NEMOSINE

TRAINING SESSIONS

18th October 2021

Innovative packaging solutions for storage and conservation of 20th century cultural heritage of artefacts based on cellulose derivative

HIGH O_2 BARRIER AND ACTIVE PACKAGING

ACTIVE ACID ADSORBERS

MULTI-SCALE MODELLING

GAS DETECTION SENSORS

PACKAGING WITH MODULAR DESIGN

CURATIVE PACKAGES

NEMOSINE has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760801.

Multi-Scale Hybrid Modeling to Predict Degradation Kinetics of Cellulose Acetate Based Movie Films

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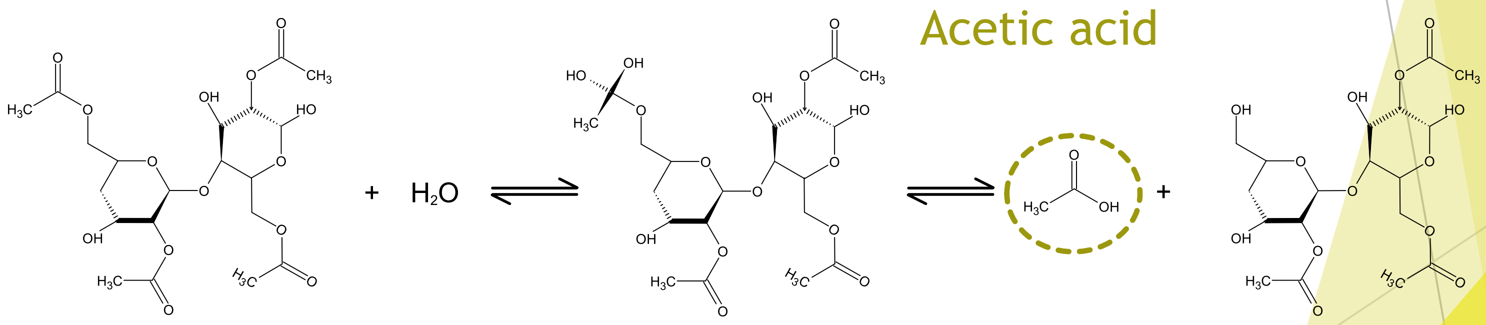
NEMOSINE has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760801.

Outline

- The Problem
- First-principles model for cellulose acetate polymer
  - Reactants' concentration determination
  - 5 tips on finding transition states (Gaussian)
  - Solving the transition state theory equations as function of time
- Hybrid model approach
  - Model presentation
  - 5 tips on Multivariate analysis models
  - Acetic acid adsorbent materials effect
- Conclusions

Problem: the "vinegar syndrome"

- A huge percentage of the recent European cultural heritage (CH) can be found in movies, photographies, posters and slides made using cellulose derivates, are in danger to be lost due to the natural instability cellulose acetate (CA).
- Deacetylation under neutral conditions:



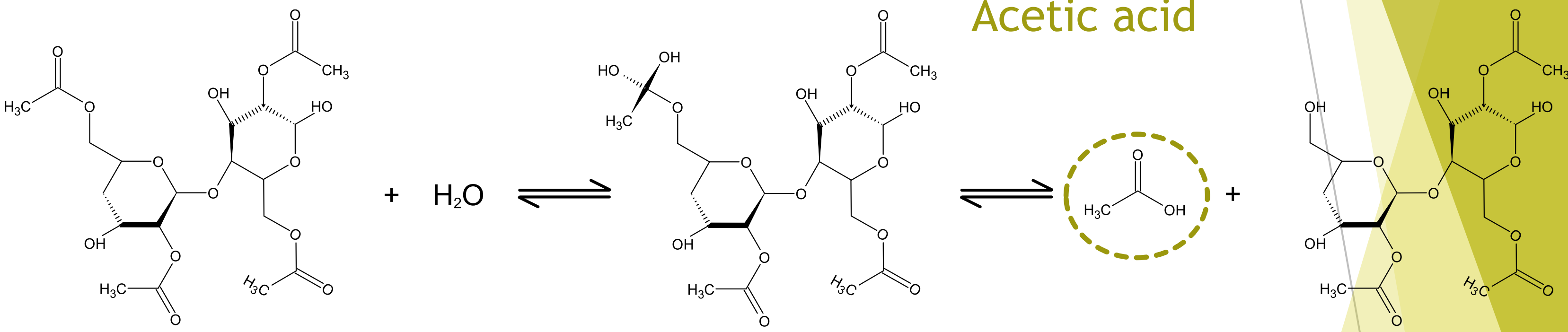
- No accurate predictions on the lifetime of the movie films to take best actions timely.

