

# Phase equilibria for biomass conversion processes in subcritical and supercritical water

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## Abstract

The description of phase equilibria for two biomass conversion processes, the hydrothermal upgrading (HTU) process and supercritical water gasification (SCWG) process, has been carried out. The HTU process is a liquefaction process under subcritical water conditions, the product contains biocrude, organic compounds, gases, and water. In the SCWG process, the product is fuel gas containing more than 50% hydrogen on a mole basis. Biocrude is the target product in HTU, and hydrogen in SCWG. The description of phase equilibria indicates the possible routes and operating conditions for separating the target product from the product mixture. For the HTU process, the task has been accomplished by properly characterizing biocrude and the application of the Statistical Associating Fluid Theory (SAFT) equation of state. The calculated result for biocrude separation is in good agreement with the experimental data. In the SCWG process, for the removal of CO<sub>2</sub> from gas product to produce higher purity hydrogen, four equations of state of PSRK, PR, SRK, and SAFT have been applied to calculate the phase equilibria. Water and 1-hexanol are the solvents for dissolving CO<sub>2</sub>. The amounts of solvent required have been indicated for achieving certain hydrogen purity in the vapor phase. The predicted comparison results show that 1-hexanol is a better solvent than water. Using the weight amount of one-tenth of water, 1-hexanol can make higher or comparable hydrogen purity in the vapor phase and less hydrogen dissolved in the liquid phase.

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*Keywords:* Biomass; Vapor–liquid equilibria; HTU; SCWG; Biocrude; SAFT; Equation of state

## 1. Introduction

The biomass fuels are potential substitutes for fossil fuels. Biomass conversion processes, pyrolysis, gasification, and liquefaction, are under development. In this work, we focus on the phase behavior and phase equilibria for hydrothermal upgrading (HTU) [1,2] and supercritical water gasification (SCWG) [3,4] processes.

The HTU process is a promising liquefaction process, it can be used for the conversion of a broad range of biomass feedstocks, which is an advantageous characteristic. The process is especially designed for wet materials, the drying of feedstock is not necessary. Treated in water in a temperature range of 300–350 °C and a pressure range of 120–180 bar, biomass is depolymerized to a hydrophobic liquid product so-called “biocrude”. Gases are also produced, consisting of CO<sub>2</sub>, H<sub>2</sub>, methane and CO. Other product includes water and organic compounds.

In SCWG, the reaction generally takes place at the temperature over 600 °C and a pressure higher than the critical

point of water. With temperature higher than 600 °C, water becomes a strong oxidant, and oxygen in water can be transferred to the carbon atoms of the biomass. As a result of the high density, carbon is preferentially oxidized into CO<sub>2</sub> but also low concentrations of CO are formed. The hydrogen atoms of water and of the biomass are set free and form H<sub>2</sub>. The gas product consists of hydrogen more than 50% on a mole basis, CO<sub>2</sub> in second quantity of about 33%, and others including CH<sub>4</sub> and CO.

In both the processes, the target products of biocrude and hydrogen need to be separated from the product mixture. Thermodynamic models of Statistical Associating Fluid Theory (SAFT) [5,6], PSRK [7], PR [8], and SRK [9] have been applied to model the phase equilibria for the reactor and separation units.

## 2. The HTU process

Goudriaan et al. [1,2,10] gave detailed descriptions of the HTU processes for the conversion of biomass to biocrude. The conversion reaction generally takes place in aqueous environment in the temperature range of 300–350 °C and

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### Nomenclature

$m$  segment number  
 $u^0/k$  temperature-independent dispersion energy of interaction between segments (K)

#### Greek letters

$\varepsilon^{AB}/k$  association energy interaction between sites A and B  
 $\kappa^{AB}$  volume of interaction between sites A and B  
 $v^{00}$  temperature-independent segment volume (cm<sup>3</sup>/mol)

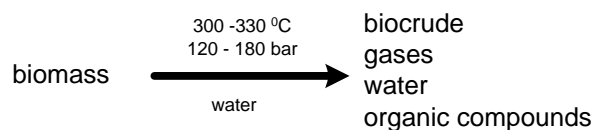


Fig. 2. Products from the HTU process.

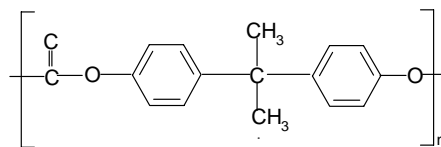


Fig. 3. Chemical repeat unit of polycarbonate.

a pressure range of 120–180 bar. The HTU process mainly consists of pre-treatment, reactor, high-pressure separator, low-pressure separator, and upgrading units, as shown in Fig. 1. In this work, the reaction temperature and pressure are specified as 330 °C and 180 bar, respectively. The operating conditions of the high-pressure separator are 230 °C and 160 bar. Low-pressure separation takes place at 80 °C and 1 bar. To better design and operate the process, we need to know more about phase behavior and phase equilibria in the reactor and separation units.

## 2.1. Phase equilibria in the HTU process

### 2.1.1. Products from HTU

As shown in Fig. 2, the biomass, with a lower energy density, is converted to biocrude with a higher energy density. The produced gases contain CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and CO. Organic compounds include mainly alcohols and acids. Oxygen in biomass is removed largely as CO<sub>2</sub> and water.

