

Applicability of the common equations of state for modeling hydrogen liquefaction processes in Aspen HYSYS

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Abstract: Liquid hydrogen will likely play a significant role in the future of energy as its applications are growing fast. Due to the low efficiency of the existing liquefaction plants, many studies are dedicated to the liquefaction processes. The accuracy of the simulations crucially depends on the fluid package and prediction of thermodynamic properties. Four common equations of state implemented in Aspen HYSYS used for hydrogen liquefaction, including PR, MBWR, SRK, and BWRS, are investigated to find their accuracy for estimating volumetric and calorimetric properties, that are essential for precise simulation of hydrogen liquefaction processes. Results show that MBWR is the best choice for hydrogen liquefaction processes, which are simulated by Aspen HYSYS. MBWR predicts the thermodynamic properties of hydrogen and parahydrogen very well, in the whole range of temperature and pressure typically met in the liquefaction processes. The MBWR performs well in predicting enthalpy of ortho-para conversion too. Although PR performs better than SRK and BWRS, none of them yields reliable data in low temperatures, so they could not be applied for liquefaction processes. However, they may lead to desirable results for processes that experience higher temperatures range. An innovative, simplified hydrogen liquefaction cycle is developed to be able to capture the mere effect of EOS on essential performance parameters of the liquefaction cycles such as SEC and COP. Applying PR and MBWR to the developed cycle shows that PR compared to MBWR leads to 10% and 4% deviation in SEC and COP, respectively.

keywords: Equation of state, REFPROP, Hydrogen Liquefaction, Modified- Benedict–Webb–Rubin, Aspen HYSYS.

1. Introduction

Liquid hydrogen demands have experienced rapid growth in the past decades' thanks to the increased applications (Ohlig & Decker, 2014). Hydrogen has wide applications in the petroleum and chemical industries, including hydrodealkylation, hydrodesulfurization, and hydrocracking (Qian, Jaubert, & Privat, 2013). Hydrogen could be used as a storage system for renewable energy sources faced with fluctuation during a day, such as solar and

wind (Ahmadi, Mirghaedi, & Roshandel, 2014). Moreover, hydrogen has been introduced as a promising fuel for internal combustion engines because of its renewability, efficient combustion, and nearly zero greenhouse gas emissions (Bai-Gang, Dong-Sheng, & Fu-Shui, 2012). Using hydrogen is involved with many challenges due to the low energy density (Berstad, Stang, & Neksa, 2009). Therefore, it should be solved by different methods such as liquefaction and compression. The boiling

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temperature of hydrogen is as low as 20 K and nearly one-third of its energy contents will be consumed in the liquefaction process (Yuksel, Ozturk, & Dincer, 2017). By the way, it seems to be the best method; therefore, many pieces of research are focused on this method (Asadnia & Mehrpooya, 2017; Berstad et al., 2009; Hammad & Dincer, 2018; Matsuda & Nagami, 1997; Mehrpooya, Sadaghiani, & Hedayat, 2020; Nandi & Sarangi, 1993; Sadaghiani & Mehrpooya, 2017; Valenti & Macchi, 2008; J.-H. Yang et al., 2019; Yuksel et al., 2017). Hydrogen clean energy sector, including using hydrogen in cars, buses, etc. are proliferated, so liquid hydrogen will likely play a significant role in transportation (Ohlig & Decker, 2014; Rösler, van der Zwaan, Keppo, & Bruggink, 2014). Liquid hydrogen is used directly by the aerospace industry as a fuel, and electronics and metallurgical sectors for specific production processes. Besides end-use, the liquid form of hydrogen for transportation and storage is economical, especially over long distances (Sherif, Zeytinoglu, & Veziroğlu, 1997).

For the development of hydrogen industries, accurate predictions of the thermodynamic properties of hydrogen are essential (Sakoda et al., 2010). Thermodynamic models employ the equation of state (EOS) as the relationship between pressure, temperature, and density (McCarty, Hord, & Roder, 1981) to determine how the fluid behavior deviates from that of an ideal (J.-H. Yang et al., 2019). EOS's desired criteria are accuracy, consistency, computational speed, robustness, and predictive ability outside of the fitted domain (Wilhelmsen et al., 2017).

At low temperatures and high densities, hydrogen exhibits quantum behavior; therefore, in cryogenics applications, EOS must be modified appropriately to consider this context (Sadus, 1992). One of these modifications for cubic EOSs is volume translation, which had been used since the pioneering work of André Péneloux to improve the description of volumetric properties. This technique is widely applied in process and product design, where an EOS is used to estimate densities and other thermodynamic properties (Frey et al., 2007; Jaubert, Privat, Le Guennec, & Coniglio, 2016). The calorimetric and volumetric properties of fluids for processes like compression, expansion, and heat exchange in the cryogenic region are

essential (Jacob W Leachman, Jacobsen, Lemmon, & Penoncello, 2017). The change of heat capacity and enthalpy influences the calorimetric properties, which affects the overall efficiency of the liquefaction process. The volumetric properties, such as vapor pressure and density affect the pressure changer equipment (J.-H. Yang et al., 2019). To conduct a precise simulation of the hydrogen liquefaction process, choosing a proper EOS that could yield satisfying thermodynamic properties results, is essential. Therefore, in this study, the choice of appropriate EOS for hydrogen liquefaction processes, which are simulated using Aspen HYSYS, is investigated.

The Accuracy of Aspen HYSYS has been proved in many studies around hydrogen liquefaction and similar areas (Ansarinasab, Mehrpooya, & Mohammadi, 2017; Ghorbani, Hamed, Shirmohammadi, Hamed, & Mehrpooya, 2016; Nouri, Miansari, & Ghorbani, 2020; Sadaghiani, Mehrpooya, & Ansarinasab, 2017; Seyam, Dincer, & Agelin-Chaab, 2020; Skaugen, Berstad, & Wilhelmsen, 2020; Taleshbahrami & Saffari, 2010; Thomas, Ghosh, & Chowdhury, 2011). Therefore, it is selected as the simulation tool here. Aspen HYSYS is developed by Aspen Tech and includes a set of subroutines to estimate physical properties and liquid-vapor phase equilibrium, heat and material balances, and simulating chemical engineering equipment (Belkadi & Smaili, 2018). It contains over 30 thermodynamic models and has extensive databank and powerful methods for fluid properties computation (Asadnia & Mehrpooya, 2017).

In 1949, Redlich and Kwong (Redlich & Kwong, 1949) introduced one of the most successful PVT relationships. Later, Soave (Soave, 1972) modified the Redlich-Kwong (RK) EOS successfully. The Soave-Redlich-Kwong (SRK) EOS has found widespread applications in the chemical and petroleum industries. Krasae-In et al. (Krasae-In, Stang, & Neksa, 2010) proposed a large-scale hydrogen liquefaction plant using a multi-component refrigeration system. They adopted the SRK as EOS because of its popularity, simplicity, and fast computation through the PRO/II software package. They found that the SRK model is quite the same as that of

REFPROP¹ V.8 and claimed that the SRK model is adequate for the cryogenic regions. Krasae-In (Krasae-in, 2014) simulated a large-scale liquefaction plant using SRK while he confirming that Peng-Robinson (PR) yields quite similar results. Krasae-in et al. (Krasae-in, Bredesen, Stang, & Neksa, 2011) simulated a hydrogen liquefaction test rig utilizing SRK as a fluid package. Moreover, the SRK equation of state has been applied to many studies around liquid natural gas (Hammer et al., 2003; J. B. Jensen & Skogestad, 2006; Myklebust, 2010; Nogal, Kim, Perry, & Smith, 2008).

