Finding appropriate operating conditions for hydrogen purification and recovery in supercritical water gasification of biomass

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Abstract

The gas product from biomass gasification in supercritical water contains about 55% H_2 and 33% CO_2 in mole fraction. Others like CH_4 and CO exist in the gas product with less amounts. Hydrogen is the targeted product. Its purification is a very important step. Water is generally used as the solvent to purify the hydrogen by separating CO_2 and other gases from the gas product. The hydrogen purification can be carried out through separators, generally a high-pressure separator followed by low-pressure separators. The operating conditions of temperature, pressure, and the amounts of water used have a significant effect on the efficiency of hydrogen purification. Simulation of hydrogen purification at a wide range of operating conditions has been carried out. The appropriate operating conditions have been indicated, at which, to the greatest extent, the hydrogen produced can be purified and recovered. The results of this work will have a significant contribution to the design of a process of supercritical water gasification of biomass.
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Keywords: Biomass; Hydrogen purification; Supercritical water gasification; Modeling

1. Introduction

Hydrogen is an important future fuel, as it has a great potential of application in the future, especially the application through fuel cell. Biomass conversion is an alternative approach to produce hydrogen. Among the technologies of biomass conversions, biomass gasification in supercritical water is a very promising one [1–3]. Fig. 1 shows a process of supercritical water gasification of biomass, consisting of feed pump, heat exchanger, reactor, high-pressure separator, and low-pressure separators as the major operation units; pressure swing adsorption (PSA) can be used to produce pure hydrogen. The gas product from the reactor mainly includes hydrogen, carbon dioxide, methane, and carbon monoxide. In the high-pressure separator, significant part of the CO_2 and other gases are dissolved in the water phase, and the hydrogen is purified. The high-pressure separator is a key unit of a supercritical water gasification process, in which the hydrogen is purified by dissolving CO_2 and other gases into the water phase. Operating conditions of temperature,

pressure, and the amounts of water will affect the efficiency of hydrogen purification.

The aim of this work is to find out the appropriate operating conditions at which, to the greatest extent, the hydrogen can be purified and recovered. For this purpose, the binary and ternary systems will be modeled to get the solid basis, and then the modeling of hydrogen purification in the high-pressure separator will be carried out, and the PR equation of state [4] is taken as the model for the simulation.

2. Getting binary interaction parameters

For getting reliable modeling results for hydrogen purification, we start with the modeling of the solubility of each gas component in water to get binary interaction parameters. In Fig. 2, the lines are for the results of H_2/H_2O calculated by the PR model, the symbols are for the data of H_2 solubility in water, and Fig. 3 shows the binary interaction parameter function, which is temperature dependent. The modeling results of the solubilities of CO_2, CH_4, and CO in water are shown in Figs. 4, 6 and 8, respectively, and the binary interaction parameter functions are shown in Figs. 5, 7 and 9, respectively. The data used are in a temperature range of 5–100 °C and a pressure

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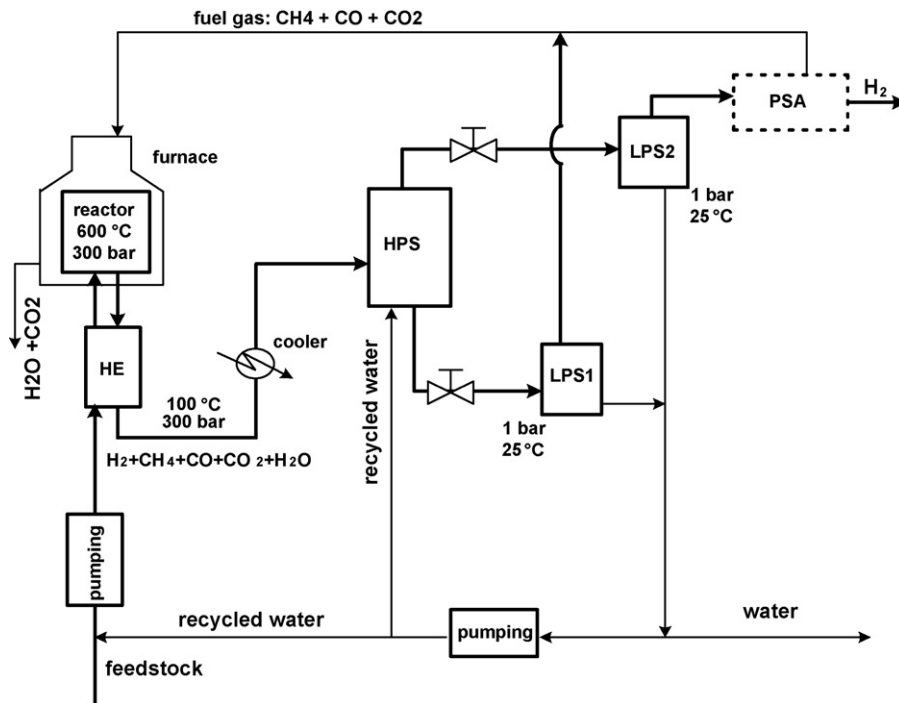*E-mail address:* fengwei@mail.buct.edu.cn (W. Feng).