The phase equilibria in the HTU process are very complicated due to the presence of water, supercritical carbon dioxide, alcohols as well as the so-called “biocrude”. As the gas product contains more than 90 wt.% of CO<sub>2</sub> [1], it is selected to represent the gases produced. Methanol and ethanol are used to represent the organic compounds. However, it is impossible to know the biocrude exactly. For description of phase equilibria in the HTU process, the biocrude has to be characterized appropriately.

### 2.1.2. Characterization of biocrude

The biocrude produced from the HTU process has its own characteristics compared to fossil fuel, such as containing more oxygen, being a mixture with a wide molecular weight distribution, consisting of various types of molecules, and being in the solid state around room temperature. By vac-

Table 1  
Products from the HTU process

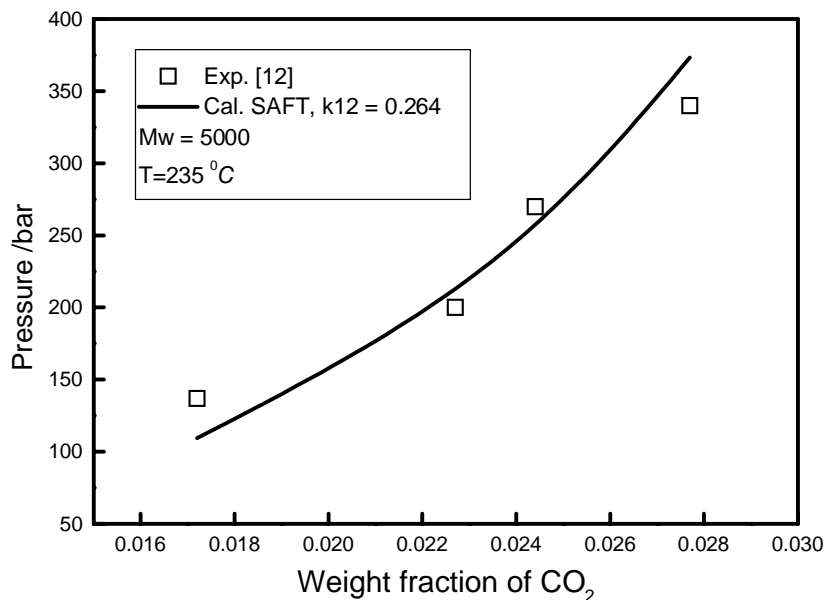
Product	Component	Molecular weight	Weight fraction (%)
Biocrude	PC760	760.00	7.5
	PC500	500.00	10.0
	PC380	380.00	17.5
	PC260	260.00	12.5
	Methyl- <i>n</i> -propyl ether	74.123	2.5
Gas	CO <sub>2</sub>	44.010	25.0
Organic compounds	Methanol	32.042	5.0
	Ethanol	44.010	3.5
Water	Water	18.015	16.5

uum flash operation, hundreds of components can be produced from the biocrude [11]. The information of elemental composition, molecular weight, and molecular weight distribution [1,10] is very useful to determine the representatives for the biocrude.

Combining the information of biocrude mentioned above, methyl-*n*-propyl ether and the polymers polycarbonate (PC) with different molecular weight are used to represent HTU biocrude. The repeat unit of PC is shown in Fig. 3. The elemental composition of the representatives of biocrude is well agreed with that of biocrude. The molecular weight of biocrude is distributed in a wide range, sometimes they could be larger than 2000 depending on the operating conditions and the feedstocks. By changing the repeat unit number of PC, the molecular weight of modeled biocrude can be easily adapted to that of biocrude. In Table 1, the weight fraction of each component is assigned to correspond to the data of the vacuum flash of biocrude [11] and the data of a pilot plant [10].



Fig. 1. Flow sheet of the HTU process. PT: pre-treatment; R: reactor; HPS: high-pressure separator; LPS: low-pressure separator; UG: upgrading unit.

Fig. 4. Swelling of PC using supercritical CO<sub>2</sub>.

### 2.1.3. Thermodynamic model and parameter determination

The products from HTU consist of biocrude, gases, and organic compounds such as alcohols and acids, and water. These products have the following characteristics:

- Including non-associating and associating components.
- Consisting of small and large molecules.
- Existing in the vapor or liquid phases.

The operating conditions are:

- Temperatures up to 350 °C.
- Pressures up to 180 bar.

The selected thermodynamic model should accommodate the above. The SAFT equation of state is selected as the thermodynamic model to describe phase equilibria. The SAFT model needs three parameters for a non-associating component, segment number  $m$ , segment volume  $v^{00}$ , segment–segment interaction energy  $u^0/k$ , and two additional parameters for an associating component, the association energy  $\varepsilon^{AB}/k$  and volume  $\kappa^{AB}$ .

