ASAE Paper Number: 056047

Thermodynamic Properties and Mold Appearance on Selected Corn Stover Components

C. Igathinathane
Alvin R. Womac
Shahab Sokhansanj
Lester O. Pordesimo

2005 ASAE Annual International Meeting
Sponsored by ASAE
Tampa Convention Center
Tampa, Florida
17 - 20 July 2005

Department of Biosystems Engineering and Soil Science, The University of Tennessee, Knoxville, TN
Oak Ridge National Laboratory, Environmental Sciences Division, P.O. Box 2008, Oak Ridge TN
USDA-ARS Instrument and Sensing Lab, 10300 Baltimore Avenue, Beltsville, MD

Introduction

Thermodynamic Properties - Usage

Understanding moisture-material interaction
monolayer moisture, bound moisture, active sites, etc.,

Heat transfer, mass transfer, energy requirement calculations
sorption / desorption heat, LH of vaporization, enthalpy, entropy, etc.,

Designing of processing and handling systems
dryers design, storage environment, packaging, etc.,

Introduction

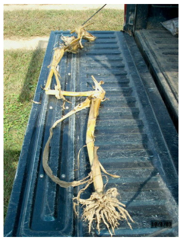
Thermodynamic Properties – Test Material

Major corn stover components (Igathinathane et al., ASAE Paper No: 041162)

Stalk (72.6%) & Leaf (20.7%)

Stalk skin   Stalk pith

Combine harvesters subject corn stalks to
crushing
twisting
and pulling actions
and expose stalk pith



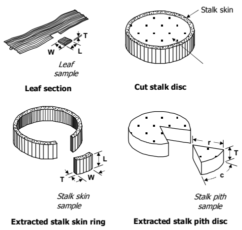
Introduction

Objectives

1. Determine thermodynamic properties
   - monolayer moisture content
   - isosteric heat of sorption
   - differential entropy
   - spreading pressure
   - net integral enthalpy
   - net integral entropy
2. Develop prediction models for the mold free days based on visual observation of mold infestation.

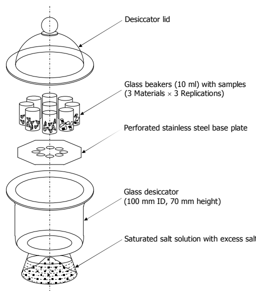
Materials and Methods

Material Preparation



Materials and Methods

Static method of sorption isotherm data collection



Temperatures used: 10, 20, 25, 30, 35, and 50°C (6 levels)
Water activity used: 11 to 98% (10 levels)

Materials and Methods

Thermodynamic Properties Determination

1. Monolayer moisture content – BET and Modified BET equation

$$M = \frac{M_w C a_w}{(1-a_w)(1-a_w+Ca_w)} \qquad M = \frac{(A+BT)Ca_w}{(1-a_w)(1-a_w+Ca_w)}$$

$$M_m = A + BT_c$$

Where:

- M = EMC % dry basis (d.b.)
- A, B, C = model constants
- T_c = temperature (°C)
- a_w = water activity (decimal)
- M_m = monolayer moisture content (% d.b.)

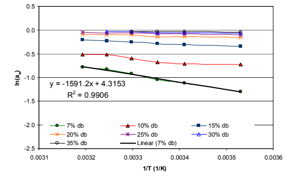
Non linear regression (Proc NLIN of SAS) evaluated model constants

Materials and Methods

Thermodynamic Properties Determination

2. Net isosteric heat of sorption - Clausius-Clapeyron equation

$$\left.\frac{\partial[\ln(a_w)]}{\partial[1/T]}\right|_M = -\frac{q_{st}}{R}$$



3. Differential entropy - Gibbs energy in Gibbs-Helmholtz equation

$$-\ln(a_w)\big|_M = \frac{-(q_{st}+\lambda)}{RT} - \frac{S_d}{R}$$

Where:

- q_{st} = water isosteric heat of sorption (kJ·mol^{-1})
- T = temperature (K)
- R = universal gas constant (0.00831434 kJ·mol^{-1}·K^{-1})
- λ = latent heat of vaporization of pure water (kJ·mol^{-1})
- S_d = differential entropy of sorption (J·mol^{-1}·K^{-1})

Slope of plot of $\ln(a_w)$ versus $1/T$ at constant M gives q_{st}
Intercept of plot of $\ln(a_w)$ versus $1/T$ at constant M gives S_d
Cubic spline interpolation produced a_w values at specified M

Materials and Methods

Thermodynamic Properties Determination

4. Spreading pressure - Iglesias et al. (1976)

$$\pi = \frac{KT}{A_m}\int_0^{a_w}\frac{M}{M_m a_w} \qquad M = \left(\frac{-a}{\ln(a_w)}\right)^{1/r}$$