First-Principles Model to Evaluate Quantitatively the Long-Life Behavior of Cellulose Acetate Polymers[1].

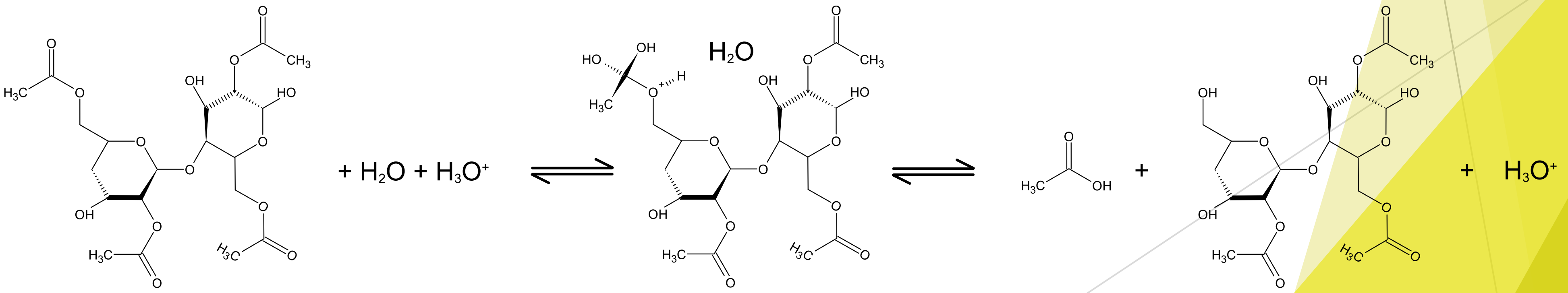
[1] Abeer Al Mohtar, Sofia Nunes, Joana Silva, Ana Maria Ramos, Joao Lopes, and Moisés L. Pinto. First-Principles Model to Evaluate Quantitatively the Long-Life Behavior of Cellulose Acetate Polymers. *ACS Omega*. **2021**. https://dx.doi.org/10.1021/acsomega.0c05438

Degradation Channels

- **Deacetylation under neutral conditions:**



- **Acid-catalyzed degradation:**



Transition State Theory

- **Determine the kinetic rate for long time-scale dynamics:**

$$\frac{dC_A}{dt} = -\frac{K_B T}{\mathrm{h}} \exp(-\frac{\Delta G^{\ddagger}}{RT}) \frac{C_A C_B}{C_0}$$

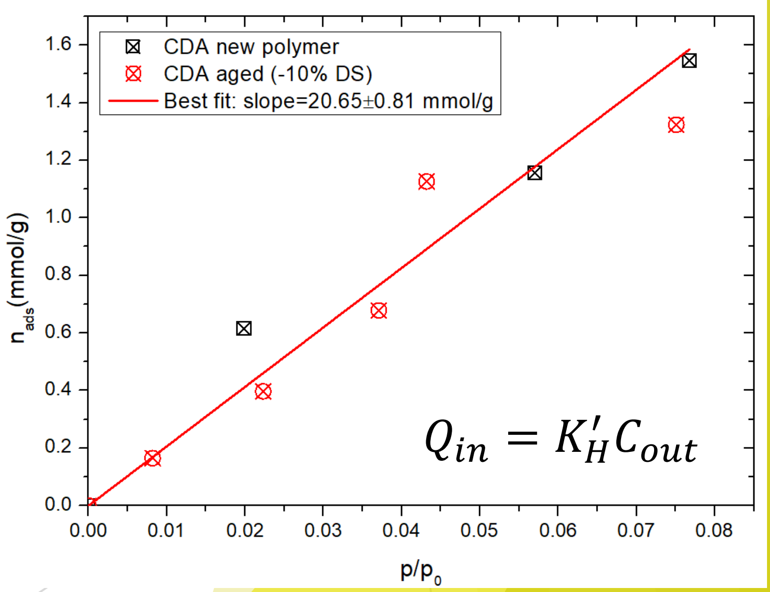
- **Water concentration from fitting literature data:**[1,2]

$$C_{H_2O} = 2.34 + 0.027 \times RH - 0.007 \times T + 3.96 \times 1011 pH^{-20.29}$$