By fitting the binary data of PC/CO<sub>2</sub> [12] and pressure–volume–temperature (PVT) data of PC [13] to the SAFT model, the parameters of PC are determined. The segment

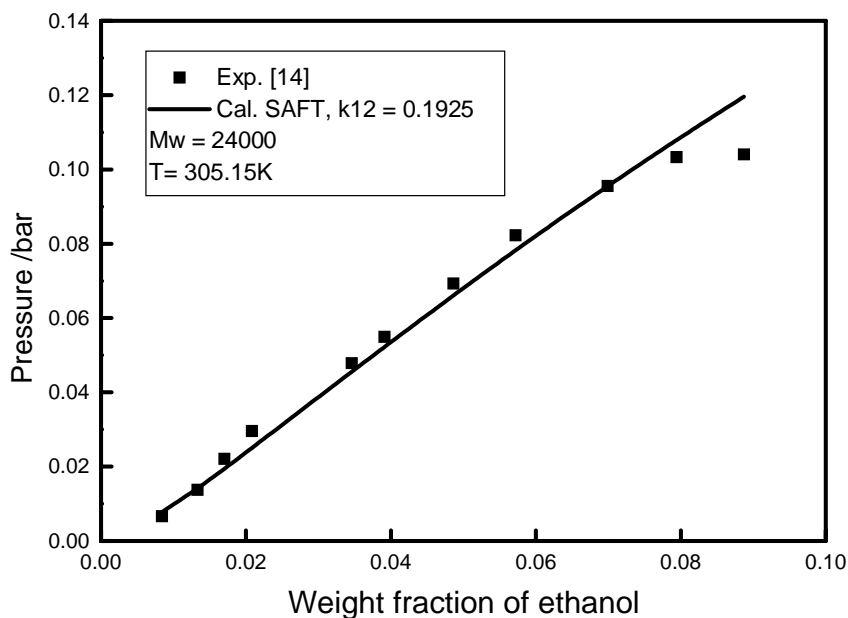


Fig. 5. Vapor–liquid equilibria for PC/ethanol.

Table 2  
The parameters of the SAFT equation of state

Component	$M_w$	$m$	$v^{00}$ (cm <sup>3</sup> /mol)	$u^0/k$ (K)	$\varepsilon^{AB}/k$ (K)	$\kappa^{AB}$	$N_{\text{ass}}^a$
PC24000 <sup>b</sup>	24000	847.20	12.0	244.700	0	0	0
PC5000 <sup>b</sup>	5000	176.50	12.0	244.700	0	0	0
PC760 <sup>b</sup>	760	26.828	12.0	260.331	0	0	0
PC500 <sup>b</sup>	500	17.650	12.0	268.461	0	0	0
PC380 <sup>b</sup>	380	13.410	12.0	275.930	0	0	0
PC260 <sup>b</sup>	260	9.178	12.0	290.204	0	0	0
Methyl- <i>n</i> -propyl ether <sup>c</sup>	74.123	4.069	10.224	208.13	0	0	0
CO <sub>2</sub> <sup>c</sup>	44.010	1.417	13.578	216.08	0	0	0
Methanol <sup>c</sup>	32.042	1.776	12.0	216.3	2714	0.04856	2
Ethanol <sup>c</sup>	46.069	2.457	12.0	213.48	2759	0.0292	2
Water <sup>c</sup>	18.015	1.179	10.0	528.17	1809	0.01593	3

<sup>a</sup> Number of association sites.

<sup>b</sup> This work.

<sup>c</sup> From literature [5].

number  $m$  has a relationship with molecular weight ( $M_w$ ) of  $m = 0.0353M_w$ ,  $u^0/k$  is equal to 244.70, and  $v^{00}$  is set to 12.0. With these determined parameters, the calculated relative deviation of liquid density for PC is 4.33% for 107 PVT data points. The binary data of PC/CO<sub>2</sub> [12] and PC/ethanol [14] have been correlated well as shown in Figs. 4 and 5. As the molecular weights of PC are smaller than 1000 in Table 1, we make use of the relationship  $m = 0.0353M_w$  to get the parameter  $u^0/k$  for each PC component with different molecular weight by fitting the PVT data of PC. The parameters needed by SAFT are listed in Table 2.

## 2.2. Results of phase equilibria for the HTU process

### 2.2.1. Vacuum flash of biocrude

The vacuum flash data of biocrude [11] are obtained at the temperature range of 160–280 °C and a pressure of 0.07 bar.

Fig. 6 shows the vaporized portion of biocrude at different temperature. The data have been reproduced well by the SAFT equation, using the components in Table 1 for representing the biocrude.

### 2.2.2. Phase equilibria and phase behavior

Feedstock is assumed to consist of 200 kg/min of dry biomass and 400 kg/min of water. The recycled water is 160 kg/min, entering the reactor together with the feedstock.