PR is the most widely used Cubic EOS in the industry. Since its publication in 1976, PR has been adopted as one of the most useful models for thermodynamic and volumetric calculations in both industrial and academic fields (Lopez-Echeverry, Reif-Acherman, & Araujo-Lopez, 2017). Many pieces of research are concentrated on the correction of PR for different materials and conditions (Abudour, Mohammad, Robinson Jr, & Gasem, 2013; Feyzi, Seydi, & Alavi, 2010; Haghtalab, Mahmoodi, & Mazloumi, 2011; Le Guennec, Lasala, Privat, & Jaubert, 2016; Le Guennec, Privat, & Jaubert, 2016; Lin & Duan, 2005). Yin et al. (Yin & Ju, 2020) presented a new cycle for hydrogen liquefaction. They used Aspen properties databanks and PR as thermo-physical properties and EOS, respectively. A novel hydrogen liquefaction process was investigated by (Asadnia & Mehrpooya, 2017). They simulated the process using Aspen HYSYS and adopted PR as EOS. Sadaghiani et al. (Sadaghiani & Mehrpooya, 2017; Sadaghiani et al., 2017) used PR as a fluid package for simulation of hydrogen liquefaction through Aspen HYSYS. Ghorbani et al. (Ghorbani, Mehrpooya, Aasadnia, & Niasar, 2019) developed a novel structure for liquefaction of 290 TPD hydrogen that consists of an absorption refrigeration system, organic Rankine cycle, and parabolic solar dishes beside the basic liquefaction cycle. They simulated the process in Aspen HYSYS V.9 and used PR as a fluid package. Ebrahimi et al. (Ebrahimi, Ghorbani, & Ziabasharhagh, 2020) performed pinch and sensitivity analyses

for the hydrogen liquefaction process in a hybridized system, including biomass gasification and air separation. They applied the pinch method on each multi heat exchanger (HX) of the hydrogen liquefaction process. Aspen HYSYS and MATLAB were used for simulation, and PR was adopted as EOS. Moreover, PR has been chosen as EOS in many other studies around hydrogen liquefaction (Mehrpooya et al., 2020; Seyam et al., 2020).

The Benedict-Webb-Rubin (BWR) expressions are based on the pioneering work of Benedict, Webb, and Rubin (1940, 1942) (Reid, Prausnitz, & Poling, 1987). The Modified Benedict-Webb-Rubin (MBWR) and Benedict-Webb-Rubin-Starling (BWRs) are two modifications of BWR (Reid et al., 1987). MBWR originally is proposed by Jacobsen and Stewart for nitrogen (Jacobsen & Stewart, 1973) and employed by Younglove (Younglove, 1982) for hydrogen. Although using the BWR series encounters some difficulties in the computation process, it is preferred in some cases because of its high precision (Thomas, Dutta, Ghosh, & Chowdhury, 2012). This EOS was implemented in the three past releases of REFPROP. Valenti and Macchi (Valenti & Macchi, 2008) used the BWRs for all hydrogen forms, in their work on a large-scale hydrogen liquefier. They used Aspen Plus for simulation and validated the results against the existing hydrogen liquefier operating parameters located in Ingolstadt, Germany. Absorption properties of hydrogen, including fugacity and compressibility factor, were evaluated by Zhou and Zhou (Zhou & Zhou, 2001) using the SRK (Soave, 1972) and BWR (Benedict, 1940).

Yang et al. (J. C. Yang & Huber, 2008; Zheng et al., 2010) used REFPROP for analyzing processes containing hydrogen. Valenti and Macchi (Valenti, Macchi, & Brioschi, 2012) investigated the influence of thermodynamic models. They developed a fluid file for REFPROP and used it as a reference case for comparison against four other considered modeling alternatives. Cardella et al. (Cardella, Decker, & Klein, 2017; Cardella, Decker, Sundberg, & Klein, 2017) used PR for hydrocarbons and nitrogen and REFPROP for pure helium, neon, and the isomeric forms of hydrogen.

Sakoda et al. (Sakoda et al., 2010) conducted a review on the thermodynamic properties of hydrogen, based on the existing equations. Thermodynamic properties of hydrogen are studied by investigating eleven

¹ Reference Fluid Thermodynamic and Transport Properties Database.

REFPROP provides the most accurate thermophysical property models for a variety of industrially important fluids and fluid mixtures, including accepted standards.

EOSs to predict different properties (Nasrifar, 2010). Ghanbari et al. (Ghanbari, Ahmadi, & Lashanizadegan, 2017) performed a comparison between the most successful cubic EOSs, i.e., PR and SRK from the modification perspective. Thermodynamic and transport properties of normal hydrogen and parahydrogen are reviewed by Jacobsen et al. (Jacobsen, Leachman, Penoncello, & Lemmon, 2007; Jacob W Leachman, Jacobsen, Penoncello, & Huber, 2007). Thomas et al. (Thomas et al., 2012) investigated the applicability of some simpler EOSs for modeling helium systems and compared the results to the MBWR.

In this research, four common EOSs in the literature, including two cubic EOSs, PR and SRK, and two non-cubic EOSs, MBWR, and BWRS are investigated to determine the best EOS for the future studies which are conducted by Aspen HYSYS. Although utilization of the volume translation method is provided in Aspen HYSYS for cubic EOSs through the “generalized cubic equation of state (GCEOS),” it is not applied here. The main goal is to compare the default EOSs implemented in the Aspen HYSYS without additional manipulating as they are employed to the common researches in this field (Ansarinassab et al., 2017; Asadnia & Mehrpooya, 2017; Ebrahimi et al., 2020; Ghorbani et al., 2019; Mehrpooya et al., 2020; Sadaghiani & Mehrpooya, 2017; Sadaghiani et al., 2017). The research's novelty is in the complete investigation of the common EOSs, which has been used for simulation of hydrogen liquefaction through different studies using Aspen HYSYS, the most popular simulation tool for hydrogen liquefaction processes. Due to the occurring heat exchange between MR streams and hydrogen streams through heat exchangers, investigating the mere effect of the EOS that is applied to the hydrogen streams is not normally possible. On the other hand, employing a unit EOS to MR and hydrogen isomers could not yield desirable results. Moreover, using a unit EOS for the whole process impose more restrictions on the simulation. In this study, an innovative, simplified configuration is developed to be able to capture the mere effect of EOS on essential performance parameters such as coefficient of performance (COP) and specific energy consumption (SEC). Therefore, it may be possible to survey the mere effect of the EOS that is dedicated to hydrogen and parahydrogen, separately.

REFPROP is considered as the base case for comparison since its accuracy has been validated through different studies (Cardella, Decker, Sundberg, et al., 2017; Valenti et al., 2012). The deviation of the estimated properties by different EOSs to the corresponding reference properties is crucial. This index has been termed as “deviation” in the rest of the paper and is defined as follows:

$$\text{deviation} = \left(\frac{\text{property}_{\text{predicted}} - \text{property}_{\text{reference}}}{\text{property}_{\text{reference}}} \right) \times 100\%$$

where $\text{property}_{\text{reference}}$ and $\text{property}_{\text{predicted}}$ stand for the desired property and the estimated property in order.

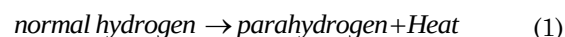
2. Ortho-para Conversion

Bonhoeffer and Harteck, about the same time as Eucken and Hiller, observed changes in property values in the samples of hydrogen, which were held at low temperatures for several hours. Since they were nearly isolated, the only possible cause was a conversion of the molecules from one spin state to another spin state (Jacob William Leachman, Jacobsen, Penoncello, & Lemmon, 2009). This observation came to no surprise when Heisenberg and Hund explained the existence of two different spin states for helium, orthohelium, and parahelium and postulated a similar occurrence for hydrogen (Farkas, 1935). Bonhoeffer and Harteck chose the names of orthohydrogen and parahydrogen. Variation in the properties of hydrogen isomers is attributed to the orientation of the nuclear spin (Jacob William Leachman et al., 2009). In general, more substantial discrepancies in the properties of orthohydrogen and parahydrogen occurs in those related to specific heat capacity such as enthalpy and entropy (Jacobsen et al., 2007). The equilibrium composition of orthohydrogen and parahydrogen varies with temperature. At room temperature and above, hydrogen has a composition of 75 % orthohydrogen and 25 % parahydrogen, which is called normal hydrogen (Farkas, 1935).

The ortho-para conversion is very slow, and if not catalyzed, the natural conversion could not proceed with proper speed. In this situation, the portion of orthohydrogen is higher than the equilibrium concentration; therefore, conversion occurs in the storage vessel. Typically, hydrogen liquefiers are designed to produce liquid hydrogen with a

parahydrogen content of more than 95% (Gupta, Basile, & Veziroglu, 2016). The ortho-para conversion at the normal boiling point generates heat of conversion equal to 703 kJ/kg. Thus, when hydrogen gas with a parahydrogen concentration of 25% is liquefied and stored, ortho-para conversion gradually occurs, generating heat of conversion equal to 527 kJ/kg. Since liquid hydrogen's latent heat of vaporization is 446 kJ/kg, substantial boil-off occurs during the long-term storage, which means that normal liquid hydrogen might be vaporized entirely even in a perfectly insulated vessel (Gupta et al., 2016; Verfondern, 2008). Orthohydrogen does not exist as pure fluid and its maximum fraction could reach 75%. The proper EOS for the orthohydrogen can just be estimated from mixing rules (Sakoda et al., 2010). In most studies conducted in the field of hydrogen liquefaction, only parahydrogen and normal hydrogen are involved. The Ortho-para conversion achieves technically by packing the hydrogen side of the heat exchangers with an appropriate catalyst (Asadnia & Mehrpooya, 2017), so theoretically, conversion of the ortho-para could be simulated through a conversion

reactor as defined in equation 1 (Asadnia & Mehrpooya, 2017; Noh et al., 2017; Sadaghiani & Mehrpooya, 2017; Sadaghiani et al., 2017).



