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Vapor Pressures and Evaporation Studies of Sugars and Sugar Alcohols

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The use of heterogeneous catalysts for conversion of sugars and sugar alcohols to value-added chemicals has been widely studied in liquid phases. Low selectivities and high costs associated with catalyst recovery have substantially limited commercialization of these processes. Gas phase packed-bed catalysis has recently been successful in overcoming these obstacles for the hydrogenolysis of glycerol to propylene glycol. In this paper, the evaporation of glucose and sorbitol was investigated to identify potential conditions for gas-phase conversions of these sugars. In our studies, vapor pressures of sorbitol were estimated in a wider temperature range of (250 to 350) °C than work done by Guido et al. (*J. Chem. Soc. Faraday Trans.* **1990**, *86*, 75−79) at (177 to 227) °C. A thermogravimetric analysis (TGA) method was used to estimate a boiling point of 362 °C for sorbitol with sorbitol's vapor pressure following a Clausius−Clapeyron model behavior. In addition, evaporation studies demonstrated sobitol evaporation and condensation on a practical level. The evaporation of sorbitol was experimentally validated with no decomposition at 0.1 bar and 294 °C and 2.5 % (mass fraction) in water. The evaporation of high-concentration sorbitol feed can be achieved by mixing with a high-temperature gas (e.g., steam). Glucose evaporated with partial decomposition at temperatures as low as 220 °C.

Introduction

Sugars and sugar alcohols have been considered as biobased feedstocks to produce many of the chemicals in common use, which are derived from petroleum feedstocks. Utilization of biobased materials will help overcome energy shortage and prevent serious environmental pollution. Heterogeneous hydrogenolysis is one means to convert sugars to value-added chemicals.[1]

Conradin et al.,[2−4] Clack et al.,[5] and Sirkar et al.[6] reported that hydrogenolysis of aqueous sorbitol solution to glycerol and propylene glycol can be carried out in the presence of a broad range of catalysts (e.g., Ni/Cu catalyst) and enhanced by the addition of base. The product distribution by mass was about 43 % glycerol and 25 % propylene glycol with 83 % conversion at (80 to 140) bar and (200 to 260) °C.

Tanikella et al.[7] and Gerrit et al.[8] described the hydrogenolysis of sorbitol and xylitol in nonaqueous solvents containing a mole fraction of 10 % of base (e.g., KOH). The catalyst used was nickel on silica/alumina. Distribution of ethylene glycol, propylene glycol, and glycerol was reported.

Gubitosa et al.[9] discussed the hydrogenolysis of polyhydric alcohols, such as sorbitol, over a ruthenium-on-carbon catalyst. In the examples, it was reported that 100 % of the sorbitol can be converted, with (41 to 51) % of the product carbon atoms in propylene glycol.

Usually, these batch hydrogenolysis reactions were carried out at (140 to 350) bar in the presence of hydrogen, at temperatures of (200 to 250) °C, with residence times in excess of 1.5 h and in the presence of a slurry of catalyst.

Liquid-phase packed-bed reactions were performed by Hellwig et al.[10] Hydrogenolysis reactions were performed in a single or multistage packed bed catalytic reactor at (100 to 300) °C temperature and (50 to 240) bar hydrogen partial pressure, 1.2 liquid hourly space velocity, and using nickel on alumina catalyst to produce 50 % mass fraction glycerol and 20 % mass fraction propylene glycol from sorbitol-type feed.

To date, low selectivities, high pressure, and catalyst recovery have limited the potential of these technologies. Thus, there is a need for new methods of converting sugars and sugar alcohols to high value chemicals such as propylene glycol and 1,3-propanediol. Gas-phase catalytic hydrogenolysis may be one feasible way in sugar conversion for achieving continuous operations with reduced reaction costs, particularly using improved catalysts in packed-bed reactors. To achieve this, it is necessary to understand how to evaporate sugars and sugar alcohols with minimal degradation prior to gas-phase catalytic hydrogenolysis in a packed-bed reactor. Traditional methods used to evaluate vapor pressures and determine boiling points cannot be used due to decomposition of C4 and higher sugars.

Guido et al.[11] reported that the vaporization of sorbitol was determined from the temperature dependence of its vapor pressure, as measured by the torsion−effusion method. In Guido's study, the vapor pressures were estimated in the temperature range of (177 to 227) °C. This paper evaluates vapor pressures at higher temperatures and uses an experimental system to validate the ability to evaporate and recover/condense sorbitol vapors. A thermogravimetric analysis (TGA) technique was adopted for the purpose of vapor pressure estimation. Goodrum et al.[12] discussed the estimation of vapor pressure and boiling points using the TGA method. A TGA laser-drilled capsule method provided a method of obtaining vapor pressures and boiling points. However, the diameter of the laser-drilled hole had a significant influence on the accuracy of this method. The laser-drilled hole must be small enough to restrict diffusion out of the sample container to a rate less than the vaporization rate inside the container, yet have sufficient diameter to prevent any self-pressurization. An alternative method was reported by Guckel et al.[13] In this method, an open sample tray instead of a laser-drilled container was evaluated using isothermal ther-

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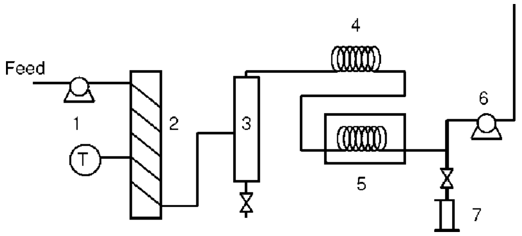


Figure 1. Evaporation system I. The different components are: 1, feed pump; 2, evaporator; 3, trap; 4, air-cooled condenser; 5, ice−water condenser; 6, vacuum pump; 7, product collector.