The results of phase behavior description and phase equilibrium prediction are demonstrated in Table 3 in detail and in Figs. 7 and 8 graphically. Fig. 8 shows an alternative process intended to separate the light portion of biocrude, which is suggested on the basis of phase equilibria results. The prediction of phase behavior in the reactor and subsequent separation units is in accordance with the real case. The prediction of the phase equilibria indicates the distributions of

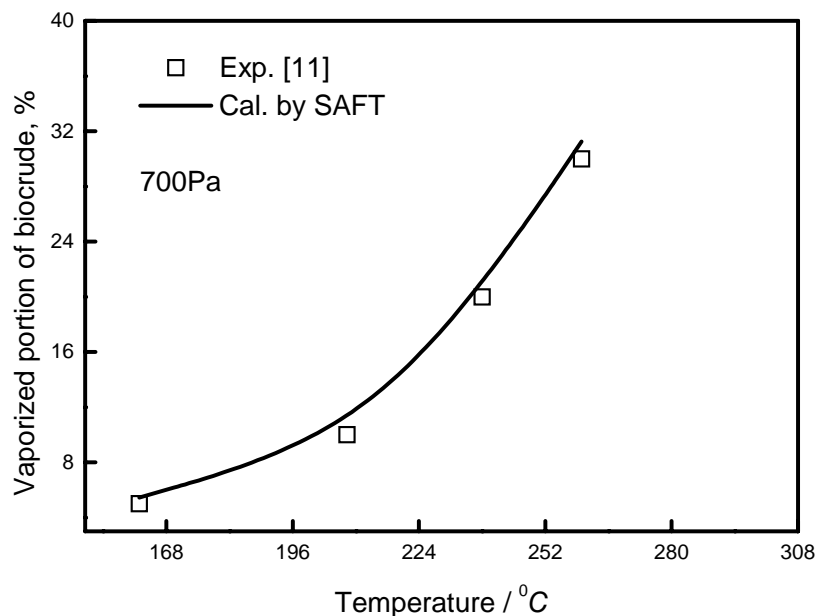


Fig. 6. Reproduced result for vacuum flash operation of biocrude.

Table 3  
Results of phase equilibria<sup>a</sup>

	Mass flow (kg/min)					
	Vapor phase		Water phase		Biocrude phase	
	Others	Biocrude	Others	Biocrude	Others	Biocrude
R (330 °C, 180 bar)	73.70	2.22	548.46	74.42	37.84	23.36
HPS (230 °C, 160 bar)			553.57	5.30	32.77	92.44
LPS (80 °C, 1 bar)	15.81	1.74	15.38	0.00	1.58	90.70
SCE <sup>b</sup> (50 °C, 200 bar)	882.48	38.67			119.10	52.03
VF (230 °C, 0.01 bar)	32.77	30.59			0.00	61.85

<sup>a</sup> R: reactor; HPS: high-pressure separator; LPS: low-pressure separator; VF: vacuum flash; SCE: supercritical CO<sub>2</sub> extraction.

<sup>b</sup> Extra CO<sub>2</sub> of 1000 kg/min is used for the supercritical CO<sub>2</sub> extraction.

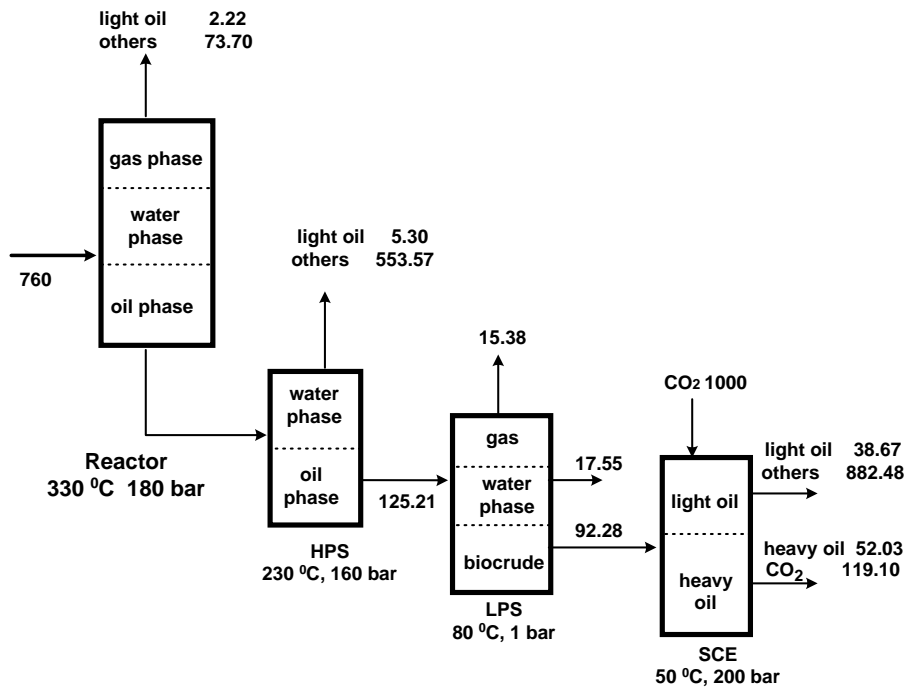


Fig. 7. Process phase behavior and phase equilibria.