The conversion progress depends on the hydrogen temperature (Asadnia & Mehrpooya, 2017 and is considered as follows (Asadnia & Mehrpooya, 2017):

$$\text{Conversion}(\%) = C_0 + (C_1 \times T) + (C_2 \times T^2) \quad (2)$$

where C_0 , C_1 and C_2 are conversion coefficients, and T is hydrogen temperature (K).

The conversion coefficients are adjusted, such that the fraction of parahydrogen in the output reactor equals experimental data (J. Jensen, Stewart, Tuttle, & Brechna, 1980). Table 1 lists the temperature and parahydrogen concentration in the inlet of converters. Moreover, the equilibrium concentration of the parahydrogen in the outlet of converters and the conversion coefficients are indicated.

Table 1. Conversion coefficient applied to the conversion reactors used for modeling ortho-para conversion

Conversion ID	Input temperature (°C)	Input parahydrogen concentration (%)	Equilibrium concentration of the parahydrogen in the outlet (%)
O-P Converter 1	-195	25 (normal hydrogen)	33
O-P Converter 2	-240	33	93.34
Conversion coefficients			
Conversion ID	C_0	C_1	C_2
O-P Converter 1	37.67	-0.06	0.0001
O-P Converter 2	94.2	-2.17	0.0497

3. Methodology

Here the capability of four common EOSs available in the Aspen HYSYS, including; PR, MBWR, BWRS, and SRK, are investigated for predicting volumetric and calorimetric properties of hydrogen and parahydrogen, including density, vapor pressure, specific heat capacity, enthalpy, and entropy. Volumetric behaviors of parahydrogen and hydrogen are the same (Pitzer, Lippmann, Curl Jr, Huggins, & Petersen, 1955) since where the volumetric properties are discussed, just the properties for one of them are reported (J.-H. Yang et al., 2019).

For validation of the results, experimental data presented by Leachman et al. (Jacob W Leachman et al., 2017) and REFPROP, which

its accuracy had been tested through different studies, are employed. Hydrogen in the liquefaction process normally experiences a continuous wide range of temperatures from 25 °C to -252.5 °C. However, the experimental data are reported only for the specific pressures and temperatures, so that it might tolerate some restriction on the range of data. By the way, as the first step, the data acquired from REFPROP are compared to the experimental data presented by Leachman et al. (Jacob W Leachman et al., 2017) for double-check. The results are shown in Table 2 and Table 3 for 1 MPa and 10 Mpa, through the common temperature range of hydrogen liquefaction processes; 20 K to 300 K.

Table 2. Enthalpy, entropy, and density from REFPROP and Ref. (Jacob W Leachman et al., 2017) for para-hydrogen.

Parahydrogen													
P=1 MPa						P=10 MPa							
(Jacob W Leachman et al., 2017)						REFPROP		(Jacob W Leachman et al., 2017)				REFPROP	
T	ρ	h	s	ρ	h	s	ρ	h	s	ρ	h	s	
(K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	
20	72.292	6.05	-0.323	72.117	4.4267	-0.2744	79.907	98.919	-1.5669	79.872	97.19	-1.5223	
30	55.303	140.91	4.992	54.75	141.5	5.0914	72.488	190.02	2.0849	72.361	189.01	2.1353	
40	7.27	590.55	18.848	7.2282	590.59	18.902	63.191	310.51	5.5316	63.037	309.91	5.5792	
50	5.2796	719.68	21.737	5.2618	719.08	21.767	52.666	456.8	8.787	52.542	456.12	8.8221	
60	4.2279	838.39	23.903	4.2168	837.47	23.92	42.864	617.03	11.707	42.752	616.02	11.728	
70	3.5511	955.49	25.708	3.5427	954.38	25.718	35.294	777.4	14.18	35.216	775.31	14.179	
80	3.0716	1075.5	27.309	3.0647	1074.3	27.316	29.873	933.62	16.266	29.828	930.44	16.246	
90	2.7113	1201.3	28.79	2.7054	1200.2	28.795	25.951	1088.1	18.086	25.92	1084.6	18.058	
100	2.4293	1334.5	30.193	2.4243	1333.7	30.199	23.007	1244.2	19.73	22.977	1241	19.703	
110	2.202	1475.6	31.537	2.1977	1475.2	31.545	20.714	1403.7	21.25	20.682	1401.3	21.229	
120	2.0145	1623.9	32.828	2.0108	1624	32.837	18.872	1567.4	22.674	18.839	1565.9	22.659	
130	1.8571	1778.4	34.064	1.8538	1778.7	34.074	17.356	1734.7	24.013	17.321	1734.1	24.004	
140	1.7229	1937.6	35.243	1.72	1938	35.253	16.083	1904.8	25.274	16.048	1905	25.268	
150	1.607	2099.8	36.362	1.6045	2100.2	36.371	14.997	2076.5	26.458	14.962	2077.4	26.456	
160	1.506	2263.8	37.421	1.5038	2264.2	37.428	14.057	2248.8	27.57	14.024	2250.1	27.57	
170	1.417	2428.4	38.419	1.4151	2428.7	38.425	13.235	2420.7	28.612	13.203	2422.5	28.614	
180	1.3381	2592.7	39.358	1.3363	2592.9	39.363	12.508	2591.5	29.589	12.479	2593.7	29.592	
190	1.2676	2756.2	40.242	1.266	2756.3	40.245	11.862	2760.8	30.504	11.834	2763.3	30.508	
200	1.2042	2918.3	41.073	1.2028	2918.4	41.076	11.282	2928.1	31.362	11.257	2931	31.368	
210	1.1468	3078.9	41.857	1.1456	3079.1	41.86	10.759	3093.4	32.169	10.735	3096.7	32.176	
220	1.0948	3237.9	42.596	1.0936	3238.1	42.599	10.284	3256.6	32.928	10.262	3260.3	32.936	
230	1.0472	3395.2	43.296	1.0462	3395.6	43.298	9.8504	3417.8	33.645	9.8308	3421.8	33.654	
240	1.0037	3550.9	43.959	1.0028	3551.4	43.961	9.4534	3577.1	34.323	9.4356	3581.4	34.333	
250	0.96364	3705.2	44.588	0.96281	3705.8	44.591	9.0883	3734.7	34.966	9.0721	3739.3	34.977	
260	0.92667	3858.2	45.188	0.92592	3858.9	45.191	8.7512	3890.7	35.578	8.7365	3895.5	35.589	
270	0.89245	4010	45.761	0.89177	4010.7	45.764	8.4389	4045.2	36.161	8.4256	4050.2	36.173	
280	0.86067	4160.7	46.31	0.86005	4161.4	46.312	8.1487	4198.5	36.718	8.1367	4203.6	36.73	
290	0.83109	4310.6	46.835	0.83052	4311.2	46.837	7.8784	4350.7	37.253	7.8675	4355.8	37.264	
300	0.80348	4459.6	47.341	0.80296	4460.2	47.342	7.6258	4502	37.765	7.616	4507.1	37.777	

Table 3. Enthalpy, entropy, and density from REFPROP and Ref. (Jacob W Leachman et al., 2017) for hydrogen.