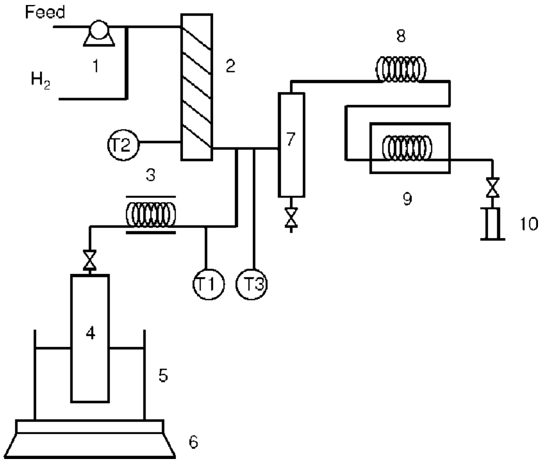


Figure 2. Evaporation system II. The different components are: 1, feed pump; 2, preheater; 3, heater; 4, steam vessel; 5, oil bath; 6, hot plate; 7, trap; 8, air-cooled condenser; 9, ice−water condenser; 10, product collector.

Table 1. Evaporation of 2.5 % (Mass Fraction) Sorbitol Feed at Different Pressures *P* with Evaporation System I[a]

t/(°C)	*p*/(bar)	recovery*/(%)	recovery/(%)
294	0.1	90.8 ± 0.4	88.6 ± 0.3
294	0.2	75.2 ± 0.6	74.3 ± 0.5
294	0.3	55.1 ± 0.5	53.9 ± 0.6
294	0.5	41.5 ± 0.3	40.2 ± 0.4
294	0.7	35.7 ± 0.6	34.3 ± 0.5
294	1.0	28.1 ± 0.5	26.9 ± 0.6

[a] Recovery* denotes the recovery of nonvolatiles from TGA analysis. Recovery denotes the recovery of sorbitol from HPLC analysis.

Table 2. Evaporation of 2.5 % (Mass Fraction) Sorbitol Feed at Different Temperatures *T* with Evaporation System I[a]

t/(°C)	*p*/(bar)	recovery*/(%)	recovery/(%)
280	0.1	51.8 ± 0.5	51.1 ± 0.6
285	0.1	64.5 ± 0.4	63.3 ± 0.4
290	0.1	77.9 ± 0.6	75.6 ± 0.5
292	0.1	83.9 ± 0.7	81.7 ± 0.5
294	0.1	90.8 ± 0.3	88.6 ± 0.7

[a] Recovery* denotes the recovery of nonvolatiles from TGA analysis. Recovery denotes the recovery of sorbitol from HPLC analysis.

mogravimetry to the measurement of evaporation rates. These evaporation rates correlated well with vapor pressures. This method provides rapid, simple, and accurate measurement.

Guckel et al.[13] suggested that the logarithm of the evaporation rate at a given temperature was linearly proportional to the logarithm of vapor pressure, as shown in eq 1. This linear relationship is independent of the sample and the temperature range of analysis. The constants, *a* and *b*, are dependent on the instrument, operational parameters (e.g., gas purge rate), and sample containment procedure.[14]

$$\ln(p/\mathrm{bar}) = a\ln(k/\%\cdot\mathrm{min}^{-1}) + b \qquad (1)$$

where p is the vapor pressure at a given temperature and k is the corresponding evaporation rate. This equation and method were adopted in this paper. Rapid evaluation, as possible with milligram samples in thermogravimetric analysis (TGA) methods, and analysis at lower temperatures reduce sugar degradation during this method.

Compared with glycerol and ethylene glycol, sugars and sugar alcohols are more difficult to evaporate since they have higher boiling points than glycerol and ethylene glycol [(290 and 197.3) °C, respectively]. Sugars and sugar alcohols tend to decompose at temperature lower than their boiling points during the evaporation process. For practical applications, degradation during evaporation can be reduced by dilution (e.g., with water or hydrogen) or by the reducing system pressure. Another means to prevent the degradation or side reactions is direct contact heating by mixing the sugars with high-temperature steam. Both of these “practical” methods were evaluated in this paper to correlate with TGA-based vapor pressure estimates.

Experimental Section

Materials. Glucose (99.9 %), sorbitol (99.9 %), sucrose (99.9 %), glycerol (99.9 %), and methanol (HPLC grade) were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade nitrogen and helium were obtained from Praxair (Dunbury, CT).

Experimental Setup. Figure 1 provides a schematic of evaporation system I, including the evaporator, trap, air-cooled condenser, and ice−water condenser, for sugar and sugar alcohol evaporation studies. The trap was for gas−liquid separation. Two condensers were used to achieve better condensation at lower pressures. The temperatures of the evaporator and trap were controlled using a single display proportional-integral-derivative (PID) controller (Winona, MN). The pressure was indicated and controlled by a GAST vacuum pump (Benton Harbor, MI). While the system reached the desired conditions, the aqueous feed (initial sugar or sugar alcohol mass fraction in solution was 2.5 %) was pumped into the evaporation system by a micropump at 200 g·h^{-1}. The evaporation samples were collected from the ice−water condenser and analyzed by thermogravimetric analysis (TGA), high performance liquid chromatography (HPLC), and gas chromatography (GC) without further delay. In this study, sugar or sugar alcohol was recovered in the condenser, accumulated in the trap, or decomposed. The recovered portion was reported; evidence of decomposition was reported if observed in GC results; and/or the amount remaining in the trap was quantified.