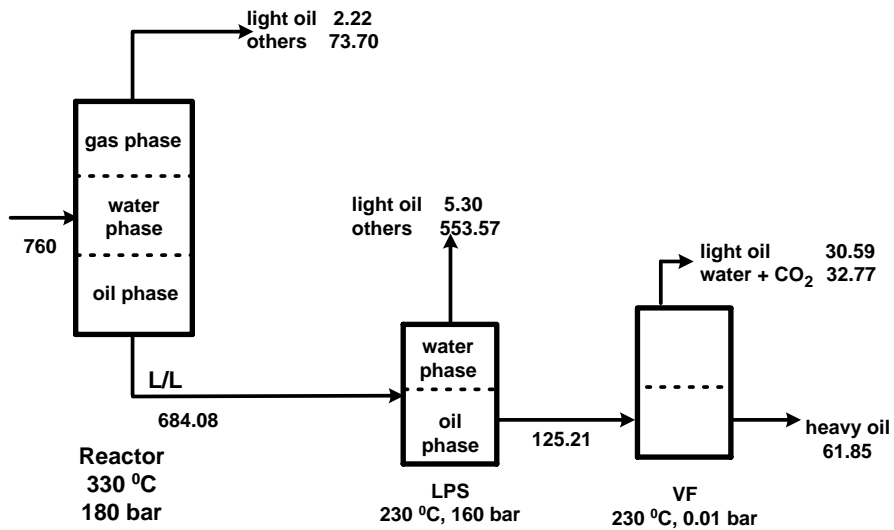


Fig. 8. Alternative process phase behavior and phase equilibria.

biocrude among the different phases. It also indicates that about 90% of the produced biocrude can be collected in the biocrude phase in low-pressure separator as shown in Fig. 7. This result is in good agreement with the experimental data [10].

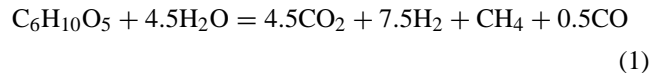
### 3. SCWG process

By treatment of biomass in supercritical water, biomass can be converted into fuel gases, which are very rich in hydrogen. As shown in Fig. 9, the pilot plant with a capacity of up to 10 kg feedstock per hour at the University of Twente (Netherlands), is taken as the reference for the scheme of the supercritical water gasification (SCWG) process. The SCWG process consists of main units as feed pumping, heat exchanger (HE), reactor, high-pressure gas–liquid separator (S1), low-pressure gas–liquid separators (S2 and S3). For further producing high purity hydrogen, pressure swing adsorption (PSA) or hydrogen membrane might be the options. In this work, we focus on the phase equilibrium descriptions in the high-pressure separators S1 in Fig. 9 and S3 in Fig. 13, respectively.

#### 3.1. Products from SCWG

We suppose that the feedstock contains 20 wt.% of cellulose and 80 wt.% of water. Cellulose is assumed to be completely converted into gas product at the temperature of

600 °C and the pressure of 350 bar as shown in Eq. (1)



The gas product consists of hydrogen (55.56%), CO<sub>2</sub> (33.33%), CH<sub>4</sub> (7.41%), and CO (3.70%) in mole fraction based on Eq. (1). Hydrogen is the target product. For producing higher purity hydrogen, the description of phase equilibrium is helpful for the process operation.

#### 3.2. Phase equilibria in high-pressure separator

High purity hydrogen can be produced by a series of subsequent separation units, which include the separation of gas product from water, the removal of CO<sub>2</sub> from gas mixture, and the production of high purity hydrogen. As shown in Fig. 9, the separation of gas mixture from water can be easily carried out in S1. Hopefully, the CO<sub>2</sub> can be removed from the gas product in a large quantity by being dissolved in water at a high-pressure of 350 bar and a low temperature of 25 °C. The description of phase equilibria is to determine the amount of water required to dissolve certain amount of CO<sub>2</sub>. Meanwhile, the dissolved hydrogen in water phase can also be known.

##### 3.2.1. Solubility of CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> in water at high-pressure

The binary data [15] of water/CO<sub>2</sub>, water/H<sub>2</sub>, water/CH<sub>4</sub>, and water/CO have been used to determine the binary