Hydrogen												
T	P=1 MPa						P=10 MPa					
	(Jacob W Leachman et al., 2017)			REFPROP			(Jacob W Leachman et al., 2017)			REFPROP		
	ρ	h	s	ρ	h	s	ρ	h	s	ρ	h	s
(K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)	(kg/m ³)	(kJ/kg)	(kJ/kg-K)
20	72.405	5.11	-0.3681	72.117	7.46	-0.2689	79.926	98.04	-1.6045	99.133	79.89	-1.6013
30	55.881	137.17	4.8439	54.75	144.54	5.0973	72.579	188.51	2.0253	72.361	192.05	2.1411
40	7.2758	592.02	18.819	7.2282	593.4	18.901	63.362	307.9	5.4399	63.037	312.71	5.5785
50	5.2763	721.64	21.72	5.2618	721.29	21.753	52.836	454.25	8.6959	52.542	458.33	8.8083
60	4.2248	839.21	23.866	4.2168	838.13	23.879	42.925	614.95	11.624	42.752	616.68	11.686
70	3.5489	952.55	25.613	3.5427	951.27	25.619	35.295	772.97	14.062	35.216	772.2	14.08
80	3.07	1064.7	27.111	3.0647	1063.5	27.114	29.86	922.12	16.055	29.828	919.59	16.045
90	2.7102	1177.3	28.437	2.7054	1176.3	28.441	25.937	1063.9	17.726	25.92	1060.6	17.704
100	2.4285	1291.4	29.639	2.4243	1290.6	29.643	22.994	1201.2	19.172	22.977	1197.8	19.147
110	2.2014	1407.7	30.747	2.1977	1407.1	30.751	20.703	1336.2	20.459	20.682	1333.1	20.435
120	2.0141	1526.4	31.78	2.0108	1525.9	31.784	18.862	1470.3	21.626	18.839	1467.8	21.606
130	1.8568	1647.6	32.75	1.8538	1647.3	32.754	17.347	1604.5	22.7	17.321	1602.7	22.684
140	1.7226	1771.3	33.666	1.72	1771.1	33.671	16.075	1739.2	23.699	16.048	1738.1	23.686
150	1.6068	1897.3	34.536	1.6045	1897.3	34.541	14.99	1874.9	24.634	14.962	1874.4	24.626
160	1.5058	2025.6	35.364	1.5038	2025.7	35.368	14.051	2011.4	25.516	14.024	2011.7	25.511
170	1.4169	2155.9	36.154	1.4151	2156.2	36.158	13.23	2149.1	26.35	13.203	2150	26.348
180	1.338	2288.1	36.909	1.3363	2288.4	36.914	12.504	2287.7	27.143	12.479	2289.2	27.143
190	1.2675	2421.9	37.632	1.266	2422.3	37.637	11.858	2427.3	27.897	11.834	2429.3	27.9
200	1.2041	2557.2	38.326	1.2028	2557.7	38.331	11.279	2567.8	28.618	11.257	2570.2	28.622
210	1.1468	2693.8	38.993	1.1456	2694.4	38.997	10.756	2709.1	29.307	10.735	2712	29.313
220	1.0947	2831.6	39.634	1.0936	2832.2	39.638	10.281	2851.2	29.968	10.262	2854.3	29.975
230	1.0472	2970.4	40.251	1.0462	2971.1	40.255	9.8485	2993.9	30.603	9.8308	2997.3	30.61
240	1.0037	3110.2	40.846	1.0028	3110.8	40.849	9.4519	3137.2	31.212	9.4356	3140.8	31.221
250	0.96362	3250.7	41.42	0.96281	3251.3	41.422	9.087	3281	31.799	9.0721	3284.8	31.808
260	0.92666	3392	41.974	0.92592	3392.6	41.976	8.7501	3425.2	32.365	8.7365	3429.2	32.374
270	0.89244	3533.8	42.509	0.89177	3534.4	42.511	8.4381	3569.8	32.911	8.4256	3573.9	32.92
280	0.86066	3676.2	43.027	0.86005	3676.7	43.028	8.1481	3714.7	33.438	8.1367	3718.9	33.447
290	0.83108	3819	43.528	0.83052	3819.5	43.529	7.8779	3859.9	33.947	7.8675	3864.1	33.956
300	0.80348	3962.2	44.013	0.80296	3962.7	44.014	7.6254	4005.2	34.44	7.616	4009.6	34.449

As it could be seen in Table 2 and Table 3, for hydrogen and parahydrogen in the considered range, there exists a negligible discrepancy in the data such that the deviation is nearly less than 1% for the whole range except enthalpy and entropy in 20 K and 30 K for 1 MPa. Although the deviation could go higher in 20 K and 30 K, it could be ignored due to the low values of enthalpy and entropy in this range. As the temperature increases, the inconsistency is reduced to less than 0.1%. Since the results are compatible with experimental data of Ref. (Jacob W Leachman et al., 2017), it is found that REFPROP could be a useful tool for validation. It should be mentioned that REFPROP could yield data continuously while the experimental data are available just in the specific points. The data for density, vapor pressure, enthalpy, entropy, and specific heat capacity of the four considered EOSs are compared with the data extracted from REFPROP as the reference case.

3.1 Density

Estimated densities for the considered cases are compared to the reference case. The results are presented in Figure 1 and Figure 2. The estimated densities for parahydrogen and hydrogen using PR, SRK, and BWRS in low temperatures are not compatible with REFPROP, while the MBWR experiences excellent consistency in this zone. The density of the parahydrogen and hydrogen estimated by REFPROP and MBWR are the same, so here only the results for hydrogen are presented through Figure 1 and Figure 2 for 1 MPa and 10 MPa. It deserves to note that this is not true for the BWRS, PR, and SRK. In other words, these EOSs estimate different values for the parahydrogen and hydrogen density. The difference between the two estimated values could go up to 26% in low temperatures, such as 30 K, but it decreased to less than 1% at higher temperatures.

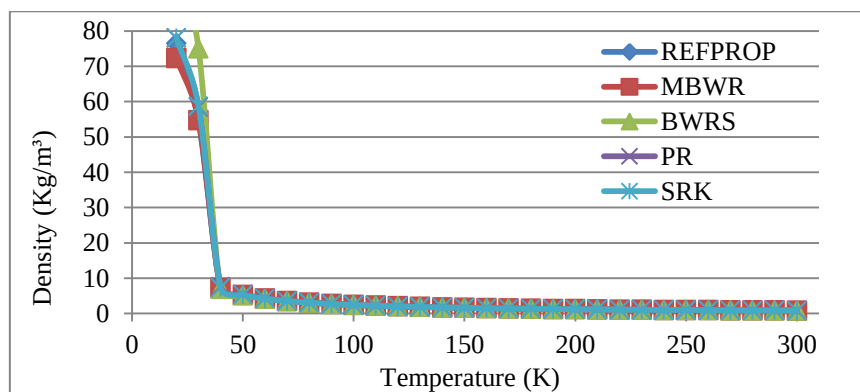


Figure 1. Estimated densities for hydrogen in 1 MPa.

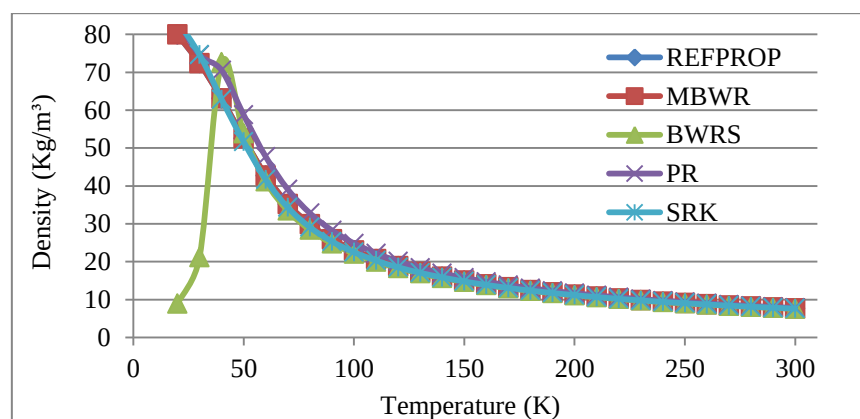


Figure 2. Estimated densities for hydrogen in 10 MPa.

For both 1 MPa and 10 MPa throughout the temperature range, MBWR leads to precise results for density such that the deviation is less than 0.05%. Among the three other EOSs,

SRK performs better for estimating density in 1 MPa and 10 MPa. For the SRK, BWRS, and PR in 1 MPa, the deviation was reduced to lower than 1% in 50 K, 60 K, and 120 K,

respectively. For 10 MPa, the deviation is higher, and it reaches less than 1 % for the SRK in 170 K and the BWRS and PR in 240 K. For PR, the deviation throughout the temperature range of 20-300 K is higher than 2%.

It could be seen that as the pressure increases or temperature decreases, the deviations increase, which is compatible with physical laws. The most significant deviation values in estimating density by Aspen HYSYS and considered EOSs, are for lower temperatures and higher pressures. As the temperature increases, the results for all three EOSs are getting more precise. In general, it could be said that all considered EOSs could

perform well except in temperature lower than 40 K; however, throughout the range, the MBWR leads to more accurate results.

