Droplet Reaction and Evaporation of Agents Model (DREAM)

Applied to HD on glass, DEM on glass and MS on glass

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Outline

• Introduction

• Model
  – Sessile drop model

• Data
  – Dutch wind tunnel (HD, DEM and MS on Glass)
  – Czech wind tunnel (HD on Glass)
  – ECBC wind tunnel (HD on Glass)

• Fitting the model to the data
4 Transport rates
**Develop in steps**

<table>
<thead>
<tr>
<th>Neat Agent</th>
<th>Thickened Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sessile Drop</strong></td>
<td><strong>Absorbed Drop</strong></td>
</tr>
<tr>
<td>Drops spread fast (seconds)</td>
<td>Drops absorb fast (minutes)</td>
</tr>
<tr>
<td>Drops spread slow (ten minutes)</td>
<td>Drops absorb slow (hours)</td>
</tr>
</tbody>
</table>

Add reactivity when significant chemical reactions are found
Sessile drop (F1)

- Drop mass over time
  \[ m(T) = m(0) - \int_{0}^{T} \dot{m}(t) \, dt \]

- Fick’s law
  \[ \frac{d m(t)}{d t} = \frac{D A(t) (C_{\text{skin}} - C_{\text{bulk}})}{L} \]

- Raoult’s law (ideal mixtures)
  \[
  P_{\text{agent in mixture}} = \text{Mol fraction}_{\text{agent in drop}} \times P_{\text{pure agent}} \\
  C_{\text{agent}} = \frac{P_{\text{agent}} \times \text{Mol weight}_{\text{agent}}}{(RT)}
  \]

- Reactivity (implemented but not yet tested)
  \[ \frac{d[X]}{d[t]} = A_e e^{(-E/RT)} [X]^x [Y]^y \]
Diffusivity, $D$ in air

- How ‘mobile’ are the molecules in air?
  - Depends on temperature, pressure, molecular mass, molecular volume, and air properties

- Two estimation methods found
  - Fuller, Schettler, Giddings method (Lyman et al. 1982)
    - All above dependencies
    - Not suitable for phosphor components: no molecular volume data
  - Simple method (Danish EPA)
    - Eliminates molecular volume dependence
Diffusivity Data and Estimations

Diffusivity data at 1 atm for DEM, MS, HD

Temperature - C

Difusivity - cm²/s

- MS
- MS,2
- MS,3
- MS,4
- DEM,2
- DEM,3
- DEM,4
- HD
- HD,2
- HD,3
- HD,4
Vapor Concentration at skin, $C_{\text{skin}}$

- Get vapor concentration from vapor pressure
  - Get ‘volatility’ using ideal gas law: $C = P \frac{M_w}{(R \cdot T)}$

- Depends on
  - Agent
    - from data (if available)
    - or estimation methods
  - Temperature
    - Antoine equation (used for model)
      - three constants $a, b, c$ fitted to data

**Antoine equation**

$$P = 133.322 \times 10^{a-b/(T+c)}$$

**Clausius-Clappleron

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
Diffusion layer thickness, L

- Depends on
  - wind speed
  - temperature (viscosity air)
  - pressure
  - on turbulence
  - drop size

- Empirical in semi-empirical model
  - Constant diffusion layer thickness for an experiment
  - ~ laminar layer thickness
  - order of magnitude: 1 millimeter
  - Fitted to data
Wind speed vs Height

3 u''s to be used for comparative testing and matrix, giving 3 wind speed vs height curves

- laminar layer
- transition layer
- turbulent layer
Area of evaporation, $A(t)$

- **Volume from initial drop mass**
  - Liquid density a function of agent and of drop temperature

- **Shape over time**
  - From observed shape and time behavior of sessile drops:
    - One shape (spherical cap), but two modes needed
      - Constant base area mode
      - Constant contact angle mode
Densities of HD, DEM, MS

**Density - g/ml**

**Temperature - C**

HD,0) HD,1) HD,2) HD,3) MS,0) MS,1) MS,2) DEM,0) DEM,1) DEM,2)
Area of evaporation over time

- **Sessile drop - constant angle**
- **Sessile drop - constant base area**
- **Sessile drop - base switches to angle**

- **Initial contact angle**: 35° degree
- **Minimum Contact Angle**: 10° degree

- **Drop weight**: initial drop 6.600 mg

- **Agent**: HD

- **Temperature**: 30°C

- **Diffusion layer**: 0.5 mm

- **Pressure**: 1 atm

**CAP, Constant Angle**

**CAP, Constant Base**
Volume of drop over time

- **Sessile drop - constant angle**
- **Sessile drop - constant base area**
- **Sessile drop - base switches to angle**

**Weight initial drop agent**: 6.600 mg (HD)

**Initial contact angle**: 35°

**Minimum Contact Angle**: 10°

**Temperature**: 30 °C

**Diffusion layer**: 0.5 mm

**Pressure**: 1 atm
DATA

• Czech data
  – 30 mass over time curves HD on Glass

• Dutch data (neat and thick)
  – 42 mass over time curves DEM on Glass
  – 46 mass over time curves MS on Glass
  – 11 mass over time curves HD on Glass

• ECBC data
  – 5 mass over time curves HD on Glass

• Much more data on the way
  – UK, Czech, Dutch and ECBC
    • Establish proper tunnels performance
    • Compare effects tunnel size (and turbulence intensity)
Dutch DEM data, 42 curves

DEM on Glass - uncorrected - Neat & Thick
~ 10 - 30 Celsius, ~ 0.75 - 2.25 m/s
Dutch MS data, 46 curves

MS on Glass - uncorrected - Neat & Thick
~ 10 - 30 Celsius, ~ 0.75 - 2.25 m/s

Time [Hours]

Mass [fraction]
Dutch HD data, 11 curves

HD on Glass - Uncorrected - Neat & Thick
~ 10 - 30 Celsius, ~ 1.00 - 2.35 m/s
Fitting the model to the data

used empirical fit functions for contact angles and ‘effective average diffusion layer thickness’

- Initial angle
- Minimum angle

assumed to depend on
  - temperature
  - relative humidity

- ‘Effective average diffusion layer thickness’

assumed to depend on
  - wind speed
  - drop size
MS fit functions

- Temperature
  - Exponential
- Relative Humidity
  - Exponential
- Wind Speed
  - Inverse with offset
- Drop Size
  - Exponential
Experiment compared with Single Sessile Drop models

MS data fitted to model
Over / Under prediction of time by model

MS on Glass

Mass fraction

Over / Under prediction of time

100%  66%  200%  150%
DEM on Glass

Over / Under prediction of time by model

mass fraction

100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%

150% 200% 66%

-1.5 -1.0 -0.5 0.0 0.5 1.0 1.5

over / under prediction of time

100% 80% 60% 40% 20% 0% 20%
HD on Glass

Over / Under prediction of time by model

mass fraction

over / under prediction of time

0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%

0 0.5 1.0 1.5

200%

150%

100%

66%

-1.0 -0.5 0.0 0.5 1.0 1.5

HD on Glass

Over / Under prediction of time by model
Data space and Fit Quality's HD on Glass

The normalized square root of the summed square error.
Conclusion

• Semi–Empirical Sessile Drop model
  – Fits existing data fairly well
    • Persistence times typically within 66% to 150% of experiment
  – Work in progress
    • More sessile drop data
    • Experimental Contact angle functions
    • Reactivity not tested yet

• Semi–Empirical Absorbed drop model
  – Prototype exists, Awaiting data
MS data fitted to model

Experiment compared with Single Sessile Drop models