Fig. 1. The supercritical water gasification of biomass. HE: heat exchanger; HPS: high-pressure separator; LPS: low-pressure separator.
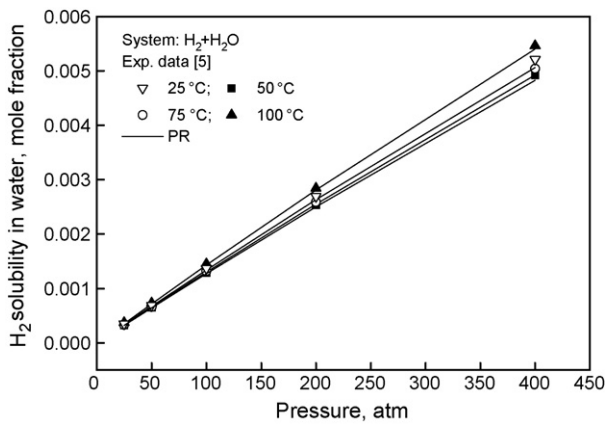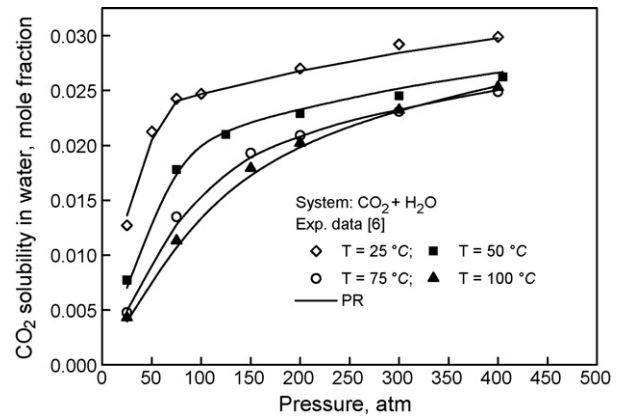

Fig. 2. Solubility of hydrogen in water [5].
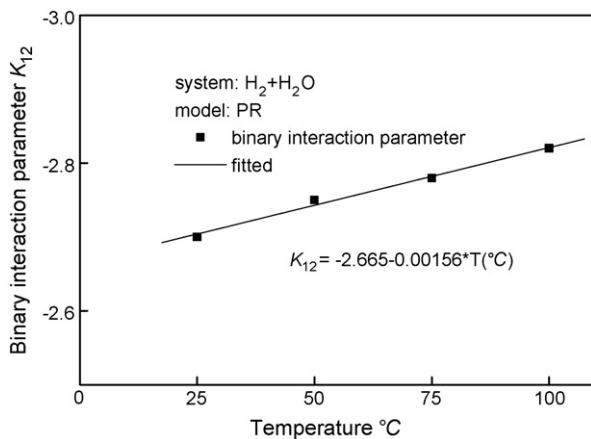

Fig. 4. Solubility of CO_2 in water [6].
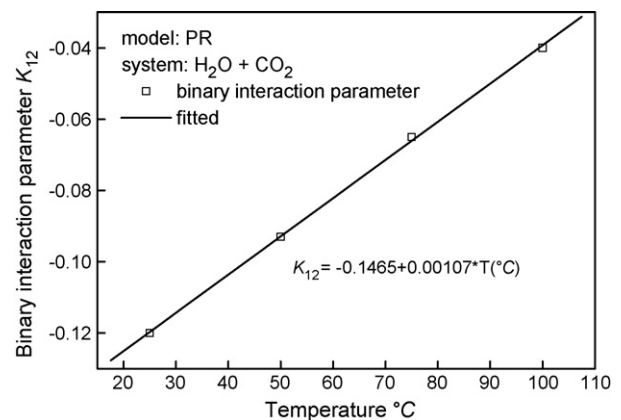

