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Chemicals Loading in Acetylated Bamboo Assisted by Supercritical CO_2 Based on Phase Equilibrium Data

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Abstract. Indonesia has a large tropical forest. However, the deforestation still appears annually and vastly. This reason drives a use of bamboo as wood alternative. Recently, there are many modifications of bamboo in order to prolong the shelf life. Unfortunately, the processes need more chemicals and time. Based on wood modification, esterifying of bamboo was undertaken in present of a dense gas, i.e. supercritical CO_2. Calculation of chemicals loading referred to ASTM D1413-99 by using the phase equilibrium data at optimum condition by a statistical design. The results showed that the acetylation of bamboo assisted by supercritical CO_2 required 14.73 kg acetic anhydride/m^3 of bamboo for a treatment of one hour.

Keywords: acetylation, bamboo, chemicals loading, supercritical CO_2

INTRODUCTION

Bamboo with the ecological benefits regards as well as auspicious material due to increasing natural resources demand with circumscribed supply. It is a sustainable material due to the high-carbon capture in the biomass, the fast growing of the plants, and it is abundantly available in Asia. Indonesia has around 135 species of bamboo [1-3]. Therefore, it would be nice to reduce the devastation of tropical forest where about 0.5 million ha are annually deforested, by the use of bamboo [4]. As consequences many research activities are trying to substitute wood with other ligno-cellulous materials, such as bamboo. Hitherto, the modification of bamboo has been conducted based on wood modification in order to extend the shelf life concerning to the durability aspect [5].

The acetylation using acetic anhydride is an accustomed chemical treatment of wood for over 50 years. The acetylation of the bamboo species Dendrocalamus asper is already reported [6]. In this work, the acetylation is supported with a surface modification using microwaves leading to increase liquid uptake. In this research bamboo modification through acetylation assisted by scCO2 without a catalyst is based upon the acetylation of wood using supercritical carbon dioxide [7].

The use of carbon dioxide in chemicals processing gained from waste gas of industries is considered as sustainable. Thus, in the context of the principles of green chemistry [8], scCO2 acts as an environmentally benign reaction medium for chemical synthesis. The density and solvent power of CO2 correspond to those of liquid, while its compressibility and transport properties are similar to a gas [9]. Therefore, scCO2 is used as auxiliary media for

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the impregnation of wood [7]. In addition, the high diffusivity allows a deep penetration of the wood and bamboo structure.

In this modification, it is required to know the solubility of acetic anhydride at a certain pressure and temperature in scCO2 as solvent to carry chemicals from the bamboo surface toward the porous bamboo interior. Moreover, this chemicals loading calculation requires the amount of absorbed and reacted chemicals in the bamboo. In this case, the weight percent gain (WPG) was obtained in order to calculate the chemicals loading. The chemicals loading represents the number of kilograms of chemicals per cubic meter of bamboo which can be absorbed and reacted inside the bamboo sample. This consideration refers to ASTM D1413 – 99 (ASTM 1999) by using the equation (1) to calculate the chemicals loading.

$$Retention = \frac{G.C}{V} \tag{1}$$

The G refers to grams of chemicals (acetic anhydride) which absorbed and reacted in bamboo; the C is the grams of chemicals (acetic anhydride) in 100 g treating solution of CO2, and the V is the volume of the bamboo sample in cm^3.

By using the carrier medium of scCO2, it is notable to observe the amount of acetic anhydride dissolving in scCO2. Moreover, its solubility in scCO2 is involved not only to elucidate the process but also to optimize by statistical.

The main objective of this paper discusses further to use the phase equilibrium data in order to calculate the chemicals loading of acetic anhydride during the acetylation of bamboo.

MATERIALS AND METHODS

All experiments including the phase equilibrium and the acetylation assisted by scCO2 have been executed at Particle Technology Department of University Bochum in Germany. In the following paragraph, the used materials, the experimental setup and the method to achieve the objective are briefly explained.