Halsey isotherm model

$$\pi = \frac{KT}{A_m}a^{\frac{1}{r}}\left[\frac{1}{\left(\frac{1}{r}-1\right)\left(-\ln(a_w)\right)^{\frac{1}{r}-1}}\right]_{0.05}^{a_w} \qquad \pi = \frac{KTM}{A_m M_m}$$

First a_w interval: 0.05 to a_w Second a_w interval: 0.0 to 0.05

Where:

- π = spreading pressure, (J·m^{-2})
- K = Boltzman's constant (1.380 × 10^{-23} J·K^{-1})
- T = temperature (K)
- A_m = surface area of a water molecule (1.06×10^{-19} m^2)
- a, r = Halsey isotherm models constants

Materials and Methods

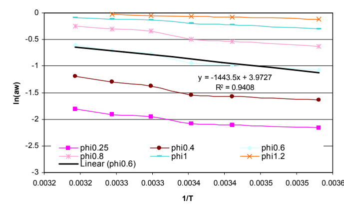
Thermodynamic Properties Determination

5. Net integral enthalpy – Based on Gibbs equation

$$\left.\frac{\partial[\ln(a_w)]}{\partial[1/T]}\right|_\pi \approx -\frac{Q_{in}}{R}$$

6. Net integral entropy – Clausius-Clapeyron equation

$$S_{in} = \frac{-Q_{in}}{T} - R\ln(a_w^*)$$



Where:

- Q_{in} = net integral enthalpy (kJ·mol^{-1}).
- S_{in} = net integral entropy (J·mol-1·K-1)
- a_w^* = geometric mean water activity at constant π

Slope of plot of $\ln(a_w)$ versus $1/T$ at constant π gives Q_{in}
Cubic spline interpolation produced a_w values at specified π

Materials and Methods

Mold Free Days Analysis

Mold growth on samples during sorption experiments was observed.

Day of first appearance of mold in the form of visible network of mycelium was recorded.

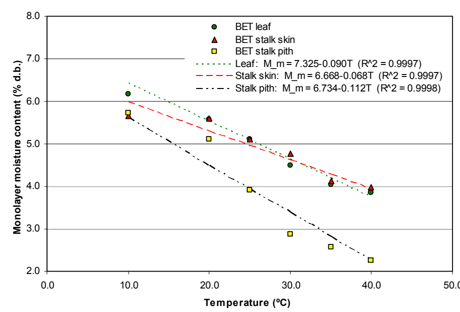
MFD = Day of first mold appearance - 1

Exponential spoilage model for MFD in terms of temperature and water activity (Herrman and Loughin, 2003; Sokhansanj et al., 2003)

$$MFD = \exp\,(A + B{\times}T + C{\times}a_w)$$

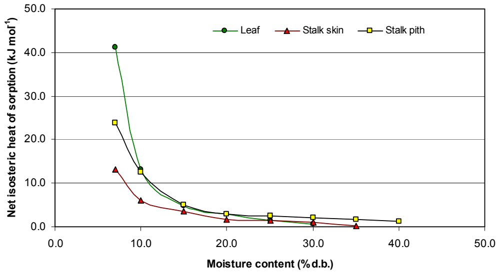
Results

1. Monolayer moisture content



Results

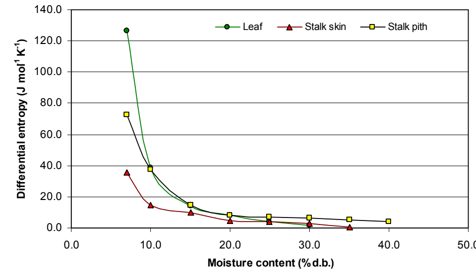
2. Net Isosteric Heat of Sorption



Low moisture – high sorption heat – highest binding energy for moisture removal

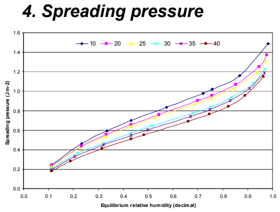
Results

3. Differential entropy



Results

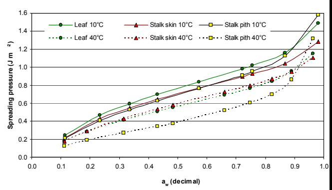
4. Spreading pressure



Eg. Leaf at different temperatures

Force in the plane of surface that exerted perpendicular to each unit length of edge to keep surface from spreading

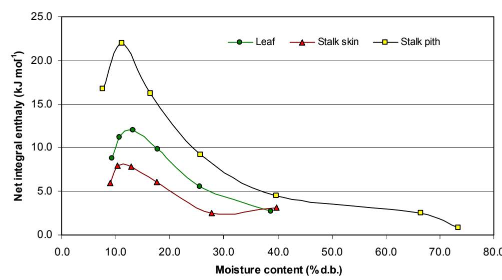
Spreading pressure decreases with increase in temperature