Figure 2 shows a schematic of evaporation system II, in which sorbitol was evaporated by mixing with high-temperature steam. The aim of this system was to reduce sugar degradation that can result for prolonged exposure of concentrated sugar on hot surfaces. In addition, the use of fine sprays can significantly reduce the time the sugar exists as a liquid before evaporating. The flow rate of steam was controlled by a valve. The steam temperature and sorbitol feed (mass fraction is 67 %) preheated temperatures were controlled using a single display proportional-integral-derivative controller. The temperature after mixing was recorded as were the feed temperatures (as controlled). The vapors were condensed after passing through the trap, and the sugar content of the condensate was evaluated as previously described.

Thermogravimetric Methodology. Condensate samples were taken at regular time intervals and analyzed with a Q50 Series Thermogravimetric Analyzer (TGA) with TA5000 Advantage

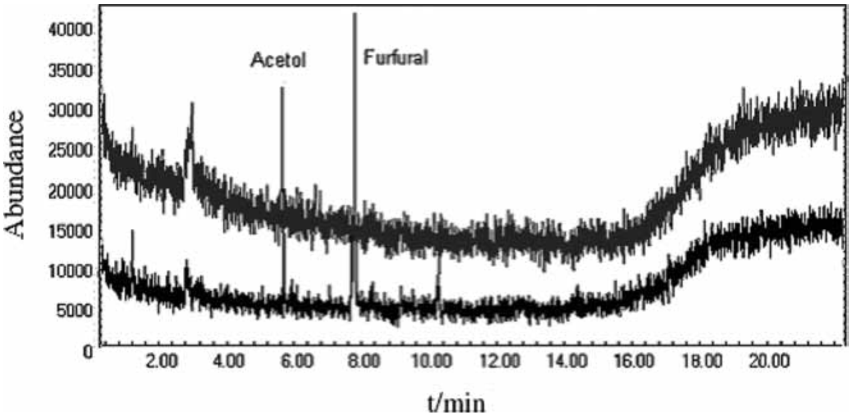


Figure 3. Gas chromatography of evaporation samples of sorbitol and glucose. The upper curve is for the sorbitol evaporation sample. The lower curve is for the glucose evaporation sample.

Table 3. Evaporation of 67 % (Mass Fraction) Sorbitol Feed at Different Feed Flow Rates *Q* with Evaporation System II[a]

Q/(g·h^{-1})	$t1$/(°C)	$t2$/(°C)	$t3$/(°C)	C/(%)	recovery/(%)	$C\dagger$/(%)
54	250	120	243	10.4 ± 0.3	91.2 ± 0.5	9.7
84	250	120	229	5.1 ± 0.2	28.5 ± 0.3	4.9
120	250	120	210	1.4 ± 0.2	5.3 ± 0.2	7.4

[a] Feed flow rate, *Q*; steam temperature, *t*1; sorbitol feed temperature, *t*2; mixing temperature, *t*3; sorbitol mass fraction in effluents, *C*; recovery denotes the recovery of sorbitol from HPLC analysis. *C*† denotes the simulated sorbitol mass fraction in effluents at the same mixing temperature.

Table 4. Evaporation of 67 % (Mass Fraction) Sorbitol Feed at Different Steam Temperatures *T* with Evaporation System II[a]

Q/(g·h^{-1})	$t1$/(°C)	$t2$/(°C)	$t3$/(°C)	C/(%)	recovery/(%)	$C\dagger$/(%)
54	210	120	206	0.2 ± 0.1	1.7 ± 0.2	1.0
54	230	120	221	3.4 ± 0.2	29.7 ± 0.3	3.2
54	250	120	243	10.4 ± 0.3	91.2 ± 0.5	9.7

[a] Feed flow rate, *Q*; steam temperature, *t*1; sorbitol feed temperature, *t*2; mixing temperature, *t*3; sorbitol mass fraction in effluents, *C*; recovery denotes the recovery of sorbitol from HPLC analysis. *C*† denotes the simulated sorbitol mass fraction in effluents at the same mixing temperature.

Table 5. Simulation Results of Evaporation of 67 % (Mass Fraction) Sorbitol Feed at Different MFR[a]

$t1$/(°C)	$t2$/(°C)	$t3$/(°C)	MFR/(%)	C/(%)	recovery/(%)
250	120	254	0.17	9.7	100
250	120	242	0.26	7.9	52.9
250	120	232	0.38	5.0	23.5

[a] Steam temperature, *t*1; sorbitol feed temperature, *t*2; mixing temperature, *t*3; mass flow ratio of feed over steam, MFR; sorbitol mass fraction in effluents, *C*; recovery denotes the recovery of sorbitol from HPLC analysis.

Table 6. Simulation Results of Evaporation of 67 % (Mass Fraction) Sorbitol Feed at Different Steam Temperatures[a]

$t1$/(°C)	$t2$/(°C)	$t3$/(°C)	MFR/(%)	C/(%)	recovery/(%)
210	120	237	0.17	6.1	60.7
230	120	243	0.17	8.4	85.4
250	120	254	0.17	9.7	100

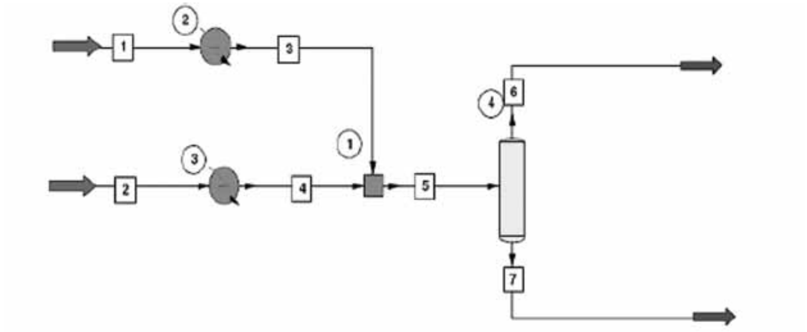
[a] Steam temperature, *t*1; sorbitol feed temperature, *t*2; mixing temperature, *t*3; mass flow ratio of feed over steam, MFR; sorbitol mass fraction in effluents, *C*; recovery denotes the recovery of sorbitol from HPLC analysis.

