

Supplementary Materials

Glycerol dehydration to acrolein catalyzed by silicotungstic acid: effect of mesoporous support

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Vaporization of glycerol solution

Glycerol decomposition starts at 290 °C [37]. Usually above 350 °C, pyrolysis is the primary reaction occurring in the system. The boiling point of pure glycerol is 290 °C, while its dilution in water lowers its partial vapor pressure. Therefore, it is necessary to determine what is the low-end temperature limit to conduct the glycerol dehydration and ensure a gas-phase reaction.

The Antoine equation describes the relationship between vapor pressure and temperature for a pure substance, as shown in Equation S-1. The constants and applicable temperature range of the equation for water and glycerol are listed in Table S-1.

$$\log_{10} P = A - \frac{B}{C + T}$$

Equation S-1

where P is the vapor pressure (mm Hg), T is the temperature ($^{\circ}\text{C}$), and A , B , and C are the constant parameters fitted to each substance.

Table S1. Antoine coefficients and the temperature range for glycerol and water [38,39].

	A	B	C	T_{\min} ($^{\circ}\text{C}$)	T_{\max} ($^{\circ}\text{C}$)
Water	8.14019	1810.94	244.485	99	374
Glycerol	7.01621	1448.81	62.4928	96	576.85

Based on Antoine equation, the vapor pressure of pure substance glycerol or water can be calculated for any temperature in the range. Figure S-1 shows the plot of vapor pressure of glycerol and water as a function of temperature.

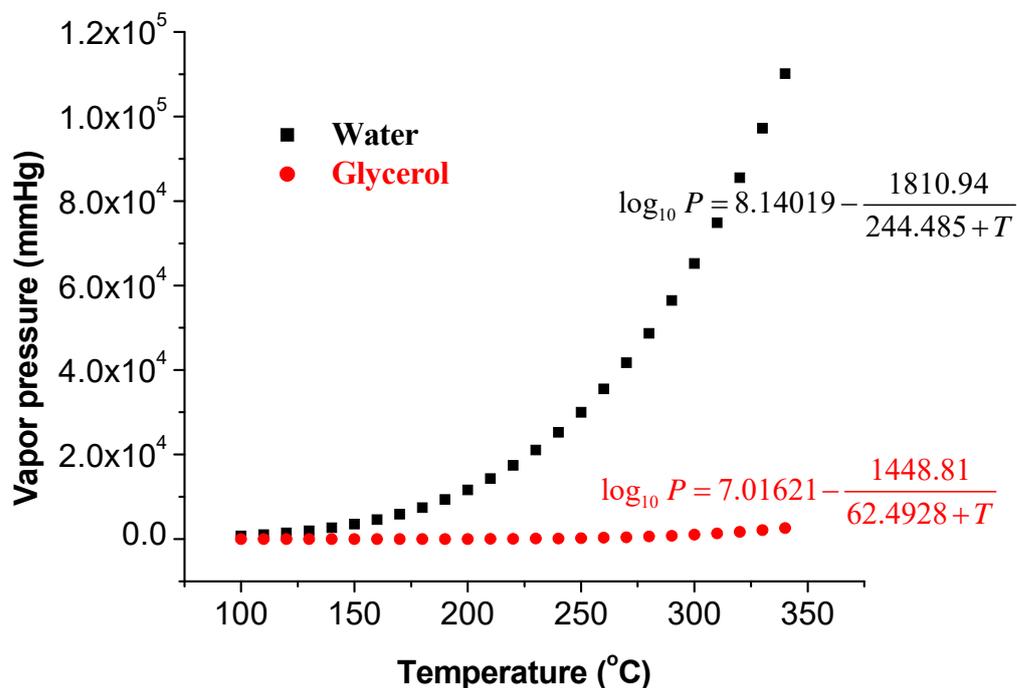


Figure S1. Vapor pressure as a function of temperature for water and glycerol calculated via Antoine Equation.

Considering the 20 wt.% glycerol in water (equivalent to a molar percentage of 4.6632%) as an ideal solution, then according to Raoult's law, there are following relationships for the two-component system (Equations S-2 and S-3):

$$P_t = P_{water}^* \cdot x_{water} + P_{glycerol}^* \cdot x_{glycerol} \quad \text{Equation S-2}$$

$$P_{water} = P_{water}^* \cdot x_{water} \quad \text{and} \quad P_{glycerol} = P_{glycerol}^* \cdot x_{glycerol} \quad \text{Equation S-2}$$

where p_t is the total vapor pressure in the two-component system, p^* is the vapor pressure of the pure component (water or glycerol, as specified by the subscript), and p is the partial vapor pressure of each component (specified by the subscript). x is the molar percentage of each component ($x_{water} = 95.3368\%$ and $x_{glycerol} = 4.6632\%$) in the liquid phase, which is the composition of our feed solution.