Fig. 3. Binary interaction parameter function for H_2/H_2O.
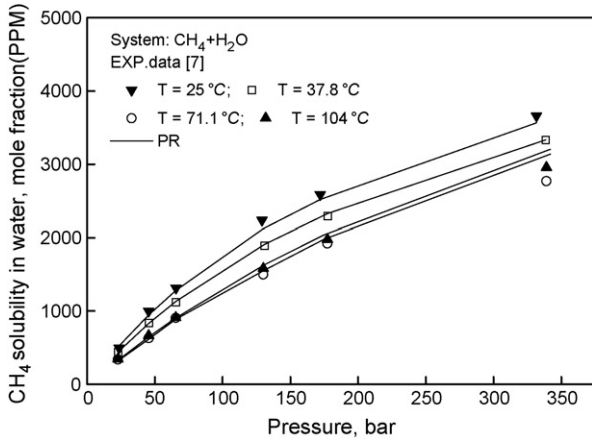

Fig. 5. Binary interaction parameter function for CO_2/H_2O.

Fig. 6. Solubility of CH_4 in water [7].

Fig. 8. Solubility of CO in water.

range of 25–400 bar. The modeling results show that the solubility of H_2, CO_2, CH_4, and CO in water, respectively, has been described very well by the PR model with the binary interaction parameters (Fig. 6).

The obtained binary interaction parameter functions in Figs. 3, 5 and 7 have been applied to the ternary systems of $CH_4/CO_2/H_2O$ and $H_2/CO_2/H_2O$. The predicted results by the PR model for the system $CH_4/CO_2/H_2O$ are listed in Table 1, including equilibrium methane mole fraction in gas mixture, CH_4 and CO_2 mole fractions, as well as the mole fraction of the mixture of $CH_4 + CO_2$ in the water phase. Fig. 10 presents the results of the system $H_2/CO_2/H_2O$. The results show that the ternary systems have been predicted very well by applying the binary parameter functions.

3. Modeling of hydrogen purification in the high-pressure separator

Based on the experimental data [1–3], Eq. (1) is used to express the biomass conversion reaction in supercritical water, the conversion reaction typically takes place at a temperature over 600 °C and an operating pressure around 300 bar.
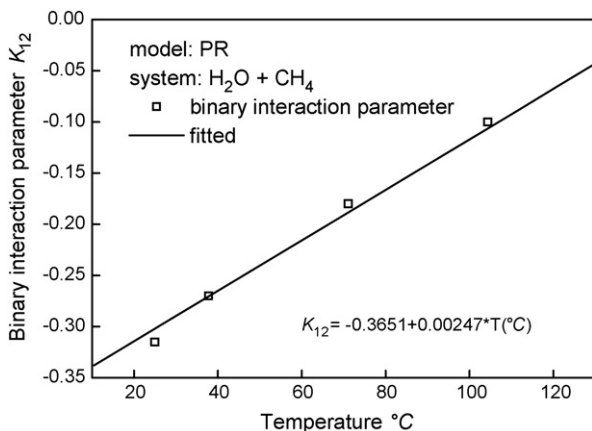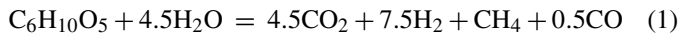
$$C_6H_{10}O_5 + 4.5H_2O = 4.5CO_2 + 7.5H_2 + CH_4 + 0.5CO \quad (1)$$
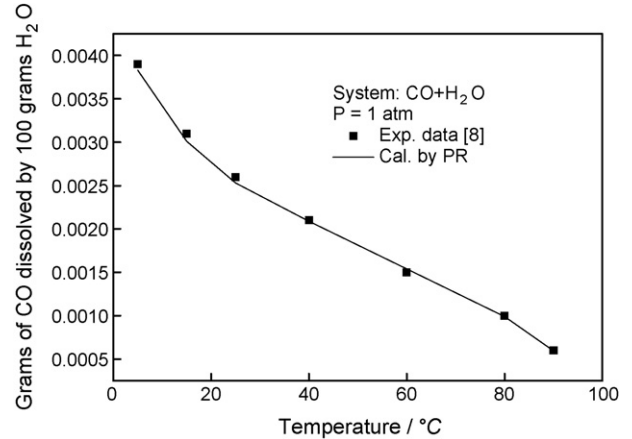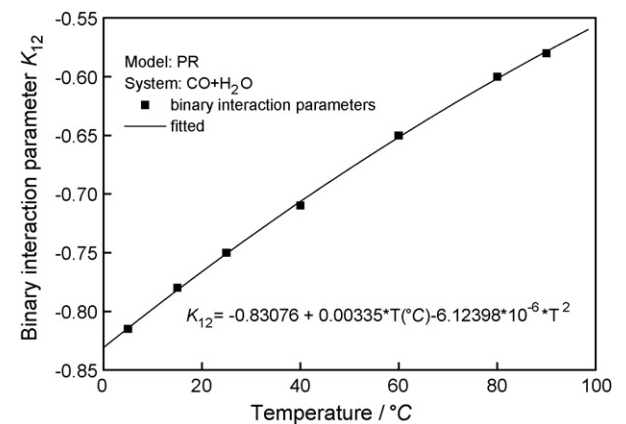