software to determine the mass concentration of nonvolatiles in the samples. Samples were first equilibrated at 25 °C, heated up to 400 °C at the rate of 10 °C·min^{-1}, and maintained 400 °C for 10 min. Thermogravimetric analysis was carried out under a nitrogen purge at a constant rate of 50 mL·min^{-1} to prevent any oxidation of samples. The mass fraction of nonvolatiles was determined from TGA. Recovery of nonvolatiles was calculated assuming all the water fed to the system condensed in the condenser and was defined as the ratio of the mass of nonvolatile matter in the condensate divided by the mass of sugar or sugar alcohol fed to the system (based on measured flow rates and mass fractions in each stream).

To estimate vapor pressure using the isothermal TGA method, the sample was heated from 25 °C to the desired temperature at a heating rate of 50 °C·min^{-1} and held at the desired temperature for 30 min. The sample mass fraction loss was monitored with time throughout the experiment. The evaporation rate at a given temperature was obtained by calculating the rate of mass fraction loss with time.

Chromatographic Analysis. For sugar analysis, the samples were analyzed with a Hewlett-Packard 1100 high performance liquid chromatograph with an Alltech ELSD 500 evaporative light-scattering detector (Alltech Associates, Inc., Deerfield, IL). An Alltech HPLC silica-based column (Apollo, 250 mm × 4.6 mm, 5 μm) was used for separation. The ELSD drift tube temperature was set at 75 °C. The nitrogen gas flow rate of the nebulizer was set at 4.97 L·min^{-1} and a pressure of 0.56 bar. Autoinjection was in a 30 μL loop. The eluent flow rate was 1 mL·min^{-1} at room temperature. The eluent mixture had a volume fraction of 97 % methanol and 3 % water. The samples were placed in the oven at 80 °C for (12 to 24) h to remove water and dissolved in methanol prior to analysis. The calibration curves of sugar and sugar alcohol were prepared, and the mass fractions of sugar or sugar alcohol were determined from calibration curves. Recovery of sugar or sugar alcohol is defined as the ratio of numbers of grams of sugar or sugar alcohol from the condenser to the number of grams of sugar or sugar alcohol initially present.

The samples were also analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector and mass spectra detector. A J&W Scientific, Inc. (Folsom, CA) DB-WAX 123−7033 GC column (30 m × 320 μm × 0.5 μm) was used for separation. The detector and injector temperatures were (250 and 230) °C, respectively, and the oven temperature was programmed at 10 °C·min^{-1} from (45 to 200) °C and at 15 °C·min^{-1} to a final temperature of 225 °C, which was held for 10 min. Helium was used as the carrier gas at a flow rate of 1.0 mL·min^{-1}, and the split ratio was 1:120.



Stream No	1	2	3	4	5	6	7
Mass flow, g/h	318	54	318	54	372	372	0
Temp, °C	25	25	349.6	120	254.2	254.4	0
Vapor mass fraction	0	0	1	0.196	1	1	0
Vapor mass flow, g/h	0	0	318	10.6	372	372	0
Liquid mass flow, g/h	318	54	0	43.4	0	0	0
Flow rates in g/h							
Water	318	17.8	318	17.8	335.8	335.8	0
Sorbitol	0	36.2	0	36.2	36.2	36.2	0

Figure 4. Simulation results of evaporation of 67 % (mass fraction) sorbitol feed at the conditions shown below. Steam temperature *t*1: 250 °C. Sorbitol feed temperature *t*2: 120 °C. Mass flow ratio of feed over steam MFR: 0.17.

Table 7. Evaporation of 2.5 % (Mass Fraction) Glucose Feed at Different Temperatures *t* and Pressures *p*[a]

t/(°C)	*p*/(bar)	recovery*/(%)	recovery/(%)
280	0.1	1.1 ± 0.2	1.2 ± 0.1
285	0.1	2.0 ± 0.2	1.8 ± 0.2
290	0.1	4.5 ± 0.3	3.5 ± 0.3
290	0.3	2.5 ± 0.2	2.7 ± 0.3
290	0.5	1.9 ± 0.2	1.8 ± 0.2

[a] Recovery* denotes the recovery of nonvolatiles from TGA analysis. Recovery denotes the recovery of glucose from HPLC analysis.

Results and Discussion

Evaporation Study of Sorbitol. Sorbitol, a 6-carbon sugar alcohol, exists as a white powder at room temperature with a melting point of 95 °C. Preliminary studies showed that evaporation at 1 bar and (270 to 300) °C could not achieve good recovery of sorbitol. Therefore, lower pressures were applied at 294 °C. As summarized by Table 1, pressure played a significant role in the evaporation of sorbitol in water.

The highest sorbitol recovery was 88.6 %, corresponding to the lowest pressure of 0.1 bar. Recovery decreased to 26.9 % when pressure increased up to 1 bar. The sorbitol, which cannot be evaporated, accumulated in the trap. With increasing pressure, the amount of residual sorbitol in the trap increased correspondingly. This observation confirmed that lower pressure could achieve better sorbitol evaporation.

To investigate the effect of temperature on sorbitol evaporation, an evaporation experiment was performed at the pressure of 0.1 bar and the range of temperatures as summarized in Table 2. Recovery of sorbitol dropped from 88.6 % at 294 °C and 51.1 % at 280 °C. No degradation by GC analysis or discolorization was observed over this temperature range. Increased evaporation with increasing temperatures qualitatively agrees with theory.