The two-component solution should be completely evaporated at a total vapor pressure of 760 mm Hg, which is our reaction pressure. The following steps detail our approach to prove that the reactions were conducted at gas phase. 1) Assume a temperature in the range (100–290 °C), so that partial vapor pressure can be calculated for both glycerol and water using the Antoine equation and Raoult’s law; therefore, the total vapor pressure can be expressed as a function of only one variable, $x_{glycerol}$. 2) Let the total vapor pressure be equal to 760 mm Hg, then solve the equation for $x_{glycerol}$. 3) The gas-phase molar composition is then calculated via Equation S-4 by combining Dalton’s law (Equation S-5) and Raoult’s law (Equations S-2 and S-3). 4) Temperature is varied to cover more data points within the range of 100–290 °C.

$$y_{glycerol} = \frac{P_{glycerol}^* \cdot x_{glycerol}}{P_{water}^* \cdot x_{water} + P_{glycerol}^* \cdot (1 - x_{water})} \quad \text{Equation S-3}$$

$$P_{water} = P_t \cdot y_{water} \quad \text{and} \quad P_{glycerol} = P_t \cdot y_{glycerol} \quad \text{Equation S-4}$$

The T - x - y diagram of the glycerol-water system can be therefore plotted (Figure S-2), which displays the boiling point for the solution of a certain glycerol molar concentration, and the corresponding glycerol molar percentage in the vapor phase can be found. Based on this diagram, the temperature obtained from the T - x - y graph for a vapor with 4.6632% glycerol molar concentration is 210 °C. Therefore, if the reaction temperature is maintained above 210 °C, the 20 wt.% glycerol solution is completely vaporized.

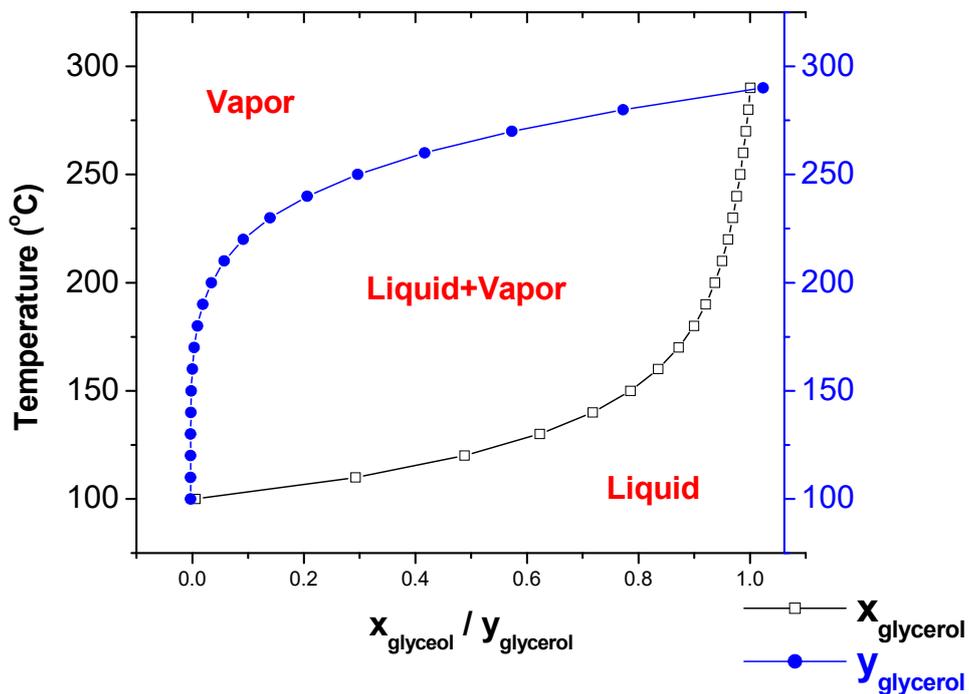


Figure S2. *T-x-y* diagram for the glycerol-water two-component system at 760 mm Hg

References

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