Fig. 9. Binary interaction parameter function for CO/water.

According to Eq. (1), the gas product consists of 55.56% hydrogen, 33.33% CO_2, 7.41% CH_4, and 3.70% CO in mole fraction.

In the high-pressure separator, water is the solvent to dissolve CO_2 and other gases into the water phase, and the hydrogen goes into the vapour phase and is purified. The hydrogen purity is defined as the hydrogen mole fraction in the vapour phase. Operating conditions have a significant effect on the results of
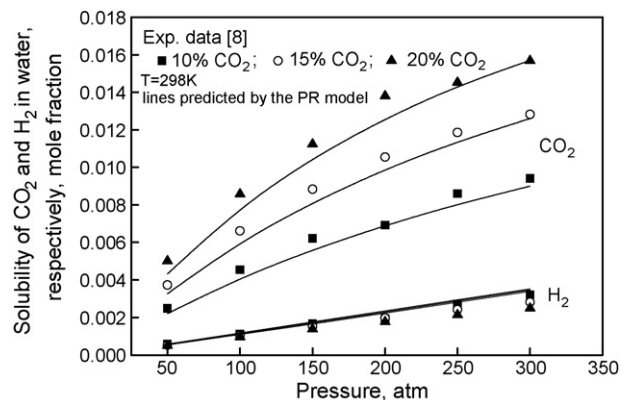

Fig. 7. Binary interaction parameter function for CH_4/H_2O.

Fig. 10. PR prediction for the ternary system of $H_2/CO_2/H_2O$. The symbols are for the mixture of $H_2 + CO_2$ with 10, 15, and 20% CO_2, respectively.

Table 1
PR calculations for the $CH_4/CO_2/H_2O$ mixture at 71 °C

P (bar)	CH_4[a]		Aqueous mole fraction of					
			CH_4		CO_2		$CH_4 + CO_2$	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
100	0.5670	0.5656	0.000776	0.000801	0.008346	0.006528	0.009122	0.007329
100	0.8045	0.8102	0.00110	0.001090	0.003555	0.002746	0.004655	0.003836
200	0.5700	0.5770	0.001310	0.001411	0.011300	0.008610	0.012610	0.010020
200	0.8102	0.0810	0.001820	0.001832	0.005390	0.003794	0.007210	0.005622
500	0.5850	0.5790	0.002434	0.002511	0.012670	0.010437	0.015104	0.012940
500	0.8205	0.8197	0.003027	0.003202	0.006265	0.004306	0.009455	0.007508
750	0.5870	0.5829	0.003027	0.003118	0.014347	0.011146	0.017474	0.014264
750	0.8260	0.8194	0.003893	0.003953	0.007105	0.004333	0.010998	0.008290
1000	0.5940	0.5877	0.00361	0.003600	0.015071	0.011610	0.018681	0.015210

Exp.: experimental data [8]; Cal.: calculated data.

