

Gasification of Trans-4-Hydroxycinnamic Acid with Ethanol at Elevated Temperatures

Shyh-Ming Chern, Wei-Ling Lin

Abstract—Lignin is a major constituent of woody biomass, and exists abundantly in nature. It is the major byproducts from the paper industry and bioethanol production processes. The byproducts are mainly used for low-valued applications. Instead, lignin can be converted into higher-valued gaseous fuel, thereby helping to curtail the ever-growing price of oil and to slow down the trend of global warming. Although biochemical treatment is capable of converting cellulose into liquid ethanol fuel, it cannot be applied to the conversion of lignin. Alternatively, it is possible to convert lignin into gaseous fuel thermochemically. In the present work, trans-4-hydroxycinnamic acid, a model compound for lignin, which closely resembles the basic building blocks of lignin, is gasified in an autoclave with ethanol at elevated temperatures and pressures, that are above the critical point of ethanol. Ethanol, instead of water, is chosen, because ethanol dissolves trans-4-hydroxycinnamic acid easily and helps to convert it into lighter gaseous species relatively well. The major operating parameters for the gasification reaction include temperature (673-873 K), reaction pressure (5-25 MPa) and feed concentration (0.05-0.3 M). Generally, more than 80% of the reactant, including trans-4-hydroxycinnamic acid and ethanol, were converted into gaseous products at an operating condition of 873 K and 5 MPa.

Keywords—Ethanol, gasification, lignin, supercritical.

I. INTRODUCTION

BIOMASS is composed of three major constituents, cellulose, hemicellulose and lignin. Among them, lignin is the hardest for conversion into more valuable products. Cellulose can be decomposed into glucose biochemically or chemically, and then be converted into ethanol through fermentation or converted into syngas through gasification [1]. However, so far, the fermentation technology has not been applicable to the conversion of lignin, probably due to the aromatic nature of the lignin. Traditionally, lignin comes mainly from the paper industry as a byproduct with an annual amount of over 100 million tons. Lately, lignin also comes from the bioethanol production processes with annual amount even greater than that from paper industries. It is utilized mainly for low-valued applications, such as dispersants in cement and water treatment. On the other hand, since lignin has a high energy content, it is suitable for conversion into higher-valued gaseous fuel.

Lignin is an extremely complicated biopolymer, often consisting of more than 10,000 units of monomers, mainly paracoumeryl alcohol, coniferyl alcohol and sinapyl alcohol. These monomers are quite similar in structure and properties.

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The model compound, trans-4-hydroxycinnamic acid (T4HA), employed in this study, is the acid version of paracoumeryl alcohol. Like lignin, T4HA is hydrophobic and essentially insoluble in water. Therefore, instead of supercritical water, ethanol at elevated temperatures is employed as a medium for the gasification of T4HA. Supercritical ethanol has been used successfully for the degradation of lignin. Patel et al. [2] employed supercritical ethanol with heterogeneous catalysts for the hydrogenation of lignin and obtained liquid products consisting mainly of phenols and substituted phenols. The conversion can be as high as 98% (Ru/ γ -Al₂O₃, 573 K and 20 hr). Other studies concerning the conversion of lignin are mostly based on supercritical water [3]-[5]. Studies on the conversion of lignin into gaseous products based on ethanol are scarce. Zhao et al. [6] investigated the conversion of kraft lignin in ethanol into both liquid and gaseous products, and achieved a very high H₂ selectivity with the use of catalyst (82 vol. %, Rh/La₂O₃/CeO₂-ZrO₂, 623 K, 4 hr). However, most ethanol-based lignin conversion studies employed a moderate temperature of no greater than 623 K, where ethanol essentially does not react and acts as a solvent. On the other hand, the present study adopted elevated temperatures, 673-873 K, where ethanol decomposes and participates in the gasification reaction of lignin vigorously.

II. EXPERIMENTS

A. Materials

Reagent-grade trans-4-hydroxycinnamic acid (T4HA), 98 wt. % purity from ALFA, and ethanol, 99.5 wt. % purity from Nihon Shiyaku Reagent, were used as the organic reactant. 99.999 % pure helium gas was used as carrier gas for GC-TCD, and as the purge gas for expelling air out of the reactor at the beginning of an experimental run.