- **Acetic acid concentration: mass balance equation**

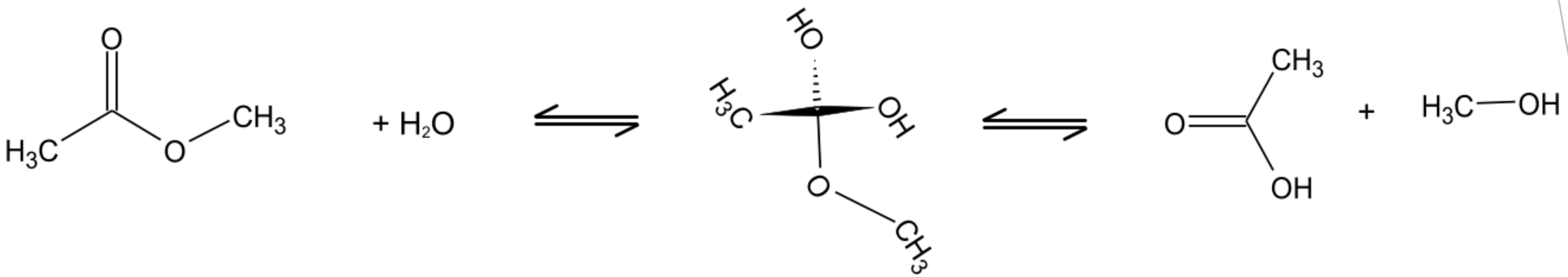
$$m(Q_{in} - Q_0) = V(C_0 - C_{out})$$

$$Q_{in} = \frac{VC_0 + mQ_0}{m + \frac{V}{K'_H}}$$

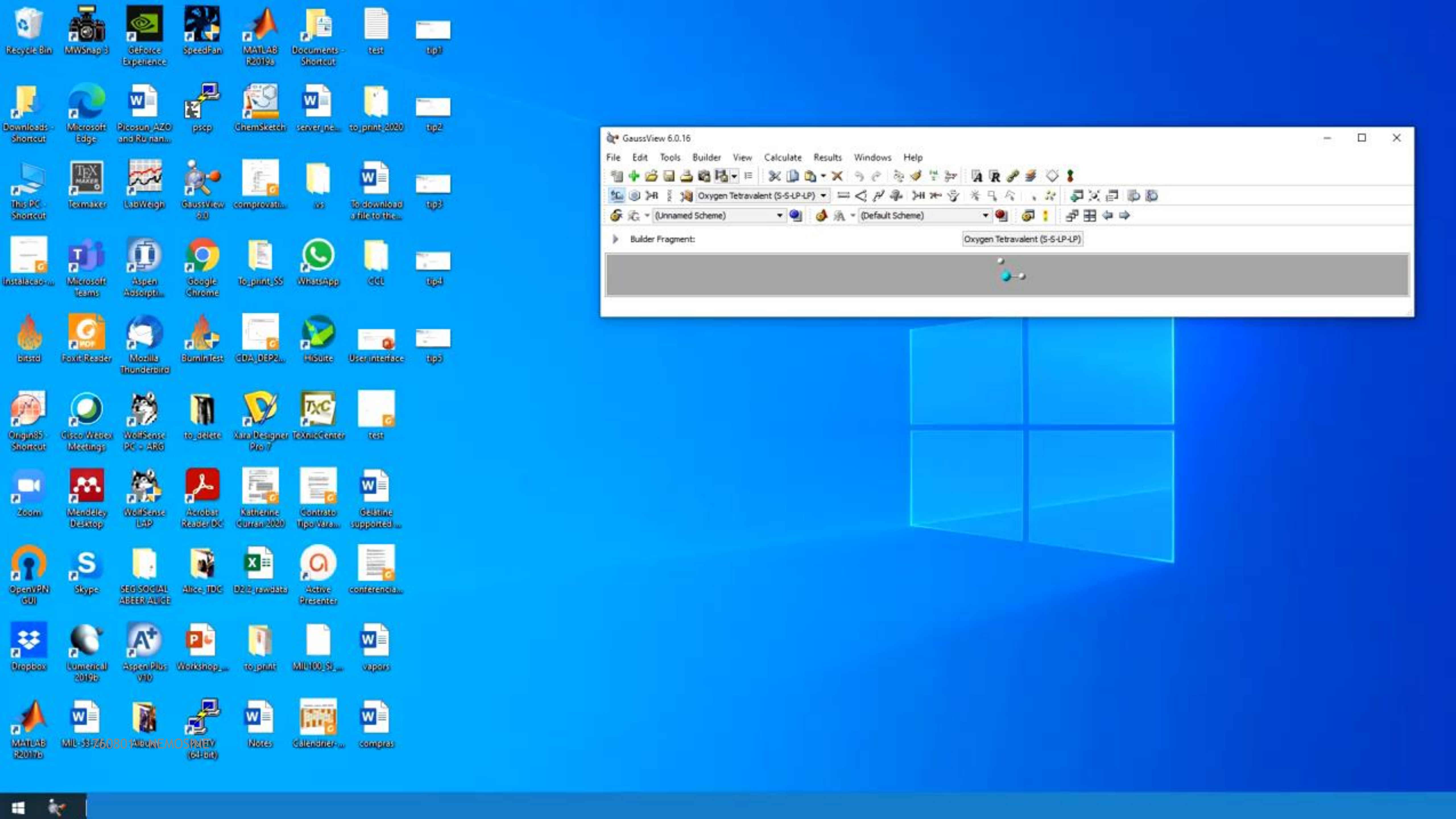


[1] P.Z. Adelstein et al."Moisture relationships of photographic film." (1997)
[2] N.S. Allen et al. "The Degradation and Stabilization of Historic Cellulose Acetate/Nitrate Base Motion-picture Film." *The Journal of Photographic Science* 36.3 (1988): 103-106.

5 Tips on Finding the Transition State Using "Gaussian": Simple Example



- Choose a good level of theory.
- Use QST3 method: provide a smart initial guess for the calculations.
- Choose calcfc keyword: it calculates the forces at the first point.
- Start at low level of theory, then go up.
- Do IRC to check if the right transition state is found.