Figure 3 shows the GC analysis of the effluent condensate. The GC will not pick up the sorbitol and verifies the absence of more volatile decomposition products. HPLC analysis of the condensate confirmed a high yield of sorbitol. No discoloration of the condensate was observed at lower pressures.

Evaporation system II was used to evaluate direct contact evaporation for comparison to the Table 1 and Table 2 results. In this study, the flow rate of steam was maintained at 318 $g\cdot h^{-1}$, and the temperature of the preheated 67 % mass fraction of sorbitol feed was maintained at 120 °C. The evaporation experiments were performed at different sorbitol feed flow rates of (54 to 120) $g\cdot h^{-1}$ and steam temperatures of (210 to 250) °C. Tables 3 and 4 summarize the sorbitol recoveries. When the feed flow rate increased (Table 3), the sorbitol mass fraction in the effluent decreased from 10.4 % to 1.4 % and the recovery of sorbitol decreased from 91.2 % to 5.3 %, which was due to higher flow rates causing lower temperatures after the mixing of the steam with the sorbitol. The mixture temperature and pressure are the intensive properties that specify the vapor–liquid equilibrium in the trap.

Increasing steam temperatures caused the sorbitol fraction in the effluent to increase dramatically (Table 4). The GC analysis verified the absence of decomposition products. The condensate from evaporation system II contained up to 10 % mass fraction of sorbitol, which is considerably greater than the maximum of 2.3 % for evaporation system I.

Sorbitol evaporation in the evaporation system II would be characterized as direct contact heating with steam followed by adiabatic flash separation. This process was simulated using ChemCad simulation software. Simulation results for evaporation of 67 % mass fraction of sorbitol feed with high-temperature steam are summarized in Table 5, Table 6, and Figure 4. This simulation confirmed the significant effect of feed flow rate and steam temperature. The simulations were performed prior to experimentation to confirm that experiments were being conducted at temperatures and pressures that would produce a vapor containing up to 10 % mass fraction of sorbitol.

The simulated recoveries and adiabatic mixing temperatures were higher than with the experimental data. Lower experimental temperatures were likely due to heat losses from the tubing. Tables 3 and 4 include simulation results adjacent to the experimental results where the simulation was modified to provide the same adiabatic mixing (effluent) temperature as was observed in the experimental system.

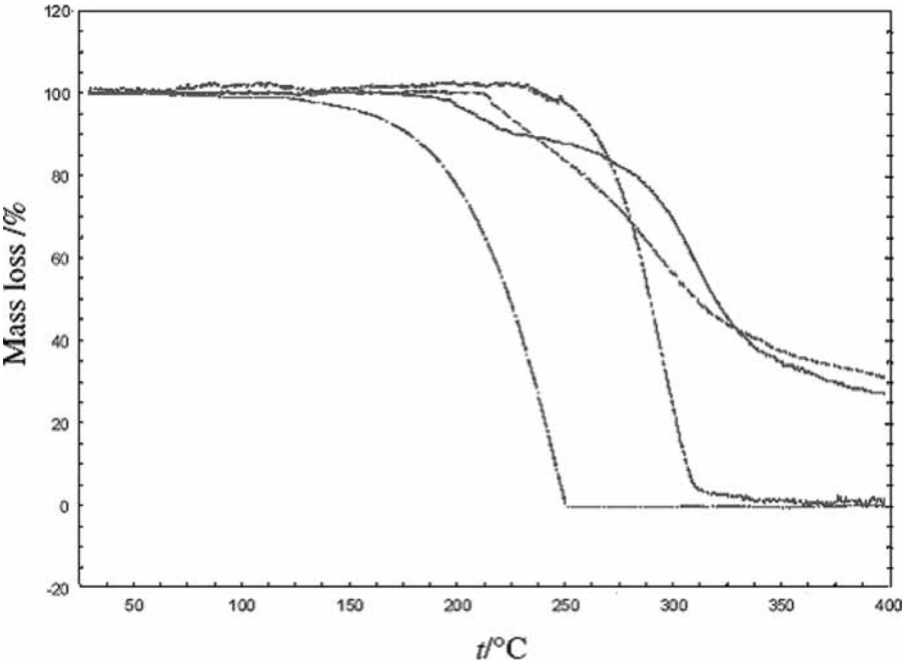


Figure 5. Mass fraction loss analysis of glycerol, sorbitol, glucose, and sucrose. —, glucose; - - - -, sucrose; — -•, glycerol; — - -, sorbitol.

