK model, which is suitable to describe the behavior of electrolytes in aqueous solution at low pressure levels; and a subsection, represented in Figure 8, using the PR model, which is suitable to describe the behavior of the gas phase at high pressure levels.

bottom of the column is mixed with fresh solvent (MAKE-UP) in V-101 and it is partially recycled back to the scrubber unit, partially recycled back to the alkaline electrolyzer.

The gas stream exiting the scrubber must be compressed up to the R-101 operating pressure, i.e., 33 bar-a. The compression from atmospheric pressure to 33 bar-a is performed in three stages, each with a compression ratio of $\beta = 3.19$ (see Figure 8). Downstream of each compression stage, cooling is performed, with subsequent condensate collection (see Figure 8). Cooling down to 35 °C occurs for the first and second stages, while cooling to 45 °C occurs during the third stage. A pressure drop of 10 kPa is assumed for each exchanger.

The gas stream obtained (3A in Figure 8) is heated to a temperature 5 °C higher than its dew point, before being fed to the deOxo reactor (R-101 in Figure 8). In this unit, O₂ is converted into H₂O, assuming an almost complete conversion, as reported in the literature [24,37]. The O₂-free hydrogen stream (4 in Figure 8) is cooled and, after condensate removal (V-105 in Figure 8), is fed to the dryer (V-106 in Figure 8), a PSA unit able to achieve deep water removal [17]. All condensate streams are collected, to be recycled back to the electrolyzer.

Table 5 provides the material balance for the atmospheric pressure electrolyzer purification train. Demineralized water was assumed to be available at 30 °C, as well as the cooling water. The solvent flow rate was selected to ensure that the temperature of the water stream returned to the electrolyzer was around 60 °C, to comply with the operating conditions of the alkaline electrolyzer [19]. Hydrogen compression needs 7375 kJ/kg H₂ to be produced.

As can be observed, the KOH content in the outlet gas is practically zero: the species dissociates completely in the liquid phase without migrating into the gas phase.

It should be noted that a non-negligible quantity of water is collected as a condensed phase (stream COND in Table 5). This stream could be recirculated to the electrolyzer, reducing the make-up of fresh water.

3.2. High-Pressure Alkaline Electrolyzer

For the high-pressure electrolyzer, operating at around 30 bar-a, the hydrogen, whose conditions are specified in Table 6, is assumed to be much purer than that obtained under atmospheric pressure (KOH content is negligible). As a result, the ENRTL-RK property package is no longer required and only the PR model is used. Also, the simulated purification train shown in Figure 9 is simplified: the scheme includes a first cooling combined with gas–liquid separation, oxygen removal and residual water removal. This high-purity product is achieved at the expense of the higher energy intensity of the high-pressure alkaline electrolyzer.

Table 6. Material balance for the process shown in Figure 9.

	UoM	H2-IN	3	2	4	H2-OUT	COND
Flow rate	kmol/h	973	500	971	969	967	3
Temperature	°C	78	31.72	41.87	83	40	40
Pressure	bar-a	30	30	30	30	30	30
Composition	mol%						
H ₂		99.40	-	99.69	99.69	99.999	0.01
O ₂		0.30	-	0.002	0.0005	0.0005	-
H ₂ O		0.30	1	0.30	0.3	0.0005	99.99
KOH		5×10^{-6}	-	-	-	-	-

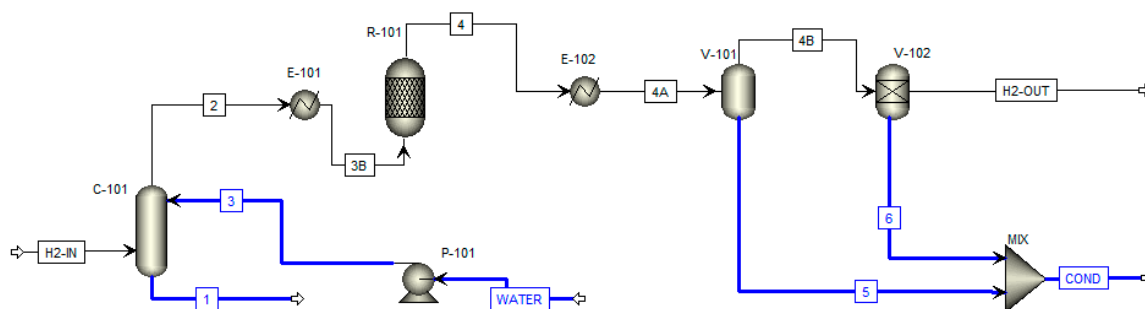


Figure 9. Purification train of H_2 from pressurized electrolyzers. Simulation in Aspen Plus® V11.

With reference to Figure 9, demineralized cold water is pumped and routed to the column, C-101 in Figure 9, to counter-currently contact the H_2 stream. The gaseous top product, stream 2, is heated and fed to R-101 for O_2 abatement. Downstream of the deOx reactor, the gaseous hydrogen stream is dehydrated with the same logic used in Section 3.1. The purified hydrogen is recovered (stream H2-OUT), while condensate is collected to be recycled back to the high-pressure electrolyzer.

Table 6 provides the material balance for the process shown in Figure 9.

In this case, the amount of water circulating in the system is drastically reduced with respect to the atmospheric pressure electrolyzer, again, at the expense of the high operating costs of the reaction unit.

From a process engineering perspective, both for atmospheric and high-pressure alkaline electrolyzers, no critical issues were highlighted in the simulation: the design of the purification train is straightforward. As for the energy balance, in both cases the following are required: cooling water, for the cooling of the process streams above the ambient temperature; electricity, to drive the compressors and electrolyzers; and hot water, for use as the heating medium in the R-101 reactor, whose operating temperature is, however, below $100\text{ }^\circ\text{C}$ (for this reason, low-pressure steam is not necessary). As a result, purification train operating expenses are expected to be negligible in the overall H_2 production economics. The electrolyzer remains the bottleneck for enabling H_2 production at the industrial level.

4. Conclusions

Hydrogen purification downstream of water electrolysis is crucial for enabling H_2 's implementation as an energy carrier on a large scale. Purification trains downstream of PEM electrolyzers are more straightforward due to the higher initial purity of the hydrogen thus produced. For this reason, in this work, hydrogen purification trains downstream of alkaline electrolyzers are analyzed. A detailed technical assessment is performed in Aspen Plus® V11 simulation environment after implementing an appropriate thermodynamic model to ensure accurate predictions. Specifically, for electrolyzers operating under atmospheric pressure, the process simulation includes two sections: one to model low-pressure electrolytes in the liquid phase using the ENRTL-RK model, and one to model high-pressure H_2 -rich gas using the PR model. Two case studies are discussed that involve the practical application of the methodology developed, namely atmospheric pressure alkaline electrolyzers and high-pressure alkaline electrolyzers, and material balances are retrieved for both of these. The high-pressure alkaline electrolyzer allows for the production of purer hydrogen and a simplified purification train, at the expense of the higher energy intensity of the high-pressure reaction section. For an in-depth comparison of the two alternatives, the systems' responses to renewable energy fluctuation should be taken into account. Future work will cover dynamic response simulations involving fluctuations in renewable energy.

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