GaussView 6.0.16
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View
Calculate
Results
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Help
Oxygen Tetravalent (S-S-LP-LP)
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MATLAB R2019a
Documents - Shortcut
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Mozilla Thunderbird
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HiSuite
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tip5
Origin85 - Shortcut
Cisco Webex Meetings
WolfSense PC - ARG
to_delete
Xara Designer Pro 7
TeXnicCenter
test
Zoom
Mendeley Desktop
WolfSense LAP
Acrobat Reader DC
Katherine Curran 2020
Contrato Tipo Vara...
Gelatine supported ...
OpenVPN GUI
Skype
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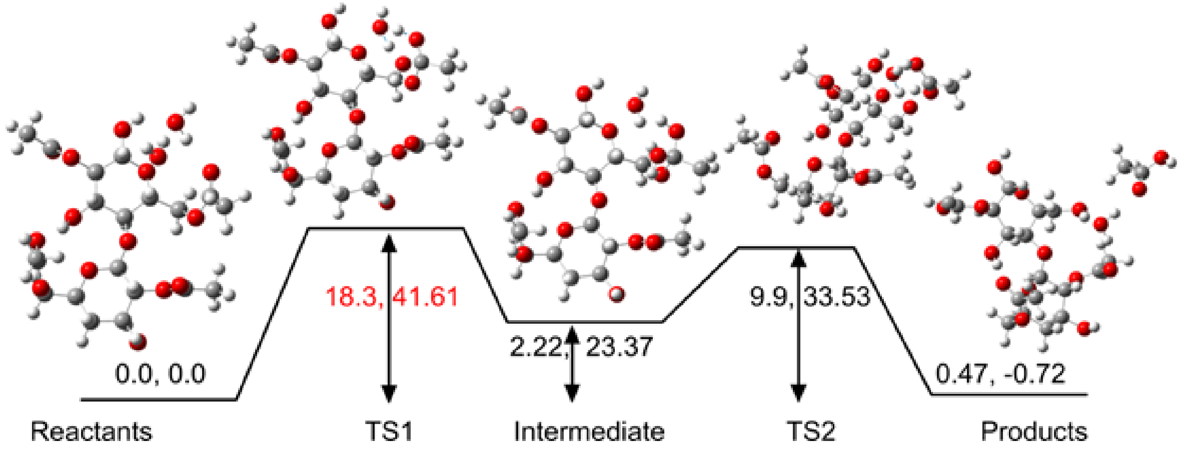
First-Principles Model: Density Functional Theory