3.2 Vapor pressure

Vapor pressure for considered cases near the boiling point is reported in Figure 3. The data predicted by considered EOSs show excellent compatibility with experimental data. It should be noted that the deviation for BWRS is more prominent than other EOSs. For vapor pressure as a volumetric property, the hydrogen behavior is similar to parahydrogen (Pitzer et al., 1955), so here only the data related to parahydrogen are reported.

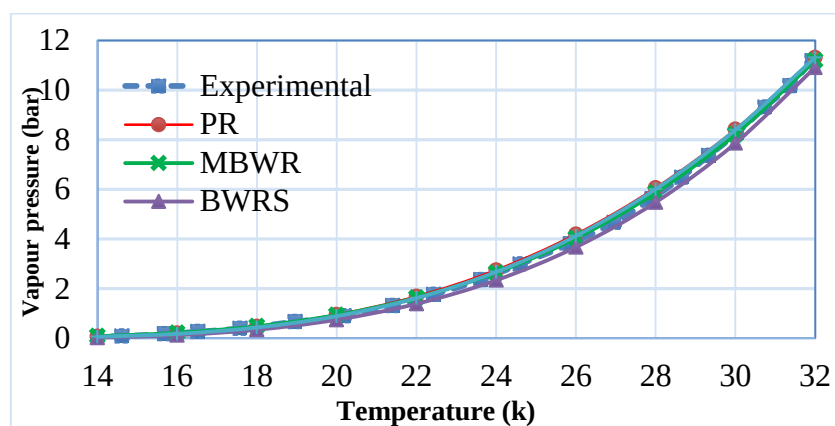


Figure 3. Vapor pressure predicted for parahydrogen by four considered EOSs through Aspen HYSYS and experimental data.

3.3 Enthalpy and entropy

The enthalpy and entropy for considered EOSs are compared in Tables 4-7. For removing the effect of reference values in different models, the enthalpy and entropy increments (Δh & Δs) are analyzed and reported. The enthalpy and entropy values are essential in energy and exergy analyses. At the same time, the other thermo-physical properties are not as crucial as these properties.

For parahydrogen, MBWR is the best choice. Although deviations for this EOS will increase for higher pressures and lower temperatures, it performs well enough through the whole range of temperature and pressure. The average deviation for MBWR is nearly less than 0.05% for both enthalpy and entropy. For

1 MPa pressure, the estimated enthalpies and entropies for the PR, BWRS, and SRK are almost identical. These models for both entropy and enthalpy could yield acceptable results in higher temperatures, while in low temperatures, they lead to high deviations. Although the pressure could affect the deviations proportionally, its effect is lower than that of the temperature. In 10 MPa, the PR and SRK are nearly the same and significantly better than the BWRS. In other words, pressure has a positive impact on the estimated results by the BWRS and a negative effect on the calculated results by the PR and SRK. For 1 MPa and 10 MPa in temperatures lower than 120 K, they lead to deviations higher than 5%.

Table 4. Estimated enthalpy and entropy increments for parahydrogen in 1 MPa.

T ₂ -T ₁ (K)	Parahydrogen, P= 1MPa									
	Δh (kJ/kg)					Δs (kJ/kg-K)				
	REFPROP	MBWR	BWRS	PR	SRK	REFPROP	MBWR	BWRS	PR	SRK
30-20	137.073	137.077	232.22	246.39	259.96	5.3658	5.3664	9.2834	10.763	10.3066
40-30	449.09	448.873	546.19	477.79	489.5	13.8106	13.8039	16.6937	13.59	14.9591
50-40	128.49	128.184	188.81	186.21	187.04	2.865	2.8584	4.2077	4.1501	4.167
60-50	118.39	118.156	175.75	174.94	175.31	2.153	2.1496	3.1977	3.1826	3.19
70-60	116.91	116.93	169.98	169.7	169.89	1.798	1.7981	2.6151	2.6107	2.613
80-70	119.92	120.13	166.58	166.5	166.6	1.598	1.6001	2.2204	2.2193	2.221
90-80	125.9	126.05	163.24	164.25	164.29	1.479	1.4813	1.9312	1.9313	1.932
100-90	133.5	133.46	163.45	162.49	162.5	1.404	1.4032	1.709	1.7095	1.709
110-100	141.5	141.29	161	161.06	161.05	1.346	1.3441	1.5324	1.533	1.533
120-110	148.8	148.59	159.76	159.83	159.81	1.292	1.2908	1.3884	1.3889	1.389
130-120	154.7	154.69	158.69	158.75	158.73	1.237	1.2364	1.2687	1.2693	1.269
140-130	159.3	159.24	157.72	157.79	157.74	1.179	1.1786	1.1676	1.168	1.168
150-140	162.2	162.38	156.85	156.9	156.87	1.118	1.1191	1.081	1.0815	1.081
160-150	164	164.11	156.04	156.09	156.05	1.057	1.058	1.0061	1.0064	1.006
170-160	164.5	164.69	155.28	155.34	155.29	0.997	0.9976	0.9406	0.9409	0.941
180-170	164.2	164.39	154.59	154.63	154.59	0.938	0.9388	0.8829	0.8831	0.883
190-180	163.4	163.46	153.94	153.98	153.93	0.882	0.8831	0.8316	0.8319	0.831
200-190	162.1	162.13	153.32	153.36	153.32	0.831	0.831	0.7859	0.786	0.786
210-200	160.7	160.58	152.74	152.78	152.73	0.784	0.7829	0.7447	0.7449	0.745
220-210	159	158.93	152.19	152.22	152.19	0.739	0.7389	0.7075	0.7076	0.707
230-220	157.5	157.3	151.68	151.71	151.66	0.699	0.6988	0.6738	0.674	0.674
240-230	155.8	155.74	151.19	151.22	151.18	0.663	0.6624	0.643	0.6431	0.643
250-240	154.4	154.28	150.73	150.75	150.71	0.63	0.6294	0.6149	0.6151	0.615
260-250	153.1	152.95	150.29	150.32	150.28	0.6	0.5996	0.5892	0.5892	0.589
270-260	151.8	151.78	149.88	149.9	149.86	0.573	0.5725	0.5653	0.5654	0.565
280-270	150.7	150.74	149.48	149.51	149.47	0.548	0.5479	0.5434	0.5434	0.543
290-280	149.8	149.83	149.13	149.14	149.11	0.525	0.5219	0.523	0.5231	0.523
300-290	149	149.05	148.77	148.79	148.75	0.505	0.5087	0.5041	0.5042	0.504

Table 5. Estimated enthalpy and entropy increments for parahydrogen in 10 MPa.

T ₂ -T ₁ (K)	Parahydrogen, P= 10MPa									
	Δh (kJ/kg)					Δs (kJ/kg-K)				
	REFPROP	MBWR	BWRS	PR	SRK	REFPROP	MBWR	BWRS	PR	SRK
30-20	91.818	91.82	130.58	188.7	199.21	3.6576	3.658	2.8282	7.5914	8.0181
40-30	120.9	120.66	-40.94	198.55	207.13	3.4439	3.4375	-6.3595	5.6807	5.9274
50-40	146.21	145.92	240.01	205.93	213.27	3.2429	3.2361	5.3292	4.5779	4.7417
60-50	159.9	159.67	239.12	206.36	212.66	2.9059	2.9013	4.3522	3.7529	3.8679
70-60	159.29	159.31	220.4	200.67	205.65	2.451	2.451	3.3932	3.0875	3.1644
80-70	155.13	155.33	204.28	193.18	196.84	2.067	2.071	2.724	2.576	2.624
90-80	154.16	154.25	192.92	186.41	189.06	1.812	1.814	2.27	2.192	2.224
100-90	156.4	156.3	185.6	180.9	182.7	1.645	1.644	1.945	1.904	1.923
110-100	160.3	160.2	178.3	176.5	177.9	1.526	1.524	1.704	1.68	1.693
120-110	164.6	164.4	174.5	173	174	1.43	1.428	1.517	1.503	1.512
130-120	168.2	168.2	171.1	170.1	170.8	1.345	1.344	1.368	1.36	1.366
140-130	170.9	170.8	168.3	167.6	168.1	1.264	1.265	1.246	1.241	1.245
150-140	172.4	172.5	165.9	165.5	166	1.188	1.189	1.144	1.141	1.143
160-150	172.7	173	164	163.8	164	1.114	1.115	1.057	1.056	1.058
170-160	172.4	172.5	162.3	162.2	162.4	1.044	1.045	0.983	0.982	0.984
180-170	171.2	171.4	160.7	160.8	160.9	0.978	0.979	0.918	0.919	0.919
190-180	169.6	169.6	159.5	159.6	159.6	0.916	0.916	0.862	0.862	0.862
200-190	167.7	167.8	158.3	158.4	158.5	0.86	0.86	18.811	0.812	0.812
210-200	165.7	165.6	157.2	157.4	157.4	0.808	0.807	-17.233	0.767	0.768
220-210	163.6	163.5	156.3	156.5	156.4	0.76	0.76	0.726	0.728	0.727
230-220	161.5	161.4	155.4	155.6	155.6	0.718	0.718	0.691	0.691	0.691
240-230	159.6	159.5	154.6	154.9	154.8	0.679	0.678	0.657	0.659	0.658
250-240	157.9	157.7	153.9	154.1	154	0.644	0.644	0.628	0.629	0.629
260-250	156.2	156.1	153.2	153.5	153.3	0.612	0.611	0.6	0.601	0.601
270-260	154.7	154.7	152.6	152.8	152.7	0.584	0.584	0.576	0.577	0.576
280-270	153.4	153.4	152	152.2	152.1	0.557	0.557	0.552	0.553	0.553
290-280	152.2	152.2	151.5	151.7	151.6	0.534	0.534	0.532	0.532	0.531
300-290	151.3	151.4	150.9	151.2	151	0.513	0.513	0.511	0.512	0.512