At temperature limits

Results

5. Net integral enthalpy

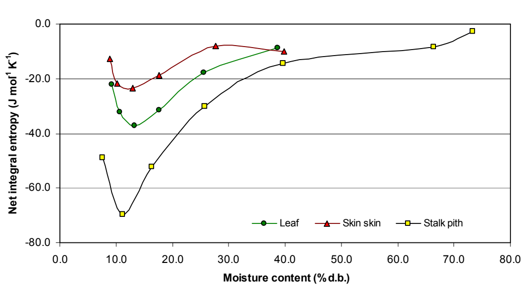


At low moisture: Exterior surface accessible sites filled; Swelling opens up new high energy sites for moisture to bound

At high moisture: Less favorable sites filled and multiple layers of sorbed water

Results

6. Net integral entropy



At low moisture: Restriction to moisture movement readily available sites were used, loss of rotational freedom; Strongest binding sites were utilized – moisture completely localized

At high moisture: More free moisture - multi layers of sorbed water offers more freedom

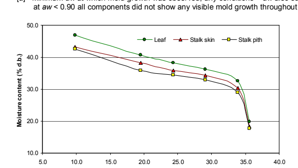
Results

7. Mold growth observation

Table 1. Storage conditions of corn stover components one day after MFD

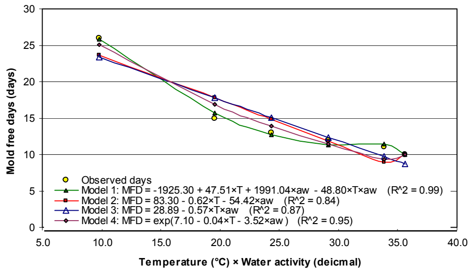
MFD	T (°C)	a_w[a] (decimal)	$T \times a_w$ (°C)	Moisture content (% d.b.) of corn stover component one day after MFD: Leaf	Stalk skin	Stalk pith
10	40	0.89	35.60	46.82	43.24	42.63
11	35	0.967	33.85	40.62	38.35	35.79
12	30	0.97	29.10	38.32	35.81	34.43
13	25	0.973	24.33	36.12	34.29	32.86
15	20	0.976	19.52	32.63	30.37	28.88
26	10	0.982	9.82	19.90	18.22	17.79

[a] Minimum *aw* at which mold growth was observed; any conditions > *aw* also sustained mold growth and at *aw* < 0.90 all components did not show any visible mold growth throughout the experimental period



Results

8. Mold free days analysis



$T \times a_w$ (t = -5.11, p = 0.0069)
T (t = -4.43, p = 0.0114)
a_w (t = 1.15, p = 0.3140)

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Conclusions

Property	Observation	Leaf	Stalk skin	Stalk pith
BET Monolayer moisture (% d.b.)	Decreased with moisture increase	**4.87 ±0.91%**	**4.87 ±0.72%**	**3.74 ±1.43 %**
Net isosteric heat of sorption (kJ·mol^{-1})	Reduced exponentially with moisture increase	**2.77**	**1.56**	**2.99**
Differential entropy (J·mol^{-1}·K^{-1})	Reduced exponentially with moisture increase	**7.79**	**4.22**	**8.81**
Spreading pressure (J·m^{-2})	Increased with water activity increase and decreased with temp.	**0.74 ±0.33%**	**0.71 ±0.31%**	**0.65 ±0.38%**
Net integral enthalpy (kJ·mol^{-1})	Increased, reached maximum and decreased with moisture increase	**8.34 ±3.58%,**	**5.58 ±2.31%**	**10.30 ±7.67%**
Net integral entropy (J·mol^{-1}·K^{-1})	Decreased, reached minimum and increased with moisture increase	**-24.84 ±10.58%,**	**-15.83 ±6.36%**	**-32.36 ±23.79%,**

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Conclusions

All stover components were affected by mold at water activity > 0.90.

For a given water activity, high temperatures were found to be conducive to mold growth.

Stalk pith was the least resistant to mold growth followed by stalk skin and leaf.

$T \times a_w$ product (p = 0.0069) was the most significant variable followed by T alone (p =0.0114) and a_w (p = 0.3140).

Developed three-parameter MFD model gave the best prediction and exponential model produced comparable prediction.

$$MFD = -1925.299 + 47.511T + 1991.037a_w - 48.797T \times a_w \quad (R^2 = 0.9937)$$

$$MFD = \exp(7.096 - 0.041T - 3.523a_w) \quad (R^2 = 0.9521)$$

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Acknowledgement

Bioenergy Feedstock Development Program of the Oak Ridge National Laboratory

Dr. Svetlana Zivanovic

Dr. Mark Radosevich

Thanks!

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Questions!

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