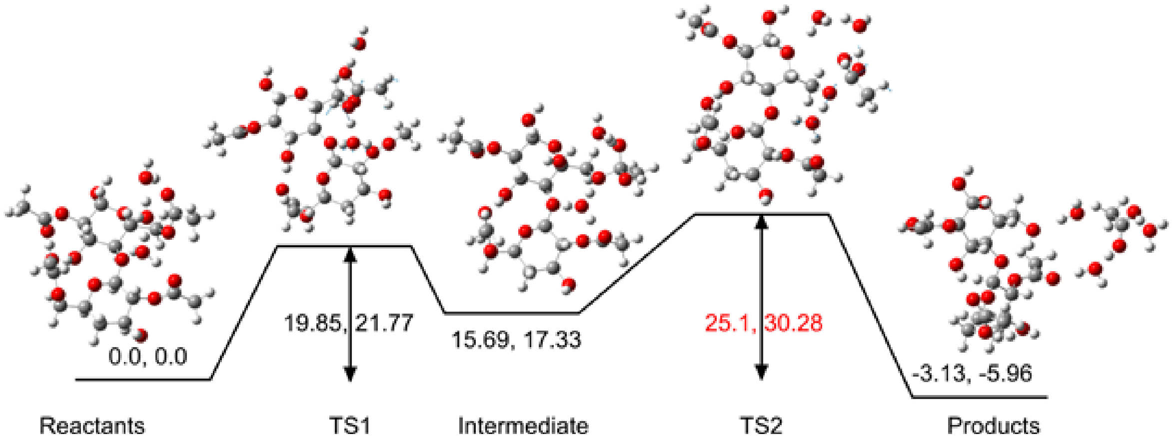
- Quantum chemical calculation of reactions activation energies (DFT-calculations)