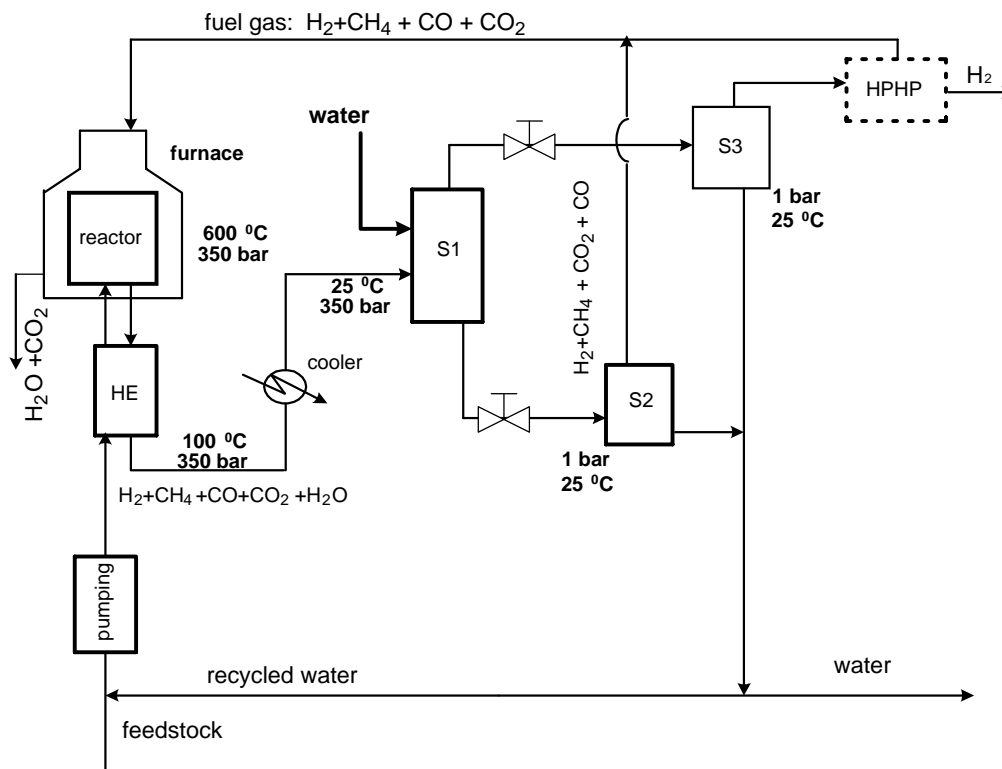


Fig. 9. Schematic flow sheet of the SCWG process. HE: heat exchanger; S: separator; H2P: high purity hydrogen production.

Table 4  
The binary parameters for SAFT, PR, and SRK at 25 °C

Substance	CO <sub>2</sub> /H <sub>2</sub> O	H <sub>2</sub> /H <sub>2</sub> O	CH <sub>4</sub> /H <sub>2</sub> O	CO/H <sub>2</sub> O
SAFT	-0.075	-0.65	-0.128	-0.34
PR	-0.120	-2.70	-0.315	0.00
SRK	-0.135	-2.80	-0.380	0.00

interaction parameters for SAFT, PR, and SRK. The SAFT parameters for hydrogen are obtained by Kreglewski [16], parameters of hydrogen are used as the SAFT parameters, which are 1.0004 (segment length), 13.625 (segment volume), and 39.171 (segment interaction energy). Table 4 lists

Table 5  
Phase equilibria results with water as the solvent at 25 °C and 350 bar

Component	Feed (kg)	Mole fraction in vapor phase			
		PSRK	SAFT	SRK	PR
CO <sub>2</sub>	1.98	0.087	0.089	0.086	0.083
CH <sub>4</sub>	0.16	0.093	0.098	0.094	0.093
CO	0.14	0.043	0.052	0.070	0.069
H <sub>2</sub>	0.15	0.777	0.760	0.749	0.754
H <sub>2</sub> O (ppm)	102.10	771	489	829	975
Percentage of total H <sub>2</sub> dissolved in liquid phase		20.68	26.73	28.75	26.77

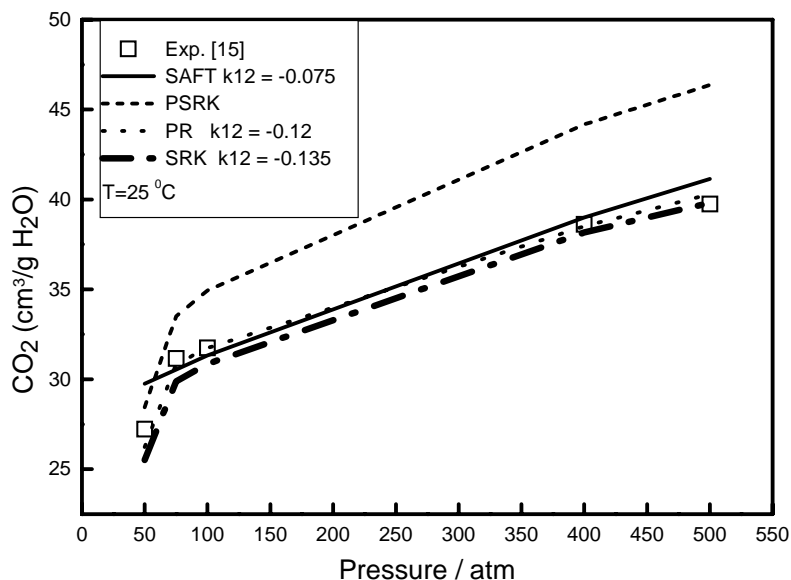


Fig. 10. Solubility of CO<sub>2</sub> in water at the temperature of 25 °C.

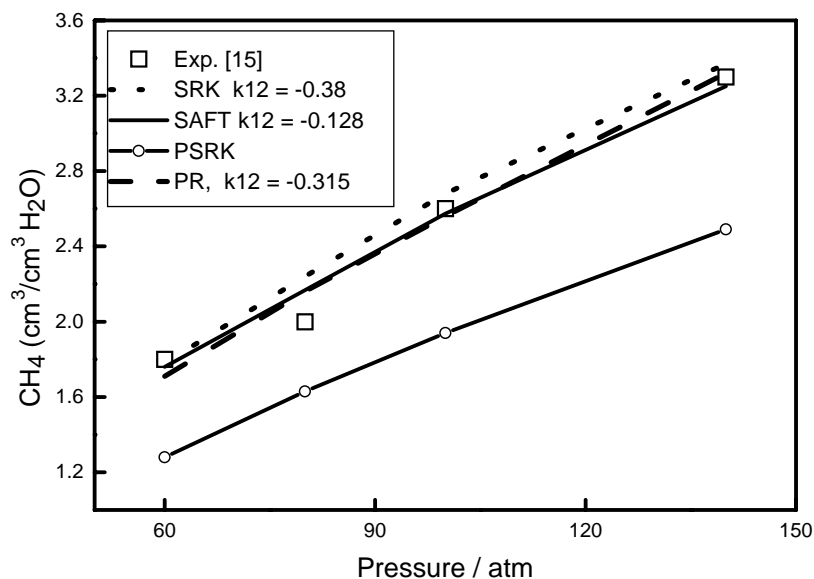


Fig. 11. Solubility of CH<sub>4</sub> in water at the temperature of 25 °C.