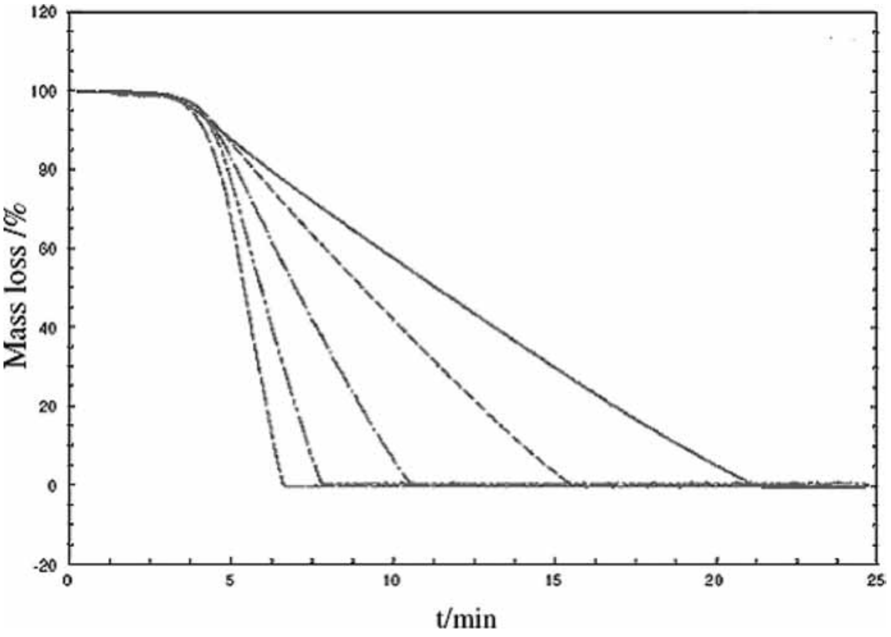


Figure 6. Mass fraction loss from isothermal thermogravimetric analysis of glycerol. —, 190 °C; - - -, 210 °C; —- •, 230 °C; —- -, 250 °C; — —, 270 °C.

Evaporation Study of Glucose. The evaporation of glucose was evaluated at (280 to 290) °C and at (0.1 to 0.5) bar. The results are summarized in Table 7. Figure 3 compares the gas chromatography of the glucose condensate to the sorbitol condensate. The presence of decomposition products (e.g., acetol, furfural), a dark tint to the condensate, and smell of burnt sugar all substantiate that the glucose underwent decomposition. Increasing decomposition of glucose to nonvolatile components at higher temperatures was qualitatively observed as would be expected.

The glucose studies were repeated with a 1 % mass fraction of aqueous glucose feed at (220 to 280) °C and pressure of 0.1 bar. Less than 10 % of glucose was recovered in the condensate.

On the basis of the data of Tables 1 through 4, sorbitol can be successfully evaporated at mass fraction up to 10 %, while glucose degraded at pressures as low as 0.1 bar. This did confirm that sorbitol was undergoing a true evaporation as opposed to entrainment in the vapor. If the experimental system promoted entrainment, sorbitol and glucose should have experienced similar degrees of entrainment.

Vapor Studies. TGA analysis of glycerol, sorbitol, glucose, and sucrose was performed at a constant heating rate of 10 °C·min^{-1}. As the results (Figure 5) indicate, the thermograms of glycerol and sorbitol exhibit a rapidly increasing rate of mass fraction loss with increasing temperatures until no sample remains—characteristic of an evaporation process. However, the thermograms for glucose and sucrose have multiple inflection points and do not proceed to zero mass at the temperature range of the study—characteristic of decomposition with eventual formation of char.

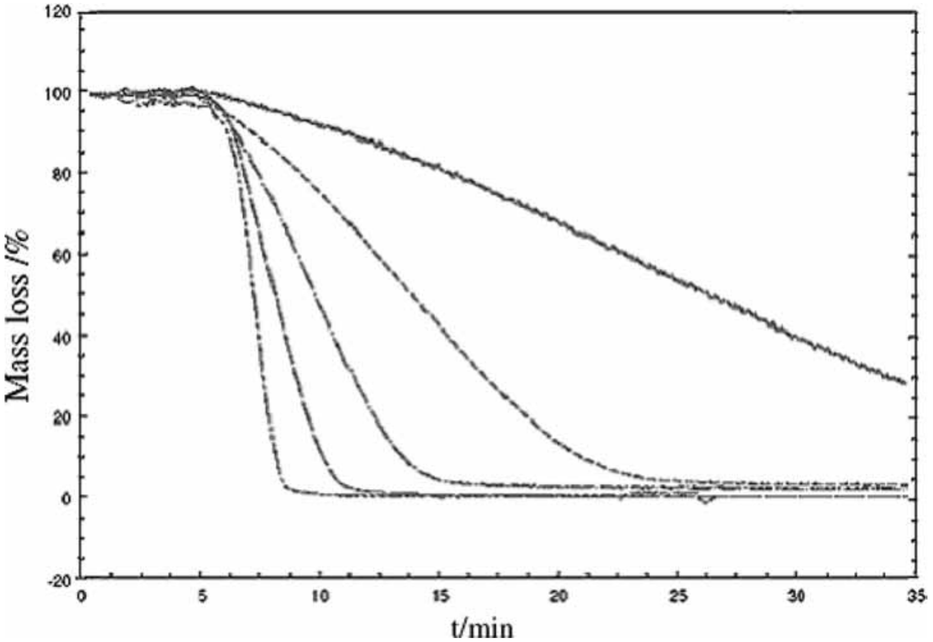


Figure 7. Mass fraction loss from isothermal thermogravimetric analysis of sorbitol. —, 250 °C; - - -, 275 °C; —- •, 300 °C; —- -, 350 °C; — —, 350 °C.