B. Methods and Procedures

Batch-type autoclave reactors were employed for the experiments. A reactor assembly consists of a 16-ml cylindrical autoclave body, a valve on its top, and a tubing connecting them, all made of 316L stainless steel. It is capable of withstanding pressure up to 140 MPa at ambient temperature. The gasification is driven by external heating that vaporizes ethanol inside the reactor and pressurizes the reaction system. Similar experimental procedures were detailed in previous studies [7]. A typical experimental run takes 90 minutes of heating, including a temperature ramp-up of about 25 minutes and a residence time of about 65 minutes at the reaction temperature. Measured data include the weight, the volume, and the composition of the product gas, which is determined to

comprise mainly H_2 , CO , CH_4 , CO_2 , C_2H_4 , and C_2H_6 with a gas chromatogram/thermal conductivity detector (GC/TCD, ThermoQuest TRACE 2000).

The main operating parameters are reaction temperature, reaction pressure and the concentration of T4HA in the feed, a solution of T4HA in ethanol. In order to enhance the gasification reaction, elevated operating temperatures were employed, from 673 to 873 K at 50 K intervals. The pressure in the reactor is not directly controllable. Instead, it is indirectly controlled by setting the temperature and assuming the pressure is the same as the vapor pressure of ethanol inside the reactor. The vapor pressure of ethanol in elevated temperatures is estimated by an empirical equation of state for ethanol [8]. However, ethanol is unstable and will decompose into lighter gases at temperatures above 673 K, as can be seen later in Fig. 1. As a result, the actual pressure in the reactor is lower than that calculated by the equation of state. Three level of pressures, 5, 15, and 25 MPa, were employed in the experiments. For safety reason, the highest pressure, namely 25 MPa, was only employed up to 773 K. Four levels of T4HA concentration in ethanol, 0, 0.25, 0.5 and 1.0 M, were tested in the experiments to investigate loading effect of T4HA in ethanol.

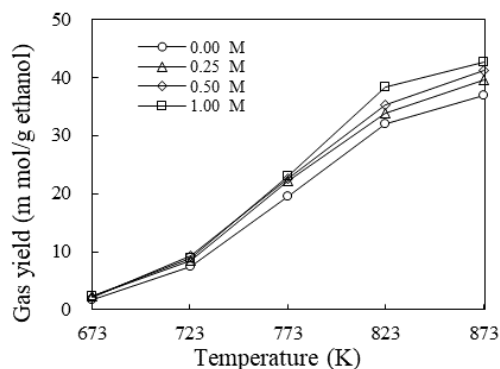


Fig. 1 Dry gas yield versus temperature with T4HA concentration as the parameter under 5 MPa

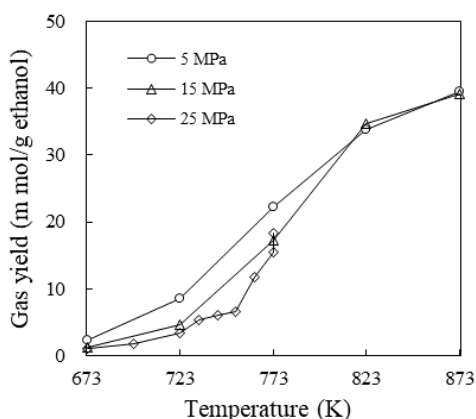


Fig. 2 Dry gas yield versus temperature with pressure as the parameters at 0.25 M T4HA concentration

III. RESULTS AND DISCUSSIONS

To facilitate the comprehension of the results, a number of terms are defined as follows. Gas yield is the millimols of the dry gas produced on the basis of one gram of ethanol fed to the reactor. Higher heating value (HHV) of the dry gas is the heat of combustion per mole of dry product gas, assuming H_2O in the combustion product is in liquid state. Gas conversion is ratio of the mass of the product gas to the mass of the feed, T4HA and ethanol. Energy conversion is the ratio of the heating value of the product gas to the heat value of the feed, T4HA and ethanol.