Materials

This research used petung bamboo (Dendrocalamus asper) originally delivered from Sumedang, East Java, Indonesia. All samples were further dried (ISO 2004)at a temperature of 378 K for 24 hours after sizing into 10 mm x 10 mm x 10 mm. Afterwards, the dried samples were subjected to a scCO2 extraction, prior to the modification. YARA/HYDRO company provided scCO2 with a purity of 99.9%v/v. Acros Organic supplied the acetic anhydride by with a 99+% purity.

Phase Equilibria

Figure 1 presents the experimental setup (View cell, NWA GmbH, Germany). The acetic anhydride (AAH) was put in the view cell and heated up to the reaction temperature with a heating coil. The phase equilibrium measurements were made by sampling, using a static analytical method. The previous research [5] has briefly described complete procedure. The weight of CO2 in both phases was calculated from the difference in the glass tube weight after sampling and degassing the glass tube as well as by additional volume calculations of CO2 measured with a flow meter. Similarly, the weight of acetic anhydride was determined with a weight difference between degassing glass tube and initial glass tube weight.

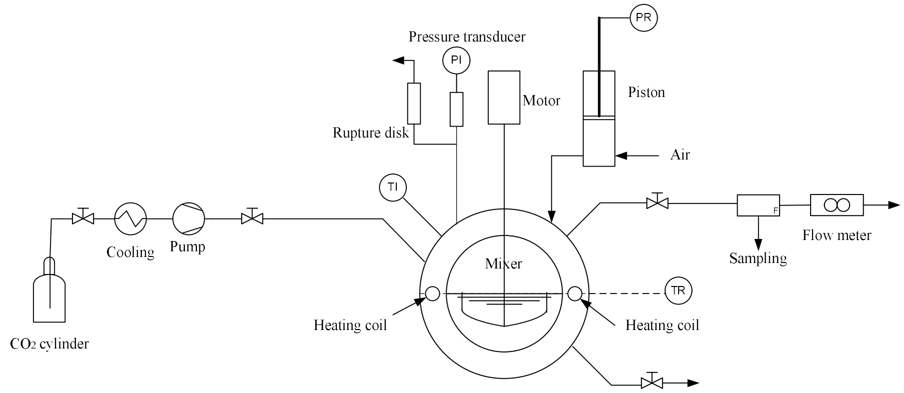

FIGURE 1. Experimental setup for the high-pressure phase equilibrium

Not only the experimental determination of the phase equilibrium, the vapor-liquid equilibria was modeled with the Peng-Robinson Styrjek Vera Equation of State (PRSV EOS) by use of an isothermal bubble point algorithm. The algorithm referred to Orbey & Sandler (1998) [11]. Experimental data of the vapor pressure were taken from Dortmund Data Bank [12]. Critical properties of all components have used compilation data by Poling, et.al, 2001 [13]. In this paper, the PRSV-EOS used a two-parameter van der Waals model [11] in order to examine the consistency of the data through the average absolute deviation (AAD) [14].

Acetylation

Pre-treated bamboo was placed on a net in the middle of the autoclave. By using a syringe, acetic anhydride in the required amount was injected into the autoclave. The detailed process was already published in [5]. Figure 2 shows schematically the equipment used for the batch wise acetylation of bamboo (View cell, NWA GmbH Germany). All experiments were designed by a statistical in order to obtain the optimum condition through factorial design with 3 variables, i.e. pressure, temperature, and time. The results were examined using Design Expert 8.0.6 (Stat-Ease, Inc) as statistical software.

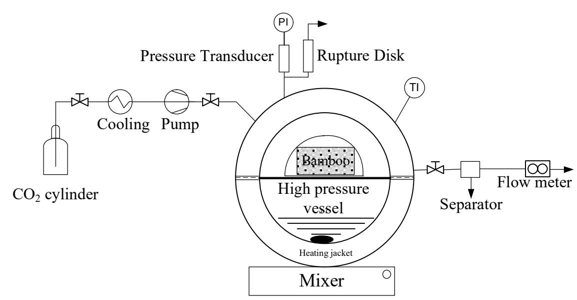

FIGURE 2. High-pressure experimental setup for batch acetylation of bamboo

Chemicals loading

The chemicals loading was calculated according to equation (1). The G-value used the weight percent gain (WPG) at a temperature of 393 K and a pressure of 165 bar for 1 (one) hour. The solution volume (V) considered using the view cell with a volume of 14.27 cm3. The C-value referred to the solubility of used acetic anhydride in the scCO2. The volume of the bamboo sample used estimation value from the initial weight of bamboo divided by the average bulk density of bamboo (Pascal Porosimeter 140, Thermo Electron, S.p.A, Italy).