Table 6. Estimated enthalpy and entropy increments for hydrogen in 1 MPa.

Hydrogen, P= 1MPa										
T2-T1 (K)	Δh (kJ/kg)					Δs (kJ/kg-K)				
	REFPROP	MBWR	BWRS	PR	SRK	REFPROP	MBWR	BWRS	PR	SRK
30-20	185.199	137.07	211.61	184.24	218.45	8.1397	5.366	8.4645	8.8564	10.6384
40-30	448.86	448.84	566.95	467.54	529.67	13.8037	13.8032	17.7697	14.4488	16.4155
50-40	127.89	127.88	159.72	165.83	169.98	2.852	2.8517	3.5587	3.7253	3.8283
60-50	116.84	116.83	149.96	153.74	155.78	2.126	2.126	2.7283	2.8099	2.8517
70-60	113.14	113.13	145.95	148.69	149.94	1.74	1.7403	2.245	2.2939	2.3148
80-70	112.23	112.19	143.87	145.97	146.73	1.495	1.495	1.9176	1.9493	1.9607
90-80	112.8	112.76	142.67	144.32	144.81	1.327	1.3257	1.6775	1.6993	1.7059
100-90	114.3	114.3	141.91	143.24	143.55	1.202	1.2022	1.4929	1.5085	1.5122
110-100	116.5	116.44	141.41	142.5	142.71	1.108	1.108	1.3459	1.3574	1.3597
120-110	118.8	118.87	141.09	141.98	142.1	1.033	1.0328	1.226	1.2346	1.2359
130-120	121.4	121.4	140.85	141.62	141.67	0.97	0.9704	1.1261	1.1328	1.1334
140-130	123.8	123.86	140.71	141.34	141.36	0.917	0.9064	1.0416	1.0468	1.047
150-140	126.2	126.21	140.6	141.16	141.14	0.87	0.8802	0.969	0.9732	0.9732
160-150	128.4	128.39	140.54	141.02	140.98	0.827	0.8277	0.9062	0.9096	0.9093
170-160	130.5	130.4	140.51	140.92	140.87	0.79	0.7898	0.8511	0.8538	0.8536
180-170	132.2	132.23	140.5	140.86	140.8	0.756	0.7551	0.8024	0.8046	0.8043
190-180	133.9	133.87	140.51	140.83	140.75	0.723	0.7232	0.759	0.761	0.7606
200-190	135.4	135.34	140.54	140.82	140.74	0.694	0.6936	0.7203	0.7219	0.7214
210-200	136.7	136.65	140.57	140.82	140.73	0.666	0.6662	0.6854	0.6867	0.6863
220-210	137.8	137.82	140.62	140.85	140.75	0.641	0.6407	0.6537	0.6548	0.6544
230-220	138.9	138.85	140.68	140.87	140.776	0.617	0.6168	0.6249	0.6259	0.6855
240-230	139.7	139.75	140.73	140.92	140.819	0.594	0.5943	0.5986	0.5994	0.539
250-240	140.5	140.54	140.81	140.97	140.869	0.573	0.5734	0.5744	0.5752	0.5748
260-250	141.3	141.23	140.88	141.02	140.927	0.554	0.5536	0.5522	0.5529	0.5524
270-260	141.8	141.84	140.95	141.09	140.994	0.535	0.535	0.5317	0.5322	0.5319
280-270	142.3	142.35	141.05	141.17	141.065	0.517	0.5174	0.5127	0.5131	0.5128
290-280	142.8	142.8	141.13	141.24	141.143	0.501	0.5008	0.495	0.4954	0.4951
300-290	143.2	143.18	141.22	141.32	141.226	0.485	0.4852	0.4785	0.4789	0.4785

Table 7. Estimated enthalpy and entropy increments for hydrogen in 10 MPa.

Hydrogen, P= 10MPa										
T2-T1 (K)	Δh (kJ/kg)					Δs (kJ/kg-K)				
	REFPROP	MBWR	BWRS	PR	SRK	REFPROP	MBWR	BWRS	PR	SRK
30-20	94.01	92.943	64.94	108.68	129.08	3.7456	3.7138	0.4845	6.6622	7.9252
40-30	120.66	120.66	-81.44	151.53	182.55	3.4374	3.4373	-6.7057	5.1347	6.1815
50-40	145.62	145.59	239.66	179.17	212.2	3.2298	3.2294	5.325	4.3199	5.1125
60-50	158.35	158.35	224.93	191.56	218.08	2.8777	2.8775	4.0979	3.6418	4.1485
70-60	155.52	155.51	198.27	189.9	206.64	2.394	2.394	3.0539	3.0034	3.2725
80-70	147.39	147.39	180.49	182.11	192.03	1.965	1.965	2.407	2.474	2.613
90-80	141.01	140.96	169.48	174.15	180.29	1.659	1.658	1.994	2.076	2.152
100-90	137.2	137.2	162.42	167.72	171.72	1.443	1.443	1.709	1.783	1.828
110-100	135.3	135.3	157.6	162.7	165.5	1.288	1.288	1.5	1.562	1.589
120-110	134.7	134.7	154.3	159	160.8	1.171	1.171	1.341	1.39	1.408
130-120	134.9	134.9	151.8	156.1	157.4	1.078	1.078	1.214	1.255	1.266
140-130	135.4	135.4	149.9	153.8	154.7	1.002	1.003	1.11	1.144	1.15
150-140	136.3	136.4	148.6	152.1	152.5	0.94	0.939	1.024	1.051	1.056
160-150	137.3	137.2	147.4	150.5	150.8	0.885	0.885	0.95	0.974	0.976
170-160	138.3	138.2	146.5	149.4	149.5	0.837	0.837	0.888	0.907	0.908
180-170	139.2	139.2	145.9	148.4	148.3	0.795	0.795	0.833	0.85	0.849
190-180	140.1	140.1	145.3	147.5	147.4	0.757	0.757	0.784	0.799	0.799
200-190	140.9	140.9	144.8	147	146.6	0.722	0.722	0.743	0.754	0.753
210-200	141.8	141.7	144.4	146.3	146	0.691	0.691	0.703	0.715	0.713
220-210	142.3	142.4	144.1	145.9	145.5	0.662	0.662	0.671	0.679	0.677
230-220	143	143	143.9	145.5	145	0.635	0.635	0.639	0.647	0.645
240-230	143.5	143.5	143.6	145.1	144.6	0.611	0.61	0.611	0.618	0.616
250-240	144	143.9	143.5	144.8	144.3	0.587	0.588	0.585	0.592	0.589
260-250	144.4	144.4	143.4	144.7	144	0.566	0.566	0.562	0.567	0.566
270-260	144.7	144.8	143.2	144.4	143.8	0.546	0.545	0.54	0.546	0.543
280-270	145	145	143.2	144.2	143.7	0.527	0.528	0.521	0.524	0.522
290-280	145.2	145.2	143.1	144.2	143.5	0.509	0.509	0.502	0.506	0.504
300-290	145.5	145.5	143.1	144	143.3	0.493	0.493	0.485	0.489	0.486

Applying MBWR to hydrogen, the same as parahydrogen, leads to acceptable results

throughout the whole temperature and pressure range. The estimated data for

hydrogen using PR, BWRS, and SRK EOSs are nearly the same; they all experience high deviations for low temperatures such that for lower than 190 K, the deviations are higher than 5%. It should be noted that the deviations for hydrogen are higher in comparison to the parahydrogen.