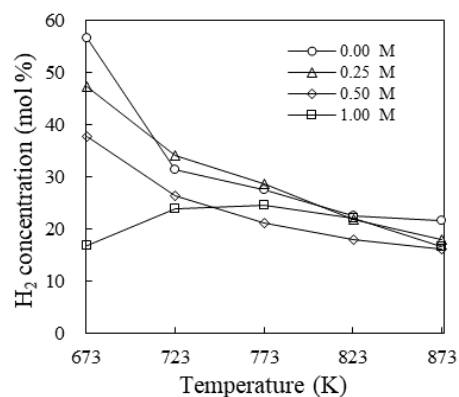


Fig. 3 H_2 concentration in dry gas versus temperature with T4HA concentration as the parameter under 5 MPa

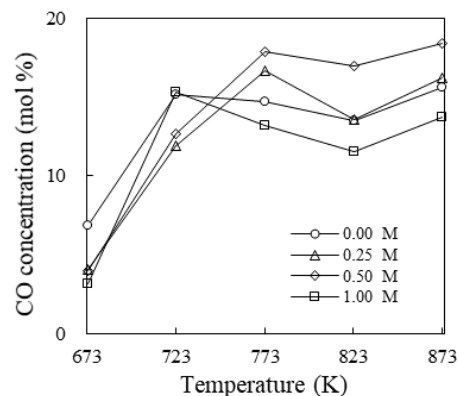


Fig. 4 CO concentration in dry gas versus temperature with T4HA concentration as the parameter under 5 MPa

Reaction temperature is the most important operating parameter for the present gasification process, as can be witnessed from Fig. 1, which displays the gas yield versus reaction temperature with T4HA concentration as the parameter. The gas yield at the low temperature end, 673 K, is very low, meaning the extent of gasification is only minimal. It then increases rapidly with rising temperature all the way to the higher temperature end of 873 K, at which it reaches about 40 mmols/g ethanol. Without the addition of T4HA, the gasification of pure ethanol serves as the back ground for the observation of the gasification of T4HA. This back ground information is needed, since both T4HA and ethanol produce

the same gas species during the gasification. Hence, on a practical point of view, it is assumed the difference between the gas yield with T4HA and that without T4HA is the gas yield of T4HA. On the basis of this assumption, it can also be seen from Fig. 1 that the gas yield of T4HA gasification also increases with rising temperature and that the marginal gas yield is shrinking with increasing T4HA concentration.

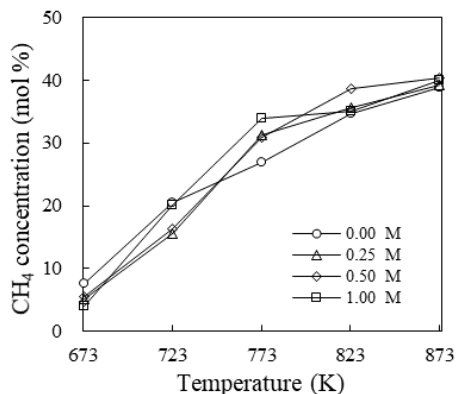


Fig. 5 CH₄ concentration in dry gas versus temperature with T4HA concentration as the parameter under 5 MPa

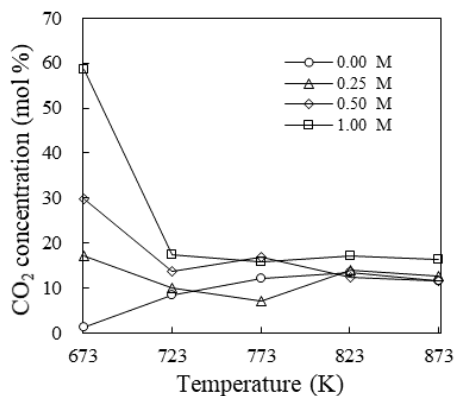


Fig. 6 CO₂ concentration in dry gas versus temperature with T4HA concentration as the parameter under 5 MPa

The effect of the reaction pressure is illustrated in Fig. 2, where gas yield is plotted against temperature with pressure as the parameter. As stated earlier, experiments under 25 MPa were not performed for temperatures above 773 K for safety. It is quite obvious that boosting pressure suppresses gasification moderately below 823 K, and has little effect above 823 K.