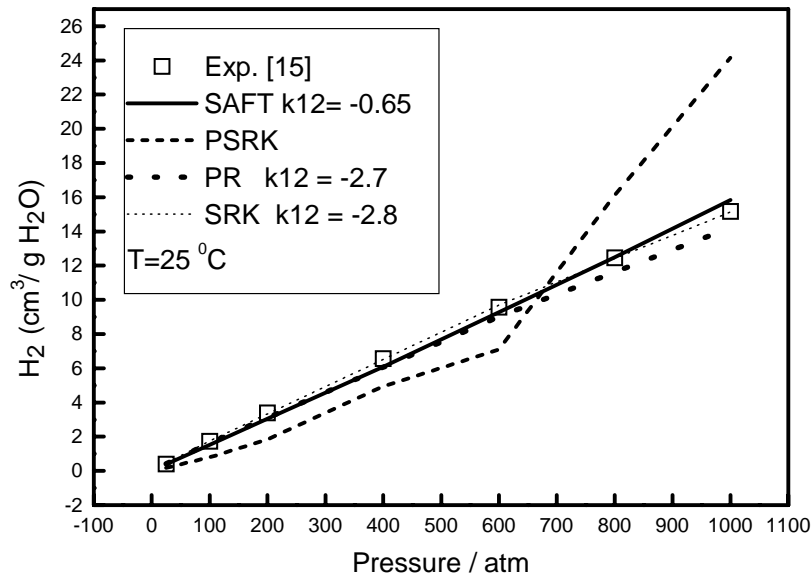


Fig. 12. Solubility of  $H_2$  in water at the temperature of  $25\text{ }^\circ\text{C}$ .

the binary parameters determined. The calculated results by PSRK, SAFT, PR, and SRK are shown in Figs. 10–12. The correlated results are quite well compared to the experimental data. However, the results are very sensitive to the values of the binary parameters, and some of them are very large, for example, for the systems hydrogen/water and methane/water.

### 3.2.2. Results of phase equilibria with water as the solvent

Table 5 shows the results of phase equilibria for the high-pressure separator S1 in Fig. 9. The water amount of 102.10 kg includes the added water of 96.43 kg and process water of 5.67 kg. The amount of the added water is about 40 times that of gas product. The calculated results of hydrogen purities in vapor phase by the four models are

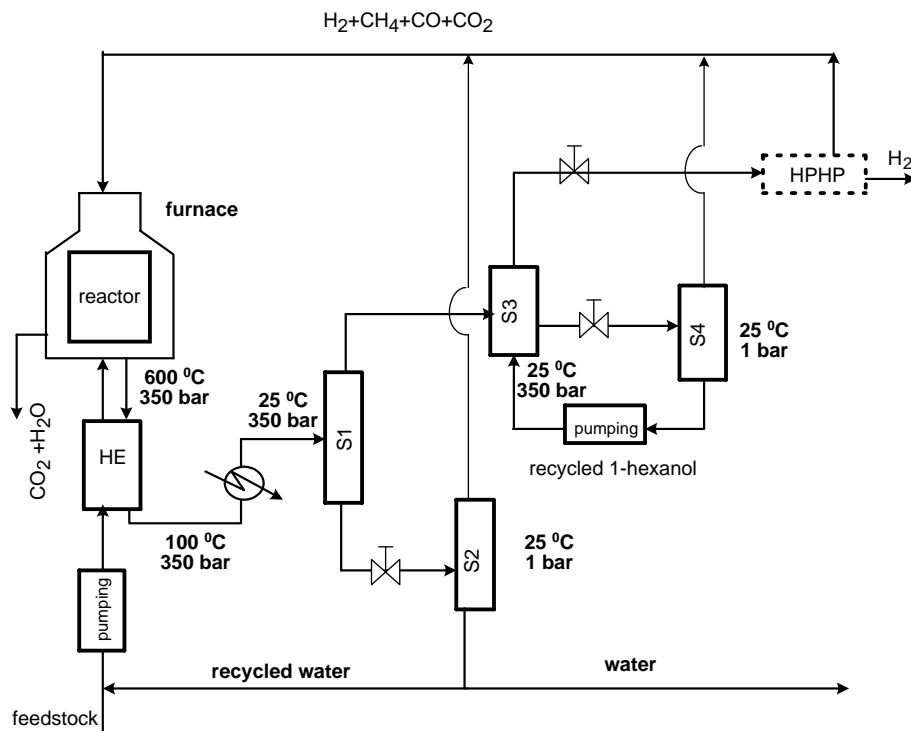


Fig. 13. The alternative SCWG process. In S3, the 1-hexanol is proposed as the solvent. HE: heat exchanger; S: separator; HPHP: high purity hydrogen production.