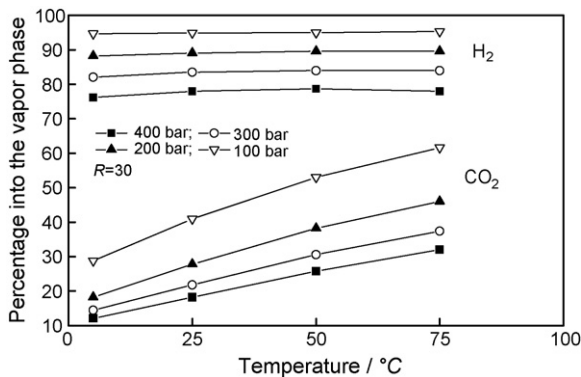[a] Equilibrium methane mole fraction in gaseous mixture.

Fig. 11. Percentage of total H_2 and total CO_2 partitioned into the vapour phase, respectively. The weight ratio of water to the gas mixture is $R = 30$.

hydrogen purification. Figs. 11–16 show the modeling results, which are in a temperature range of 5–100 °C, and at pressures up to 400 bar, for ratios $R = 30$, 40, and 50, respectively. R is the ratio of water to the gaseous product on a weight basis.

At a lower operating pressure, more hydrogen and CO_2 are partitioned into the vapour phase, and the vapour phase has a lower mole fraction of H_2 and a higher mole fraction of CO_2. At a higher ratio R or more water is used, the vapour phase has a higher mole fraction of H_2 and a lower mole fraction
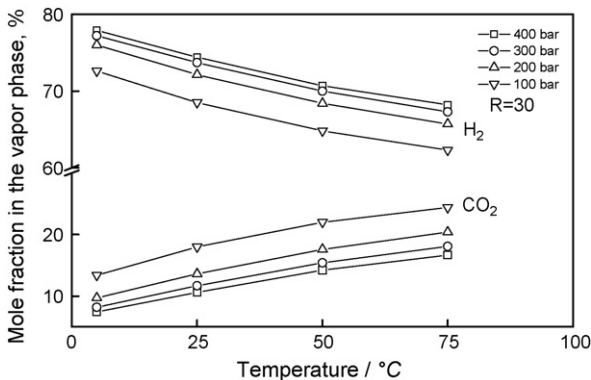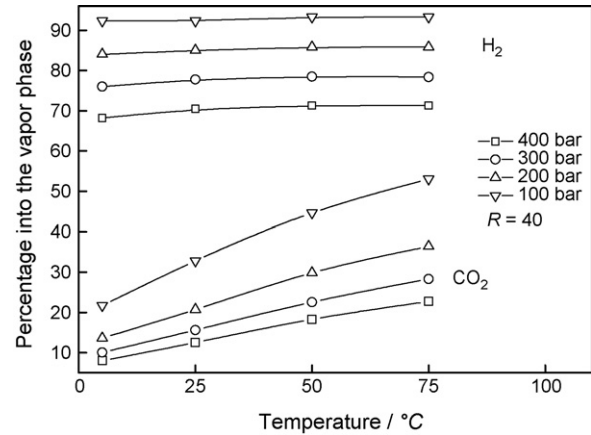

Fig. 13. Percentage of total H_2 and total CO_2 partitioned into the vapour phase, respectively. The weight ratio of water to the gas mixture is $R = 40$.

of CO_2, however, less hydrogen is partitioned into the vapour phase.

At a certain pressure and a certain ratio R, operating temperature does not have much effect on the percentage of total H_2 partitioned into the vapour phase. But at a lower operating
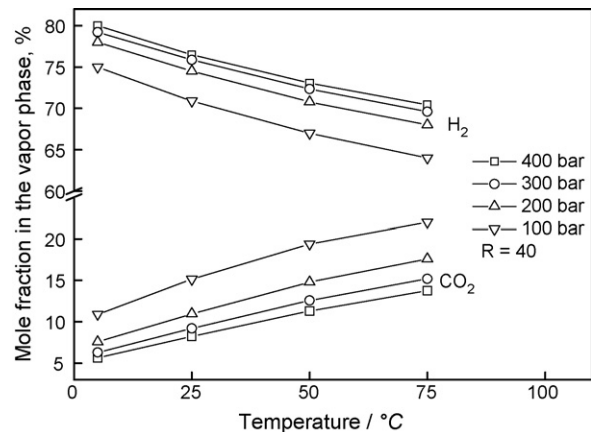

Fig. 12. Mole fraction of H_2 and CO_2 in the vapour phase, respectively. The weight ratio of water to the gas mixture is $R = 30$.