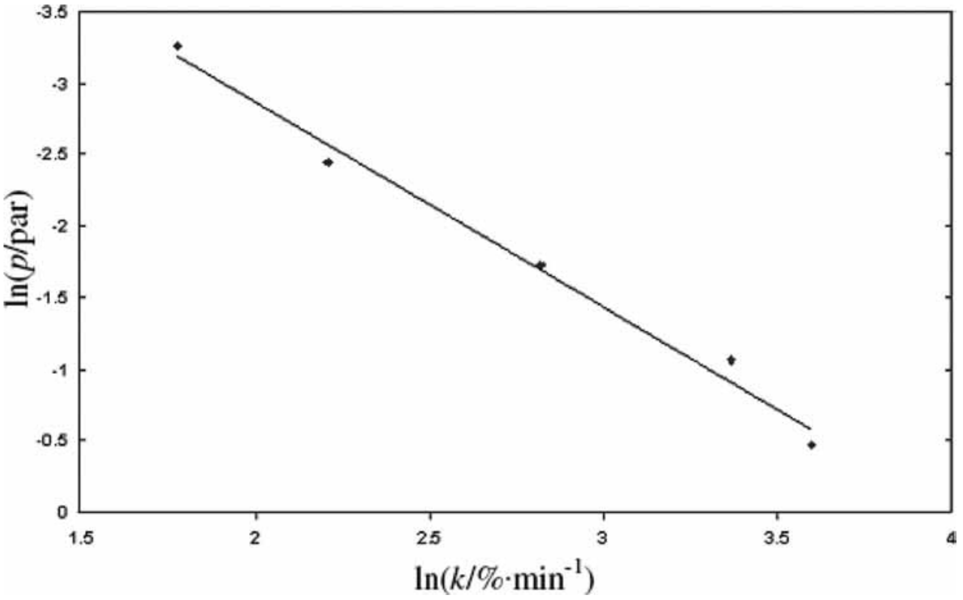


Figure 8. Linear logarithmic relationship between the evaporation rates of glycerol and the corresponding vapor pressures. The theoretical line is obtained by fitting to eq 1 using linear regression.

These results are consistent with the evaporation studies in two evaporator systems. Since the sorbitol appeared to evaporate, an isothermal TGA method was used for vapor pressure estimation.

Glycerol was used as a reference compound to calibrate the TGA instrument and experimental conditions by the method prescribed by Wiedemann.[15] Figure 6 showed a set of representative experimental time constants (TGA thermograms) depicting mass loss from (190 to 270) °C for glycerol. Figure 7 illustrates similar TGA thermograms from (250 to 350) °C for sorbitol.

The thermograms are nearly linear indicating that the evaporation followed apparent zero-order kinetics. This is consistent with an evaporation mechanism in the method developed by Guckel et al.[13] The respective zero-order rate constants for evaporation are equal to the slope of each isothermal as reported in Table 8. The slopes were estimated using linear regression. Glycerol's vapor pressure data[16] were used to obtain the constants for the characteristic equation for this TGA (see eq 1).

Figure 8 illustrates the nice correlation of glycerol's evaporation rates versus vapor pressure. The characteristic eq 1 constants were: a at 1.43 with standard deviation of 0.09 and b at −5.73 with standard deviation of 0.25 (see eq 2). As indicated earlier, these constants are instrument specific and are valid for any chemicals evaluated at the same conditions. Equation 2 was thus used to convert sorbitol evaporation rates to vapor pressures as reported in Table 9.

$$\ln(p/\mathrm{bar}) = 1.43\,\ln(k/\%\cdot\mathrm{min}^{-1}) - 5.73 \qquad (2)$$

Clausius−Clapeyron Relation. The isothermal TGA analysis of sorbitol was also carried out at (250 to 350) °C. The

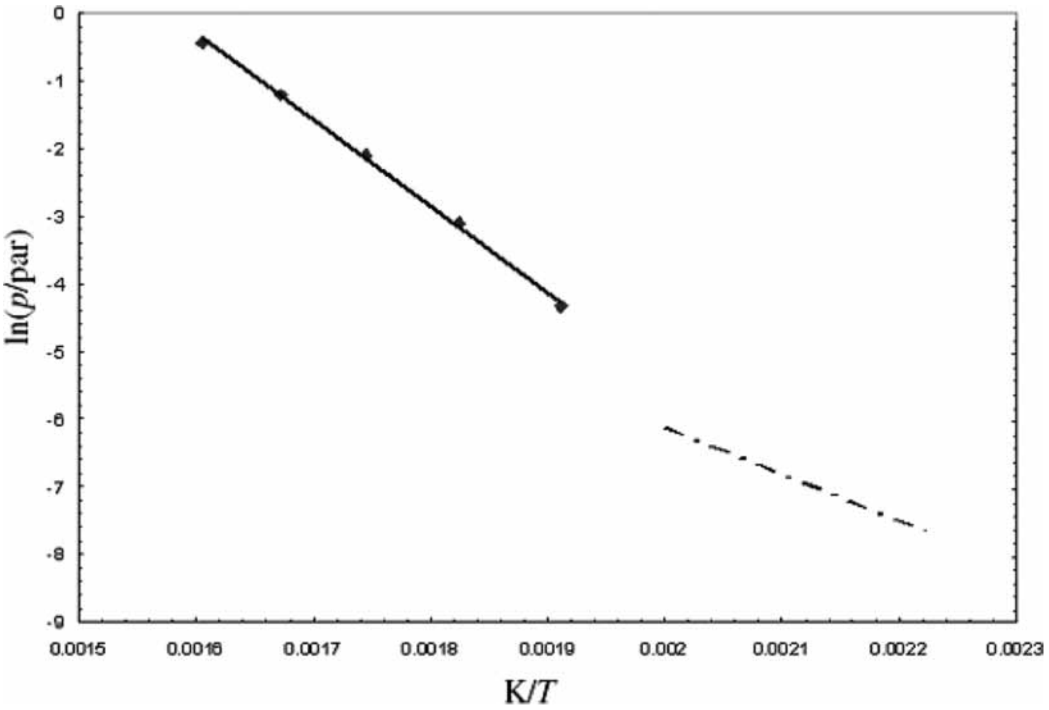


Figure 9. Temperature dependence of vapor pressure for sorbitol. Solid line denotes the regression line of vapor pressure data obtained from isothermal TGA method. Dashed line denotes the temperature dependence of vapor pressure of sorbitol in the temperature range shown in Guido's work.