The composition of the dry product gas is shown in Figs. 3-8. The hydrogen gas concentration has shown a reducing trend with increasing temperature, and does not exhibit specific trend when the T4HA concentration is raised. The data points displayed at 673 K in Fig. 3 are more scattered than those at higher temperatures. It is contemplated that the amount of gas produced from gasification at 673 K is only a few cubic centimeters, so that its collection and analysis are extremely difficult and error prone. The data values at 673 K is therefore less reliable than those at higher temperatures.

From Fig. 4, the CO concentration jumps from around 5 mol. % at 673 K to around 15 mol. % at 723 K, and stays roughly constant up to 873 K. Again, variation of T4HA concentration does not show specific trend on CO concentration.

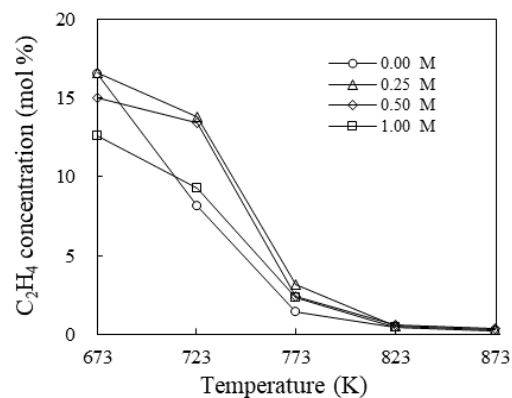


Fig. 7 C₂H₄ concentration in dry gas versus temperature with T4HA concentration as the parameter under 5 MPa

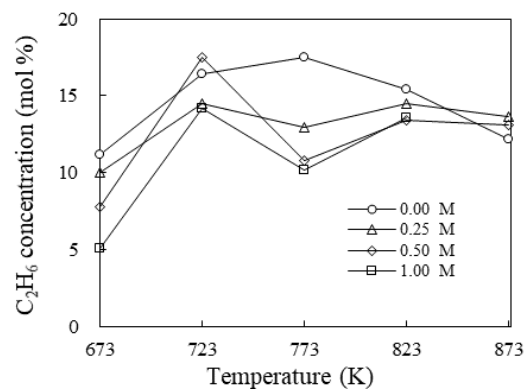


Fig. 8 C₂H₆ concentration in dry gas versus temperature with T4HA concentration as the parameter under 5 MPa

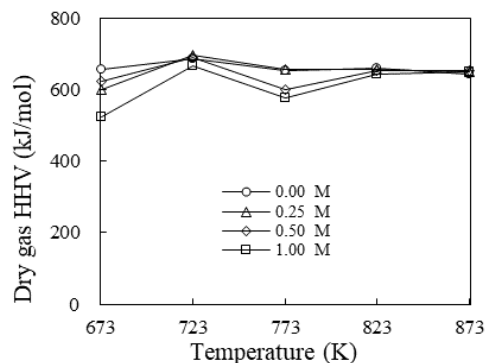


Fig. 9 HHV of the dry gas with T4HA concentration as the parameter under 5 MPa

The methane concentration is seen in Fig. 5 to rise from about 5 mol. % at 673 K all the way to about 40 mol. % at 873 K. It is a surprise that the methane concentration reaches such a high level. Raising T4HA concentration again shows no

specific trend on the methane concentration.

Carbon dioxide is the only gas component to be minimized, since it has no energy content. From Fig. 6, carbon dioxide concentration ranges around 10 to 15 mol. % from 723 to 873 K, dispersed wildly at 673 K. The wide dispersion is mostly likely due to the experimental difficulties, as explained in the previous section.

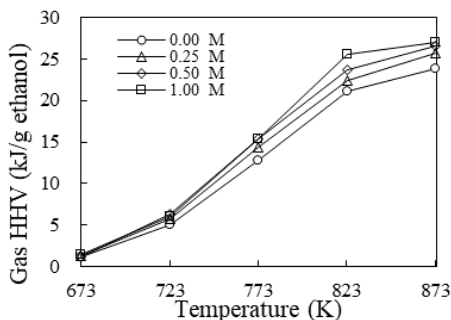


Fig. 10 Energy of the dry gas based on one gram of ethanol with T4HA concentration as the parameter under 5 MPa