Fig. 14. Mole fraction of H_2 and CO_2 in the vapour phase, respectively. The weight ratio of water to the gas mixture is $R = 40$.
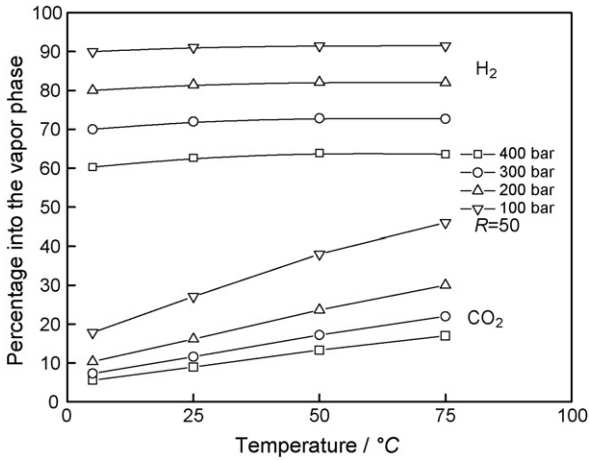
Fig. 15. Percentage of total H_2 and total CO_2 partitioned into the vapour phase, respectively. The weight ratio of water to the gas mixture is $R = 50$.

temperature, less CO_2 is partitioned into the vapour phase, and the vapour phase has a higher mole fraction of hydrogen and a lower mole fraction of CO_2. So a low operating temperature is suggested for the hydrogen purification in the high-pressure separator.

4. Finding appropriate operating conditions

From the results mentioned above, we know that low operating temperature is favoured, but maintaining an operating temperature below room temperature will cost a lot of energy, so the room temperature of 25 °C is suggested as the appropriate operating temperature for the hydrogen purification in the high-pressure separator.

For the temperature of 25 °C, Figs. 17–20 present the effect of operating pressure and the ratio R on the mole fraction of H_2 in the vapour phase, on the percentage of total H_2 partitioned into the vapour phase, on the percentage of total CO_2 partitioned into the vapour phase, and on the mole fraction of CO_2 in the vapour phase, respectively. The ratio R is limited to 170 and operating pressure is limited to 400 bar, because further increasing the ratio R and operating pressure has little effect on the mole fraction of H_2 in the vapour phase, as shown in Fig. 17.
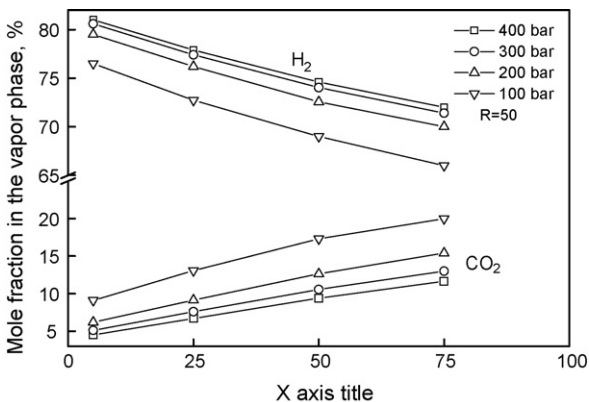

Fig. 16. Mole fraction of H_2 and CO_2 in the vapour phase, respectively. The weight ratio of water to the gas mixture is $R = 50$.
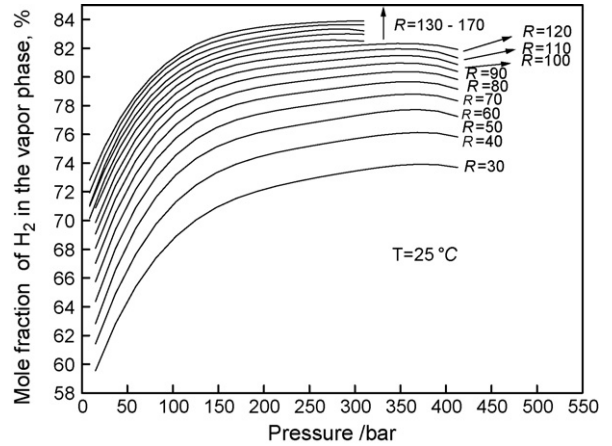