Deacetylation under neutral conditions



ΔH, ΔG (kcal/mol) at T=300 k

Acid-catalysed deacetylation



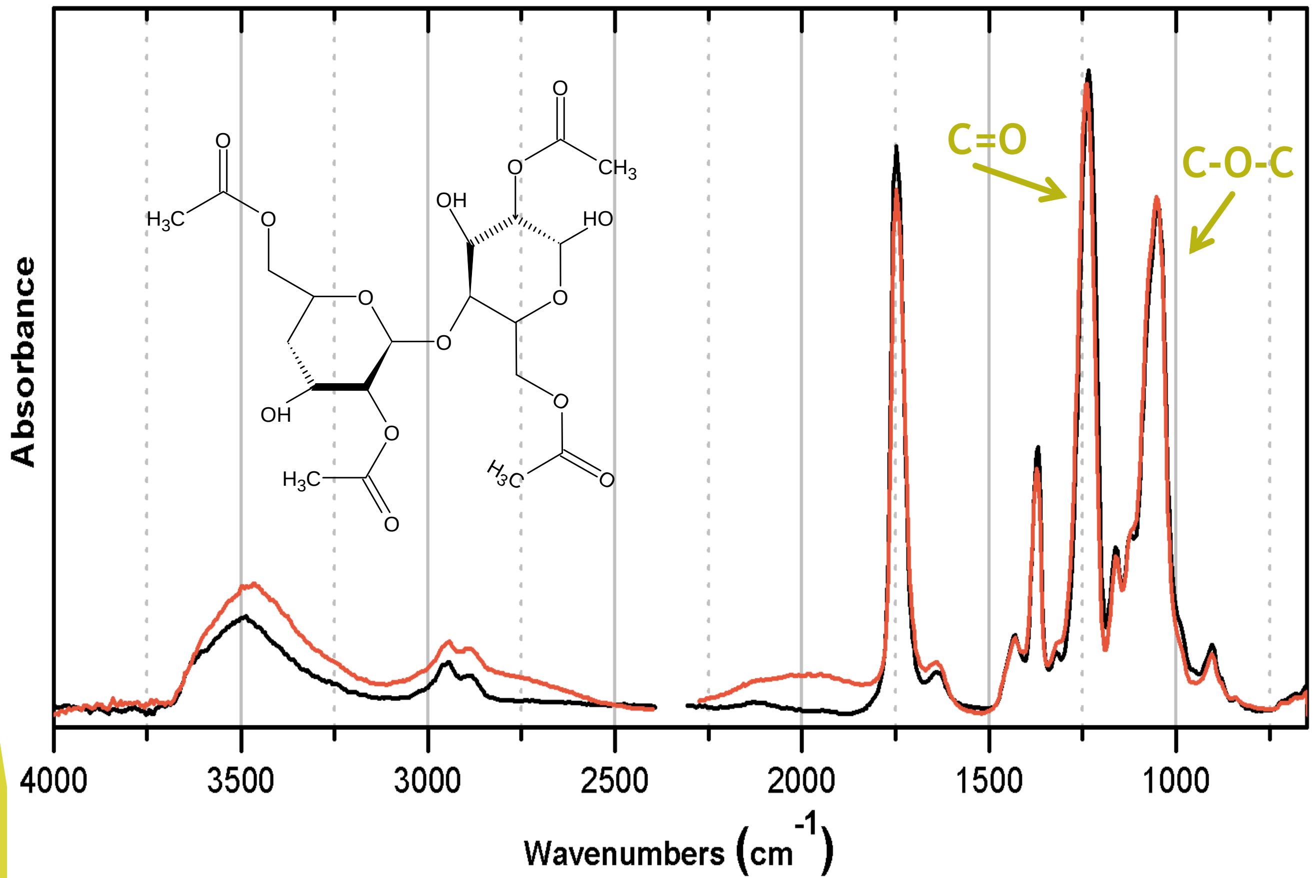
ΔH, ΔG (kcal/mol) at T=300 k

Experimental Conditions of Artificial Aging

- Two sets of experiments were performed: Thermal aging and Acidic aging
- Thermal aging conditions:
  - AA initial concentration = 0
  - Total mass = 1.2g, Volume = 11588 cm^3
  - T, RH = 80°C, 100%
- Acidic acid aging
  - A solution of 21.25 ml of acetic acid (2%) to give AA concentration= $1.79x10^{-05}$ $mmol/cm^3$ [1]
  - Total mass, Volume= 1.2 g, 2550 cm^3
  - T, RH= 70°C, 100%

[1] Abeer Al Mohtar, Sofia Nunes, Joana Silva, Ana Maria Ramos, Joao Lopes, and Moisés L. Pinto. First-Principles Model to Evaluate Quantitatively the Long-Life Behavior of Cellulose Acetate Polymers. *ACS Omega*. 2021. https://dx.doi.org/10.1021/acsomega.0c05438

µ-FTIR measurements – Degree of Substitution



- every week
- The degree of substitution (DS) was calculated from the obtained FTIR spectra, by defining the following calibration curve experimentally [1]:

$$y = 0.4916\,x + 0.1528$$

x being the DS and y the ratio between the intensity of the C=O peak (at circa 1240 cm-1) and the intensity of the C-O-C peak (at circa 1050 cm-1).

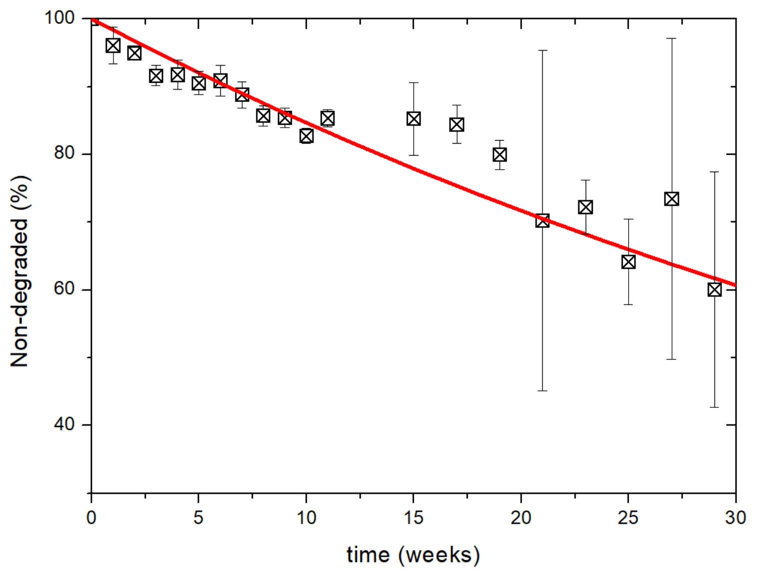
[1] Nunes, S. et al. A Diagnostic Tool for Assessing the Conservation Condition of Cellulose Nitrate and Acetate in Heritage Collections: Quantifying the Degree of Substitution by Infrared Spectroscopy. Heritage Sci. 2020, 8, No. 33.