RESULT AND DISCUSSION

The study performed the high-pressure phase equilibria measurements in this system at temperature of 363 K, 373 K, and 393 K without catalyst. As indicated in Fig.3 shows that the solubility of acetic anhydride in $scCO_2$ (gas phase) slightly increase at determined temperature and pressure, whereas the solubility $scCO_2$ in acetic anhydride (liquid phase) substantially decrease; however the measurements below 2 MPa were not investigated. In order to assess the thermodynamic consistency, the fitting of phase equilibrium data employed the PRSV/VW model. A detail explanation of this algorithm is given in Figure 4. This modeling used the modification of Peng-Robinson equation of state requiring few input (critical properties and acentric factor) to generate phase equilibria prediction data. Optimization of $\kappa 1$ parameters used the fitting the vapor pressure of all component in the system. The Peng Robinson equation of state modified by Stryjek and Vera is the most applicable to multicomponent of high pressure supercritical CO_2 systems assisted with Wong Sandler mixing rules [15,14]. In this case, the PRSV-EOS used the two-parameter van der Waals model in order to further predict the system of acetic anhydride (AAH) and supercritical carbon dioxide ($scCO_2$). In addition, the two-parameter van der Waals model used an additional parameter to enable the calculation of compositions. The binary parameter (k_{ij}) performed in this model i.e. equation (2), is a composition-dependent two parameter term. This paper outlines the assessment of the thermodynamic consistency of the obtained phase equilibrium data using the PRSV-EOS two-parameter van der Waals mixing rules [14]. The results of the two-parameter van der Waals one fluid model exhibit the average absolute deviation (AAD) below 5% over entire temperature range. Table 1 presents the thermodynamic consistency of phase equilibrium data in this research and gives k_{12}, k_{21} for the two-parameter van der Waals model. Thus, this obtained phase equilibrium data can be used to calculate the chemicals loading during the acetylation of bamboo.

$$k_{ij} = K_{ij} x_i + K_{ji} x_j \tag{2}$$

TABLE 1. Two parameters van der Waals mixing rules for the PRSV-EOS of the binary systems including AAD (%)

T (K)	k_{12}	k_{21}
363	0.0423(0.242%)	0.0122(0.242%)
373	0.0435(2.005%)	0.0845(2.005%)
393	0.0236(2.506%)	-0.0094(2.506%)