Table 6  
The predicted results of phase equilibria with 1-hexanol as the solvent

Component	Feed (kg)	Mole fraction in vapor phase			
		SRK	PR	PSRK	SAFT
CO <sub>2</sub>	1.98	0.076	0.075	0.160	0.078
CH <sub>4</sub>	0.16	0.058	0.055	0.064	0.052
CO	0.14	0.045	0.045	0.039	0.047
H <sub>2</sub>	0.15	0.820	0.825	0.736	0.823
1-Hexanol (ppm)	10.21	63	78	255	30
Percentage of total H <sub>2</sub> dissolved in liquid phase		17.23	14.65	16.34	25.20

comparable. The calculated amount of hydrogen dissolved in liquid phase by PSRK is less than that calculated by other three models.

### 3.3. 1-Hexanol as the alternative solvent

For getting the hydrogen purity of about 75% in mole fraction, much more added water has to be used as mentioned above. To reduce the amount of solvent, 1-hexanol is proposed as the alternative solvent. CO<sub>2</sub> is mainly removed in the high-pressure separator S3 in Fig. 13. The results in Table 6 are predicted using four models of SAFT, PSRK, PR, and SRK. To give a comparison, the mass flows of gases are the same as those in Table 5. The binary parameters for RKS, PR, and SAFT are set to zero. Using the weight amount of one-tenth of that of water, 1-hexanol can achieve higher or comparable hydrogen purity in the vapor phase, while less hydrogen dissolved in the liquid phase.

## 4. Conclusions

The description of phase equilibria for two biomass conversion processes has been carried out. For the HTU process, by properly characterizing biocrude produced and the application of the SAFT equation of state, the described phase behavior is in accordance with the real case, and the result of simulated biocrude separation is in good agreement with the data of a pilot plant.

For the SCWG process, four models have been applied to predicate the results of phase equilibria for the removal CO<sub>2</sub> by dissolving in water and in 1-hexanol. Compared to water, 1-hexanol can achieve higher separation efficiency. Much less amount of solvent is needed, higher or comparable hydrogen purity is obtained in the vapor phase, less produced hydrogen is dissolved in the liquid phase. However, data are

not available yet to compare with the calculated results and to determine the most suitable thermodynamic model for this process.

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## References

- [1] F. Goudriaan, D.G.R. Peferoen, Liquid fuels from biomass via a hydrothermal process, *Chem. Eng. Sci.* 45 (1990) 2729.
- [2] F. Goudriaan, et al., Thermal efficiency of the HTU process for biomass liquefaction, in: *Progress in Thermochemical Biomass Conversion*, vol. 2, Blackwell Science, Oxford, 2001, 1312 pp.
- [3] I. Lee, M. Kim, S. Ihm, Gasification of glucose in supercritical water, *Ind. Eng. Chem. Res.* 41 (2002) 1182.
- [4] M.J. Antal Jr., S. Allen, D. Schulman, X. Xu, R. Divilio, Biomass gasification in supercritical water, *Ind. Eng. Chem. Res.* 39 (2000) 4040.
- [5] S.H. Huang, M. Radosz, Equation of state for small, large, polydisperse, and associating molecules, *Ind. Eng. Chem. Res.* 29 (1990) 2284.
- [6] S.H. Huang, M. Radosz, Equation of state for small, large, polydisperse and associating molecules: extensions to fluid mixtures, *Ind. Eng. Chem. Res.* 29 (1991) 1994.
- [7] J. Chen, K. Fisher, J. Gmehling, Modification of PSRK mixing rules and results for vapor–liquid equilibria, enthalpy of mixing and activity coefficients at infinite dilution, *Fluid Phase Equil.* 200 (2002) 411.
- [8] D.-Y. Peng, D.B. Robinson, A new constant equation of state, *Ing. Eng. Chem. Fund.* 15 (1976) 59.
- [9] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, *Chem. Eng. Sci.* 27 (1972) 1197.
- [10] F. Goudriaan, Personal communication, 2001.
- [11] F. Goudriaan, Personal communication, 2001.
- [12] S.M. Gross, R.D. Givens, M. Jikei, J.R. Royer, S. Khan, J.M. DeSimone, Synthesis and swelling of poly(bisphenol A carbonate) using supercritical CO<sub>2</sub>, *Macromolecules* 31 (1998) 9090.
- [13] P. Zoller, A study of the pressure–volume–temperature relationships for four related amorphous polymers: polycarbonate, polyarylate, phenoxy, and polysulfone, *J. Polym. Phys. Ed.* 20 (1982) 1453.
- [14] S. Hwang, J. Kim, K.P. Yoo, Vapor liquid equilibrium data of binary polymer solutions by vacuum electromicrobalance, *J. Chem. Eng. Data* 43 (1998) 614.
- [15] W.F. Ed Linke, *Solubilities: Inorganic and Metal-Organic Compounds*, A Compilation of Solubility Data from the Periodical Literature, American Chemical Society, Washington, 1958, 54 pp.
- [16] A. Kreglewski, *Equilibrium Properties of Fluids and Fluid Mixtures*, University Press, College Station, Texas A and M, 1984.