Table 8. Glycerol Evaporation Rates *k* and Vapor Pressures *p*

$t/(°\mathrm{C})$	$k/(\%\cdot\mathrm{min}^{-1})$	$10^2\cdot p/(\mathrm{bar})$
190	5.89 ± 0.15	3.85 ± 0.02
210	9.08 ± 0.17	8.64 ± 0.03
230	16.7 ± 0.20	17.9 ± 0.03
250	28.9 ± 0.35	34.5 ± 0.07
270	36.5 ± 0.40	62.6 ± 0.09

Table 9. Sorbitol Evaporation Rates *k* and Estimated Vapor Pressures *p*

$t/(°\mathrm{C})$	$k/(\%\cdot\mathrm{min}^{-1})$	$10^2\ \cdot p/(\mathrm{bar})$
250	2.65 ± 0.08	1.31 ± 0.01
275	6.27 ± 0.11	4.49 ± 0.01
300	12.7 ± 0.15	12.3 ± 0.02
325	23.6 ± 0.32	30.0 ± 0.06
350	40.5 ± 0.45	65.0 ± 0.10

thermograms over this range of temperatures were consistent with evaporation without degradation.

The Clausius−Clapeyron relation is widely used in chemistry and chemical engineering to model vapor pressures of pure substances. The equation is as follows

$$\ln(p/\mathrm{bar}) = A/(T/\mathrm{K}) + B \tag{3}$$

where p is the vapor pressure and T is the absolute temperature. A and B are constants fundamentally related to the enthalpy and entropy of vaporization.[17,18] Linear regression of the Table 9 vapor pressure for sorbitol estimated A at $-12\,703$ with a standard deviation of 292 and B at 20.01 with a standard deviation of 0.51. Figure 9 illustrates the correlation of sorbitol's vapor pressure with temperature. The vapor pressures correlate well with the Clausius−Clapeyron model.

The TGA method for vapor pressure estimation is consistent with the previous work done by Guido et al.[11] (Figure 4). These regression results predict sorbitol's boiling point at 362 °C. On the basis of the previous work done by Guido et al.,[11] the predicted boiling point of sorbitol is 624 °C. The difference is due to greater extrapolation needed to project a boiling point based on Guido's data that are at lower temperatures. The results from the present TGA studies are extrapolated by about 12 °C and so are expected to be accurate to within about 2 °C.

On the basis of these results, sorbitol can be successfully evaporated either at low pressures or by mixing with high-temperature steam. This provides a possible operating window for gas-phase catalytic conversion of sorbitol to value-added chemicals.

Conclusions

Vapor pressures of sorbitol were estimated by an isothermal TGA method and modeled using the Clausius−Clapeyron equation. The results provided an improved estimate for sorbitol's boiling point at 362 °C. Evaporation studies validated that low-concentration sorbitol feed could be evaporated at high temperatures and low pressures. High pressure steam was able to evaporate concentration sorbitol feed to produce vapors of up to 10 % mass fraction sorbitol with no noticeable decomposition of the sorbitol. Experimental data accurately followed process simulation based on the estimated vapor pressures. The combined use of the TGA method, fitting to a theory-based model, process simulation of anticipated performance, and experimental validation of the process simulation provide great certainty on the ability to produce vapor-phase sorbitol at concentrations which are sufficiently high for practical packed-bed catalysis. While only 10 % mass fraction vapor phase was validated, staged evaporation−reaction approaches would allow for much higher "effective" sorbitol concentrations to be used in the gas-phase catalytic processes.

Literature Cited

(1) Nelson, L. D.; Cox, M. M. *Lehninger Principles of Biochemistry*, W H Freeman & Co., 2004.
(2) Conradin U.S. Pat. No. 2,965,679, 1960.
(3) Conradin U.S. Pat. No. 2,852,270, 1958.
(4) Conradin U.S. Pat. No. 3,030,429 1962.
(5) Clark, I. T. Hydrogenolysis of Sorbitol. *Ind. Eng. Chem.* **1958**, *50*, 1125–1126.
(6) Sirkar, A. K. U.S. Pat. No. 4,338,472, 1982.

(7) Tanikella, M. S. U.S. Pat. No. 4,404,411, 1983.

(8) Gerrit, V. L.; Alfons, J. D.; Arie, C. P.; Jozef, C. V. Continuous production of glycerol by catalytic high pressure hydrogenolysis of sucrose. *Ind. Eng. Chem. Prod. Res. Dev.* **1970**, *9*, 210–212.

(9) Gubitosa, G.; Casale, B. U.S. Pat. No. 5,600,028, 1997.

(10) Hellwig U.S. Pat. No. 3,471,580, 1969.

(11) Guido, B.; Giuseppe, D. G.; Daniela, F.; Vincenzo, P. Enthalpies and entropies of sublimation, vaporization and fusion of nine polyhydric alcohols. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 75–79.

(12) Goodrum, J. W.; Siesel, E. M. Thermogravimetric analysis for boiling points and vapor pressure. *J. Therm. Anal. Calorim.* **1996**, *46*, 1251–1258.

(13) Guckel, W.; Kastel, R.; Krohl, T.; Parg, A. Methods for determining the vapor pressure of active ingredients used in crop protection. Part IV. An improved thermogravimetric determination based on evaporation rate. *Pestic. Sci.* **1995**, *45*, 27–31.

(14) Elder, J. P. Sublimation measurements of pharmaceutical compounds by isothermal thermogravimetry. *J. Therm. Anal.* **1997**, *49*, 897–905.

(15) Wiedemann, H. G. Application of thermogravimetry for vapor pressure determination. *Thermochim. Acta* **1972**, *3*, 355–366.

(16) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC-Press: Boca Raton, FL, USA, 1998.

(17) Yau, M. K.; Rogers, R. R. *Short course in cloud physics*; Butterworth-Heinemann: Burlington, MA, USA, 1989.

(18) Herbert, B. C. *Thermodynamics and an introduction to thermostatistics*; Wiley: New York, 1985.

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