Fig. 17. Mole fraction of H_2 in the vapour phase at different weight ratios of water to the gas mixture and at different pressures.
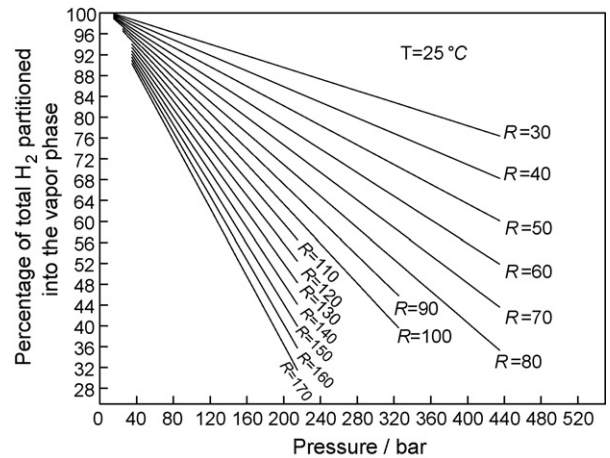

Fig. 18. Percentage of total H_2 partitioned into the vapour phase at different ratios of water to the gas mixture and different pressures.

For getting a specific hydrogen purity, or a specific mole fraction of H_2 in the vapour phase, the corresponding operating pressures and the ratios R can be found in Fig. 17. For each pair of the operating pressure and ratio R, we can find a percentage of
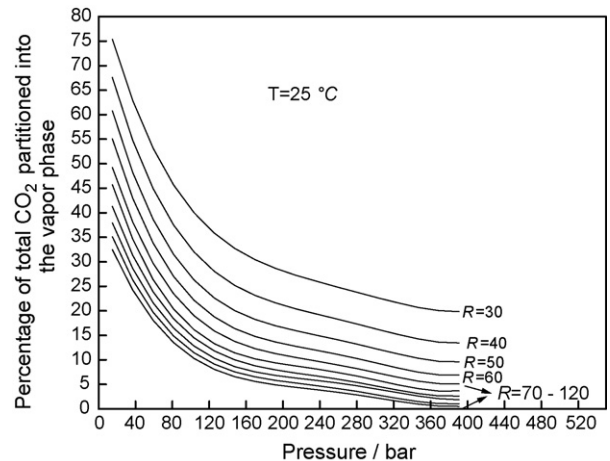

Fig. 19. Percentage of total CO_2 partitioned into the vapour phase at different weight ratios of water to the gas mixture and at different pressures.
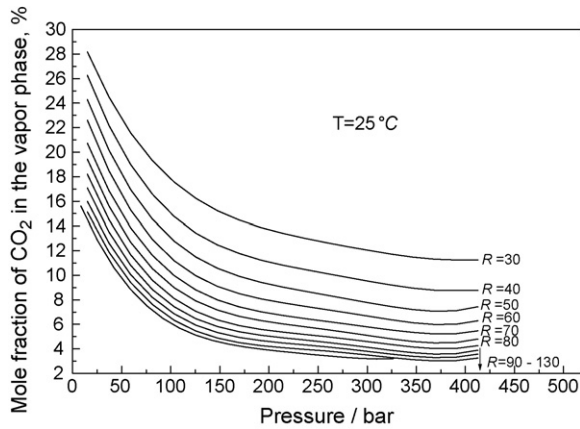
Fig. 20. Mole fraction of CO_2 in the vapour phase at different weight ratios of water to the gas mixture and at different pressures.
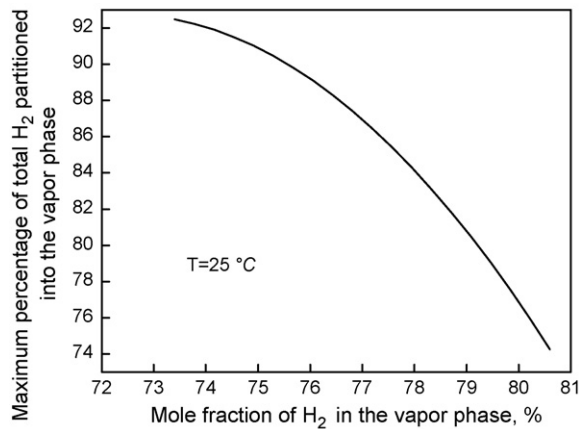

Fig. 21. Maximum percentage of total H_2 partitioned into the vapour phase corresponding to the mole fraction of H_2 in the vapour phase.