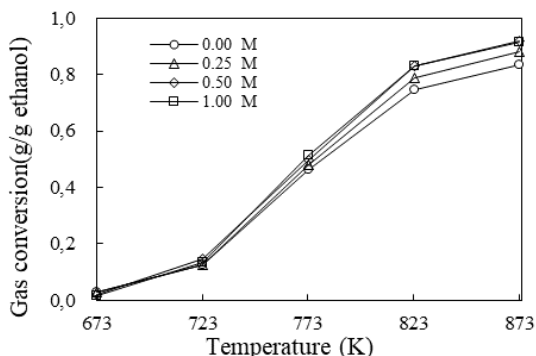


Fig. 11 Gas conversion based on one gram of ethanol with T4HA concentration as the parameter under 5 MPa

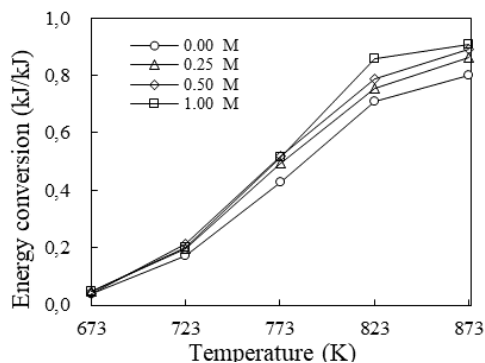


Fig. 12 Energy conversion with T4HA concentration as the parameter under 5 MPa

Ethylene gas concentration exhibits a reducing trend from about 15 mol. % at 673 K to about 0 mol. % at 873 K, as shown in Fig. 7. It indicates ethylene gas more stable at lower temperature and less stable at higher temperature. On the other hand, ethane gas is more stable at higher temperature, as

depicted in Fig. 8, where ethane gas concentration remains around 15 mol. % from 723 to 873 K and is much lower at 673 K.

The HHV per mole of the dry product gas, presented in Fig. 9, is seen to stay roughly constant at around 650 kJ/mol throughout the temperature range investigated, and only to be suppressed mildly by the addition of T4HA at lower temperature from 673 to 773 K. It is also shown the drop in HHV increases with rising T4HA concentration.

The HHV of the dry product gas from gasification on the basis of one gram of ethanol, shown in Fig. 10, displays similar trends to those of gas yield in Fig. 1. This comes as no surprise, since multiplication of gas yield from Fig. 1 by HHV from Fig. 9, which is roughly constant, gives gas HHV in Fig. 10.

The gas conversion based on one gram of ethanol increases from very low value of about 0 mol. % at 673 K to about 85 mol. % at 873 K, as seen in Fig. 11. With ethanol alone, more than 80 % of ethanol turns into gases at 873 K. Addition of T4HA adds additional percentage to the gas conversion.

The energy conversion in Fig. 12 shows similar trends to those of gas conversion in Fig. 11. The reason is obvious, since HHV of the gas is roughly constant. It should be noted that energy conversion is not on the basis of one gram of ethanol, instead on the basis of T4HA/ethanol solution.

IV. CONCLUSIONS

The gasification of a lignin model compound, trans-4-hydroxycinnamic acid, with ethanol is investigated experimentally for temperatures from 673 to 873 K and pressures from 5 to 25 MPa. The gasification of ethanol as well as trans-4-hydroxycinnamic acid proceeds vigorously with rising temperature. At the highest temperature investigated, namely 600 K, approximately 80 % of the feed turns into light product gases. The energy conversion at 873 K is also about 80 %. The product gas is composed mainly of H₂ (20–60 mol. %), CO (3–18 mol. %), CH₄ (5–40 mol. %) and CO₂ (0–60 mol. %), C₂H₄ (0–15 mol. %) as well as C₂H₆ (5–15 mol. %). The best operating condition of the present study occurred at 873 K and 5 MPa, that produces a gas yield of about 40 mmol/g ethanol, a gas conversion of about 85 %, a gas HHV of about 650 kJ/mol, a H₂ concentration of about 20 mol. %, a CO concentration of about 15 mol. %, a CH₄ concentration of 40 mol. %, a CO₂ concentration of about 10 mol. %, and a C₂H₆ concentration of about 13 mol. %. The composition of the product gas shows no specific trends with the variation of the trans-4-hydroxycinnamic acid concentration.

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