First-Principles Model: Results

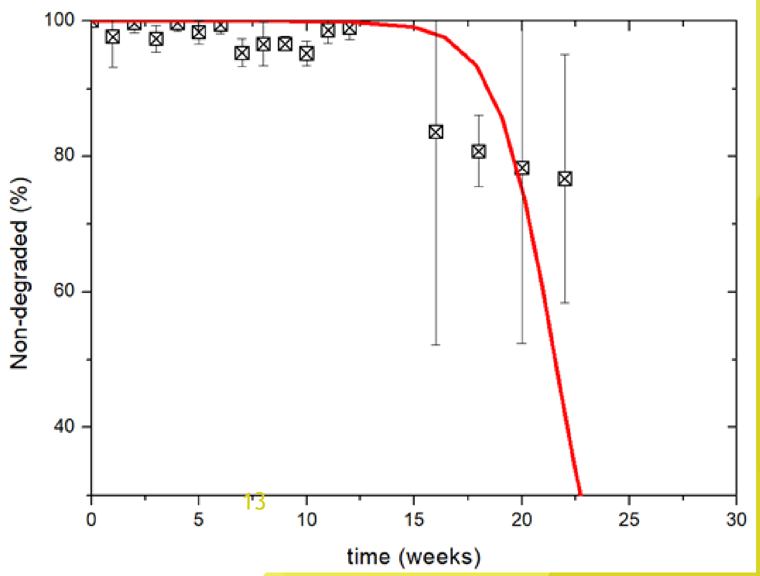
- The degradation kinetics were determined by coupling the transition-state-theory with the DFT calculations.
- The concentration of the reactants were carefully calculated.
- Model outcome agreed well with the artificial aging experiments with no adjustable parameters.