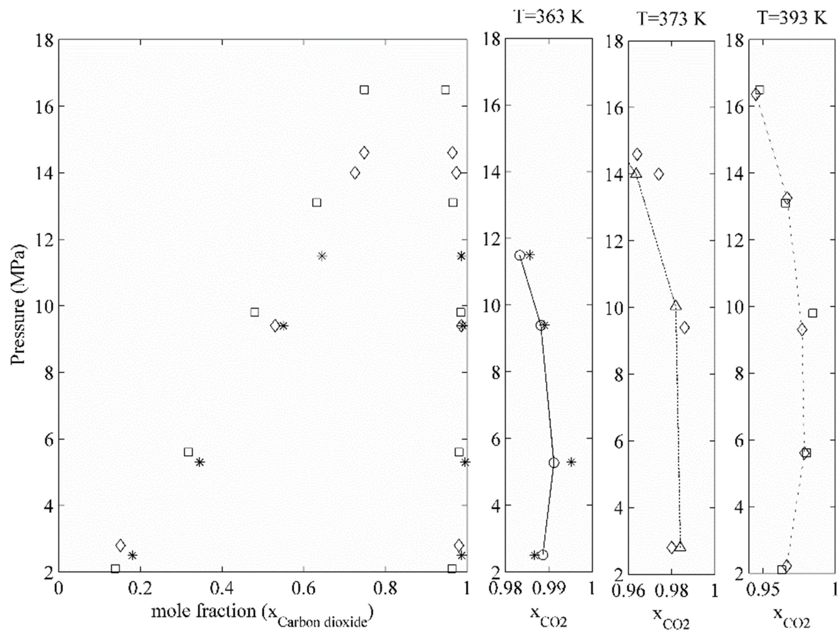

FIGURE 3. Isothermal P-x relation for acetic anhydride-carbon dioxide system. (*) observed 363 K (solid line) PRSV-VDW 2 parameters 363 K (◊) observed 373 K (dash-dot line) PRSV-VDW 2 parameters 373 K (□) observed 393 K (dotted line) PRSV-VDW 2 parameters 393 K

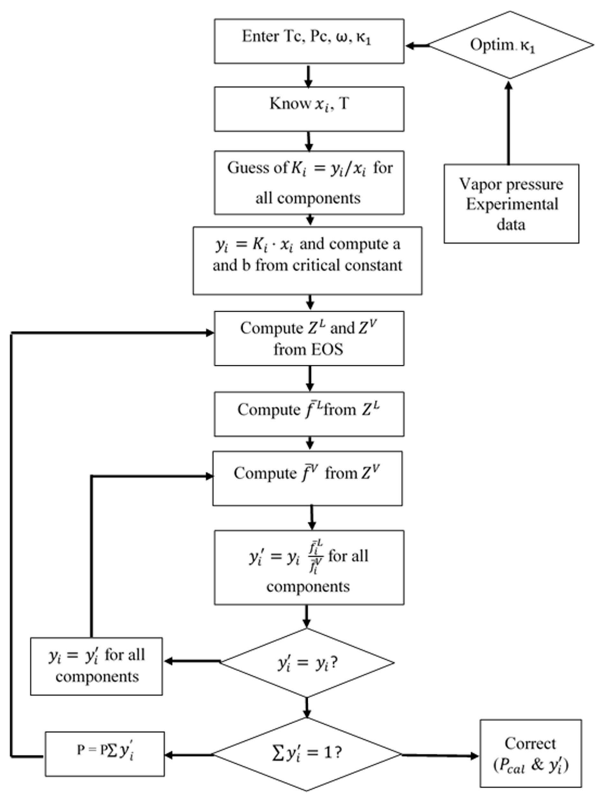

FIGURE 4. Modified algorithm of VLE calculation using the PRSV-EOS with van der Waals mixing rules (Orbey & sandler 1998)

The G-value can be obtained from statistical result under optimum conditions of acetylation achieved at 20.87% of WPG at an optimum condition with the weight difference of 0.11 g and an initial weight of bamboo of 0.54 g. The volume (V) was considered in the view cell with a volume of 14.27 cm^3. The C-value used the weight of applied acetic anhydride divided by the scCO2 in the view cell. The initial weight of bamboo divided by the average density of bamboo (0.56 g/cm^3) figured the volume of the bamboo sample. The calculation yielded chemicals loading around 14.72 kg acetic anhydride/m^3 of bamboo for one hour. This calculation denoted that acetylation assisted by supercritical CO_2 was faster than other chemicals loading of conventional bamboo modification, i.e. using borax ($Na_2B_4O_7.10H_2O$) about 11.93 kg/m^3 – 21.44 kg/m^3 of petung bamboo for 5 (five) days [17].

CONCLUSION

The estimation of chemicals loading in bamboo acetylation assisted by $scCO_2$ can be determined based on phase equilibrium data. Upon thermodynamic consistency, obtained phase equilibrium data of the system had the low percentage of average absolute deviation (below 5%) by fitting with the PRSV-EOS using the two-parameter van der Waals mixing rules. Therefore, this solubility data can be further used to predict the chemicals loading in acetylation of bamboo. The chemicals loading considered to ASTM D1413 – 99 generating the equation for the calculation. The result show that bamboo acetylation assisted by densified gas, i.e. $scCO_2$, can conserve higher amounts of chemicals in short time compared to conventional modification processes.

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