3.4 Specific heat capacity and conversion enthalpy

Specific heat capacity (C_p) for hydrogen and parahydrogen estimated by considered EOSs through Aspen HYSYS are compared to the

experimental data (Jacob W Leachman et al., 2017) in Figure 4 and Figure 5, respectively. As it is shown in Figure 4, the results for MBWR fit very well to the experimental data for the whole range of temperature typically met in the liquefaction processes. However, other EOSs could yield acceptable results only for temperature higher than 220 K. As the temperature approach to the boiling point, the deviation for MBWR increases and could reach 13%. For temperatures higher than 50 K, the deviation is less than 1%.

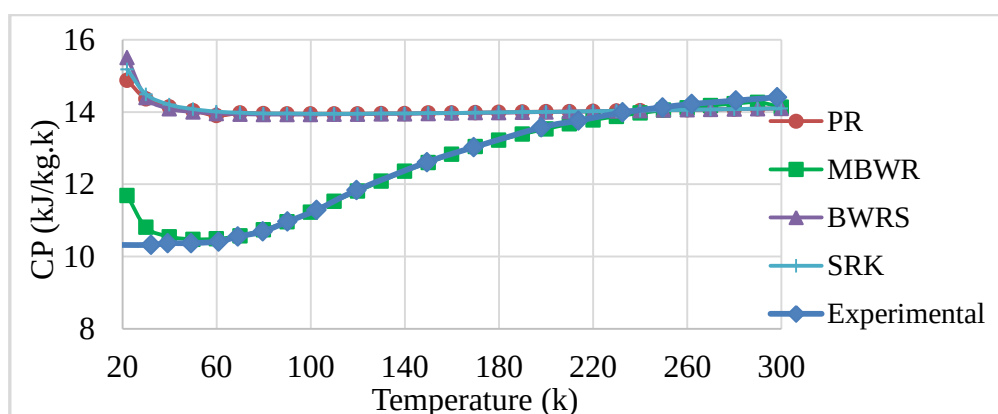


Figure 4. Comparison of estimated values of heat capacity (C_p) for hydrogen by different EOSs to the experimental data.

For parahydrogen, the same as hydrogen, the results of MBWR fit very well with the experimental data. Three other EOSs yield acceptable results only for temperature higher than 120 K. The deviation for MBWR is less than 1% except for temperature lower than 50 K that could go up to 13%.

Ortho-para conversion is of great importance in the simulation of hydrogen liquefaction processes and could lead to inaccurate results if it is not simulated correctly. The results presented in the previous

sections show that only MBWR could lead to desirable results in the whole range of temperature and pressure. Therefore, it deserves to compare the enthalpy of conversion based on the data obtained from Aspen HYSYS by MBWR with the experimental data. The results are shown in Figure 6.

To have a better understanding the results are presented in Table 8, from 20 to 280 K. Moreover, the difference between the two series of data is reported as a deviation in Table 8.

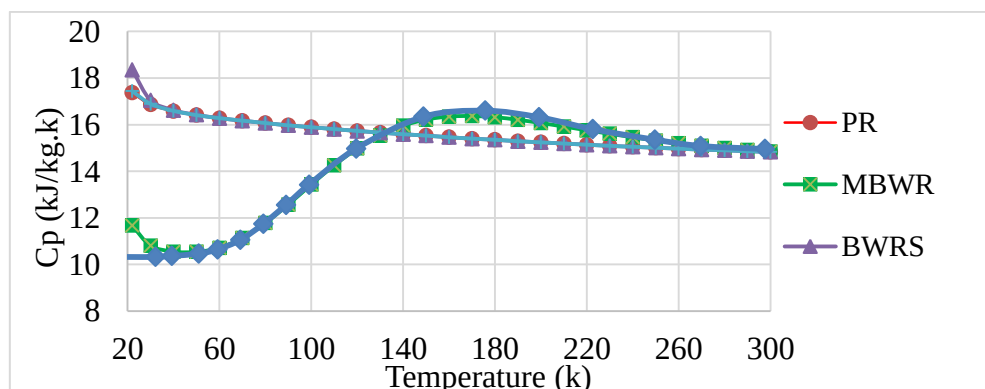


Figure 5. Comparison of estimated values of heat capacity (C_p) for parahydrogen by different EOSs to the experimental data.

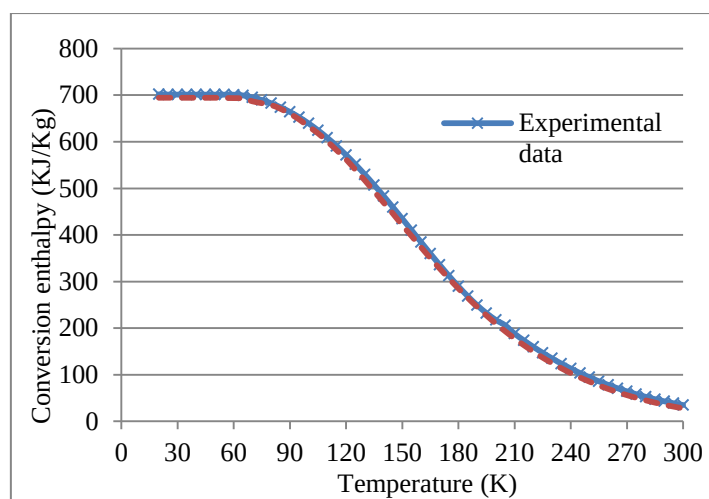


Figure 6. Comparison between results of Aspen HYSYS by MBWR and Experimental data (Jacob W Leachman et al., 2017).

Table 8. Comparison between results of Aspen HYSYS by MBWR and Experimental data from 20-280 K (Jacob W Leachman et al., 2017).

T (K)	Enthalpy (kJ/kg) - Experimental	Enthalpy (kJ/kg) - HYSYS	Deviation (%)	T (K)	Enthalpy (kJ/kg) - Experimental	Enthalpy (kJ/kg) - HYSYS	Deviation (%)
20	701.77	694.45	1.04	160	384.93	373.91	2.86
40	701.15	694.38	0.97	180	289.63	285.20	1.53
60	701.02	693.72	1.04	200	217.57	209.81	3.57
80	682.60	678.81	0.56	220	159.95	149.66	6.43
100	639.38	632.74	1.04	240	113.30	103.45	8.70
120	571.72	562.27	1.65	260	78.11	69.49	11.03
140	483.80	469.70	2.91	280	52.58	45.01	14.41

As it could be seen in Figure 6 and Table 8, the two curves are compatible very well. The difference between the two cases is in the range of 6-14 kJ/kg, which is ignorable in comparison to the power needed for liquefaction. The MBWR leads to a 1% deviation compared to the experimental data at the boiling point, which is ignorable. Although the deviation could go up to 14% at temperatures higher than 270 K, the value is lower than 8 kJ/kg and could be ignored. The results show that MBWR could estimate all the considered properties of the hydrogen and parahydrogen in the range of 20-300 K, which is typically met in the liquefaction processes.

4. Result and discussion

MBWR yields the most accurate results, while PR is the most common EOS, which has been utilized in the field of hydrogen liquefaction processes. For more understanding, EOS's effect on significant specifications of a sample liquefaction cycle, including COP and SEC, is investigated through applying MBWR and PR. For this purpose, the liquefaction concept proposed by Sadaghiani et al. (Sadaghiani & Mehrpooya, 2017), which includes two MR cycles, is considered. Due to the configuration

of this concept, any change in the hydrogen streams, such as changing the dedicated EOS, could lead to unavoidable changes in the MR cycles. Therefore, it is impossible to capture EOS's mere effect on the COP and SEC using this concept. The considered concept is simplified to remove the interaction between MR cycles and hydrogen streams for solving this problem. The simplified concept and the original one are presented in Figure 7. It is not logical to reject heat from hydrogen streams using coolers since, in this situation, indexes like COP and SEC are not valid anymore. Although the simulation in the Aspen HYSYS is based on the simplified concept in Figure 7, for calculation of the COP and SEC, it is supposed that every cooler is served by a hypothetical independent refrigeration cycle to provide a cooling effect.