total H_2 partitioned into the vapour phase in Fig. 18. Finally the "maximum" percentage of total H_2 partitioned into the vapour phase can be found out for the specific H_2 purity, and the corresponding operating pressure and the ratio R are taken as the appropriate operating conditions at the temperature 25 °C for getting the mole fraction of H_2 specified. In Figs. 19 and 20,
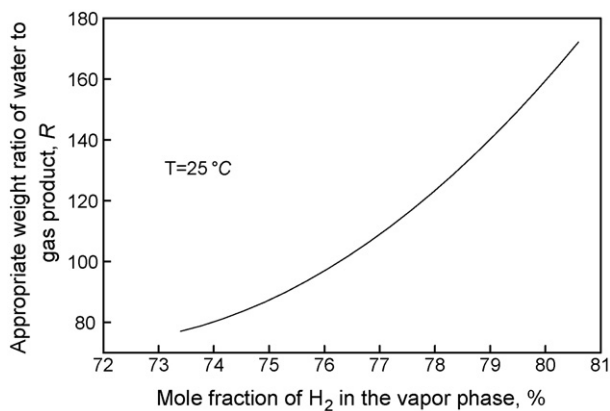

Fig. 22. Appropriate ratio R corresponding to the mole fraction of H_2 in the vapour phase.
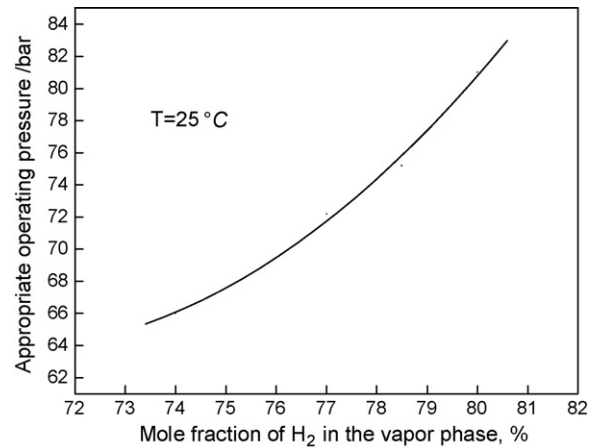

Fig. 23. Appropriate operating pressure corresponding to the mole fraction of H_2 in the vapour phase.

we can know the percentage of total CO_2 partitioned into the vapour phase and the mole fraction of CO_2 in the vapour phase, respectively, at the appropriate operating conditions.

For getting the H_2 purities of from 73 to 81%, the appropriate operating conditions have been indicated through Figs. 21–23. As shown in Fig. 21, the maximum percentage of total H_2 partitioned into the vapour phase decreases with the mole fraction of H_2 in the vapour phase. For a specific maximum percentage of total H_2, one can find the corresponding hydrogen purity (hydrogen mole fraction) in Fig. 21, and then from Figs. 22 and 23, the corresponding appropriate ratio R and operating pressure can be found, respectively.

5. Conclusions

The hydrogen purification in a supercritical water gasification process is a very important step. The operating conditions of temperature, pressure, and the amounts water used have a significant effect on the efficiency of hydrogen purification. Finding out the appropriate operating conditions to maximise the hydrogen recovery is the objective of this work.

The modeling of the hydrogen purification by removing other gases from the gas product of $H_2 + CO_2 + CH_4 + CO$ has been carried out through the description of phase equilibrium in the high-pressure separator at a wide range of operating conditions, a temperature range of from 5 to 100 °C, a ratio R range of from 30 to 170, and pressures up to 400 bar. The results include the effect of temperature, pressure, and the ratio R on the percentages of total H_2 and total CO_2 partitioned into the vapour phase, respectively, and on the mole fractions of H_2 and CO_2 in the vapour phase, respectively. These four parameters are used for measuring the efficiency of hydrogen purification. Based on the modeling results, the appropriate operating temperature is suggested at the temperature of 25 °C. Appropriate operating pressures and ratios R have been indicated for hydrogen purities from 73 to 81% in mole fraction. At appropriate operating conditions, for a specific hydrogen purity (defined as the mole fraction in the vapour phase), the percentage of total H_2 partitioned into the vapour phase can be maximised, in the meantime,

the percentage of total CO_2 partitioned into the vapour phase and the mole fraction of CO_2 in the vapour phase can be minimized.

Acknowledgement

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