These refrigeration cycles are supposed to be based on the reversed Carnot cycle with an ambient temperature of 25 °C. COP for the reversed Carnot cycle is calculated as follows:

$$COP = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Cooling effect}}{\text{Work input}} = \frac{Q_L}{W_{net}} = \frac{T_L}{T_H - T_L} \quad (3)$$

where Q_L , W_{net} , T_L and T_H stand for cooling effect (rejected heat from hydrogen

stream), work input (for the all hypothetical reversed Carnot cycles), the temperature of the cold and warm space, respectively. For every cycle Q_L is obtained from Aspen HYSYS simulation, and the W_{net} could be calculated as follows (Van Wylen, 2015):

$$W_{net} = \frac{Q_L (T_H - T_L)}{T_L} \quad (4)$$

The results are reported in Table 9 for two cases, with MBWR and PR as EOS.

For the liquefaction cycle, the COP could be calculated using Equation (3) while the SEC is defined as:

$$SEC(kWh) = \frac{W_{net}(kW)}{m(kg/s) \cdot 3600(s/h)} \quad (5)$$

The COP and SEC for the two considered cases are reported in Table 10.

Table 9. Cooling effect and work input for cases with PR and MBWR.

Cycles	PR		MBWR	
	Q_L (kW)	W_{net} (kW)	Q_L (kW)	W_{net} (kW)
Cooler1	3419.55	455.07	3428.57	456.27
Cooler2	2934.70	1482.17	2822.06	1425.28
Cooler3	4506.22	6411.29	3839.27	5462.37
Cooler4	1694.56	5655.94	1627.94	5035.88
Cooler5	2031.36	11900.67	1788.98	10480.66
Cooler6	1733.35	16170.96	1697.49	14752.99
Total	16319.74	42076.1	15204.31	37613.45

Table 10. COP and SEC for cases with the PR and MBWR as EOS.

EOS	COP	SEC
PR	0.388	3.388
MBWR	0.404	3.028

It is found that using MBWR leads to 10.63% lower SEC and 4.12% higher COP compared to PR.

5. Conclusion

Liquid hydrogen has a wide range of applications and particular usages due to its unique characteristics. Liquid hydrogen is expected to play an important role in the future of energy if it could be liquefied economically. The existing liquefaction plants have low efficiencies so many studies are dedicated to optimizing liquefaction processes and providing novel concepts. The accuracy of these studies is intensively dependent on the simulation tools and adapted models. Aspen HYSYS includes a rich data bank of physical properties and different implemented models and EOSs, so it has been chosen as the simulation tool in many pieces of research. The accuracy of the models developed by Aspen HYSYS and similar programs are crucially dependent on the selected EOS. In this study, four common EOSs, PR, MBWR, SRK, and BWRS, which had been utilized in many studies around hydrogen liquefaction, are investigated through a novel methodology to find their accuracy and the proper range of applications.

Although the results of the PR and SRK for density are acceptable through the whole range, the best results are gained by applying the MBWR. The use of the PR, SRK, and BWRS in estimating the enthalpy and entropy experience more deviations, especially in lower temperatures and higher pressures, so that

they can be used only for temperature range far from the boiling point. It deserves to note that the effect of temperature on the accuracy of the results for a specified EOS is more than the pressure. The results show that MBWR is the best EOS, which could estimate essential properties, including density, vapor pressure, entropy, enthalpy, and specific heat capacity with acceptable deviations compared to the reference case, i.e., REFPROP. Moreover, the MBWR could yield fair values for conversion enthalpy through the whole range of temperature, so it could be the right choice for hydrogen liquefaction processes, especially the ones that include ortho-para conversion. The three other considered EOSs could present nearly acceptable results for higher temperatures but are not adequate for hydrogen liquefaction processes due to the low boiling point of hydrogen and high deviations for lower temperatures. If utilizing the MBWR is not possible thanks to the computational difficulties or the processes temperature, it seems that the PR, which is a simple EOS, could perform better than the two others and lead to more accurate results. Applying the PR and MBWR to a simplified concept for liquefaction of hydrogen shows that using PR compared to the MBWR leads to 10.63% and 4.12% deviation in SEC and COP, respectively. It is advised to use the MBWR for simulation of hydrogen liquefaction processes conducted by Aspen HYSYS. This could lead to more accurate and reliable results.

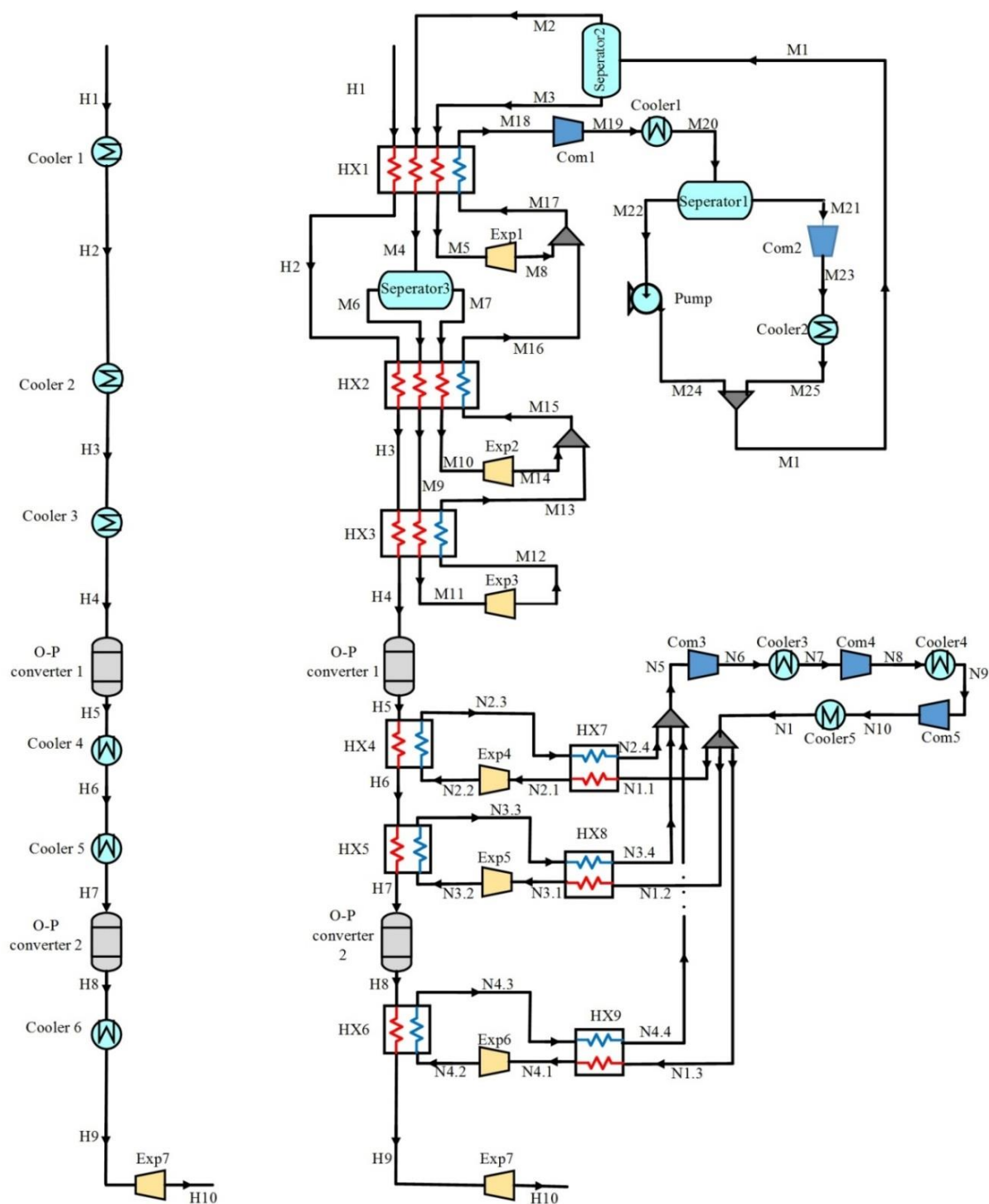


Figure 7. Schematic of the original sample liquefaction cycle (right) and simplified one (left).

Nomenclature			
Symbols	P	Pressure, MPa	BWRS Benedict-Webb- Rubin- Starling
h Specific enthalpy, kJ/kg	ρ	Density, kg/m ³	MBWR Modified-Benedict-Webb- Rubin
s Specific entropy, kJ/kg-k	Abbreviations		
Δh Enthalpy increments, kJ/kg	HX	Heat exchanger	SRK Soave-Redlich-Kwong
Δs Entropy increments, kJ/kg-k	EOS	Equation of state	GCEOS Generalized cubic equation of state
T Temperature, K	PR	Peng-Robinson	COP Coefficient of performance
			SEC Specific energy consumption

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