Collaboration with Universidade NOVA de Lisboa – accelerated aging experiments

Acidic aging conditions



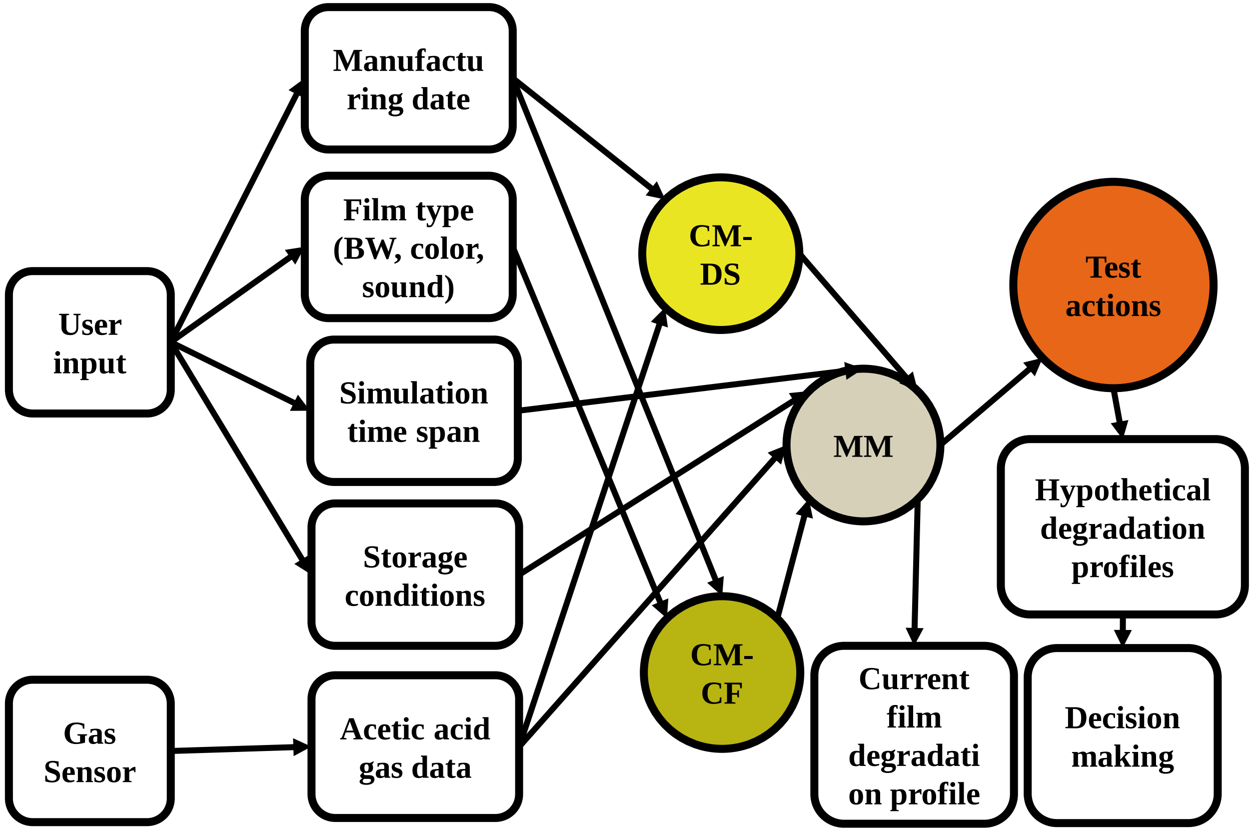
Thermal aging conditions



Decision making based on hybrid modeling approach applied to cellulose acetate based historical films conservation[1]

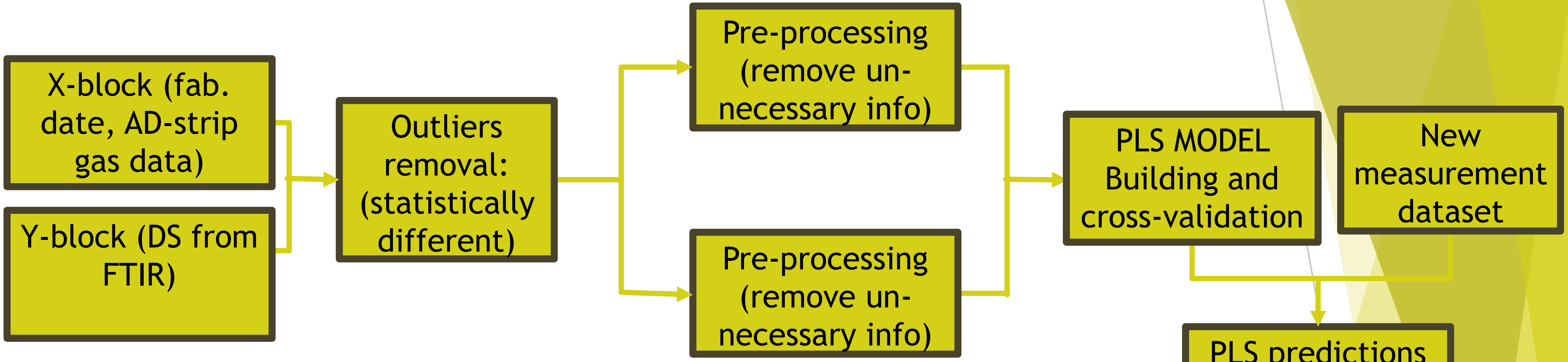
[1] Al Mohtar, Abeer, Moisés L. Pinto, Artur Neves, Sofia Nunes, Daniele Zappi, Gabriele Varani, Ana Maria Ramos et al. "Decision making based on hybrid modeling approach applied to cellulose acetate based historical films conservation." *Scientific Reports* 11, no. 1 (**2021**): 1-13.

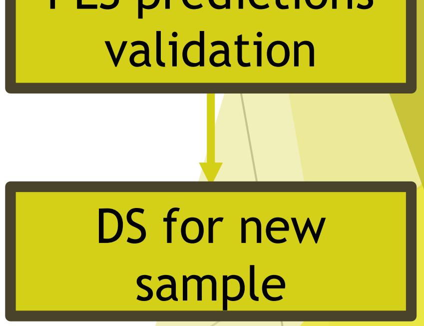
Hybrid Model Presentation



	Input	Output
MM model	Initial DS, time span, storage conditions (T, RH, mass of polymer, V box, initial AA in the atmosphere).	Degradation state evolution of pure polymer as function of time.
CM-DS	Manufacturing date, off-gas data, AD-strip	DS=current DS of the film.
Adapted MM model	Initial DS, time span, storage conditions, CF.	Degradation state evolution of plasticized polymer as function of time.
CM-CF	Manufacturing date, film type (BW, color, sound).	k_{CF}=how much the film is degrading faster than the pure polymer.
Hybrid model	CF=output of CM-CF, DS=output of CM-DS, time span, storage conditions.	Degradation state evolution of the movie film as function of time.
Hybrid model - adsorbent functionality	Mass and Henry's constant ($K_{H_{ad}}$) of the AA adsorbent, AA adsorbent replacement time.	Effect of AA adsorbent on the degradation evolution.

Machine Learning: Partial Least Square Model

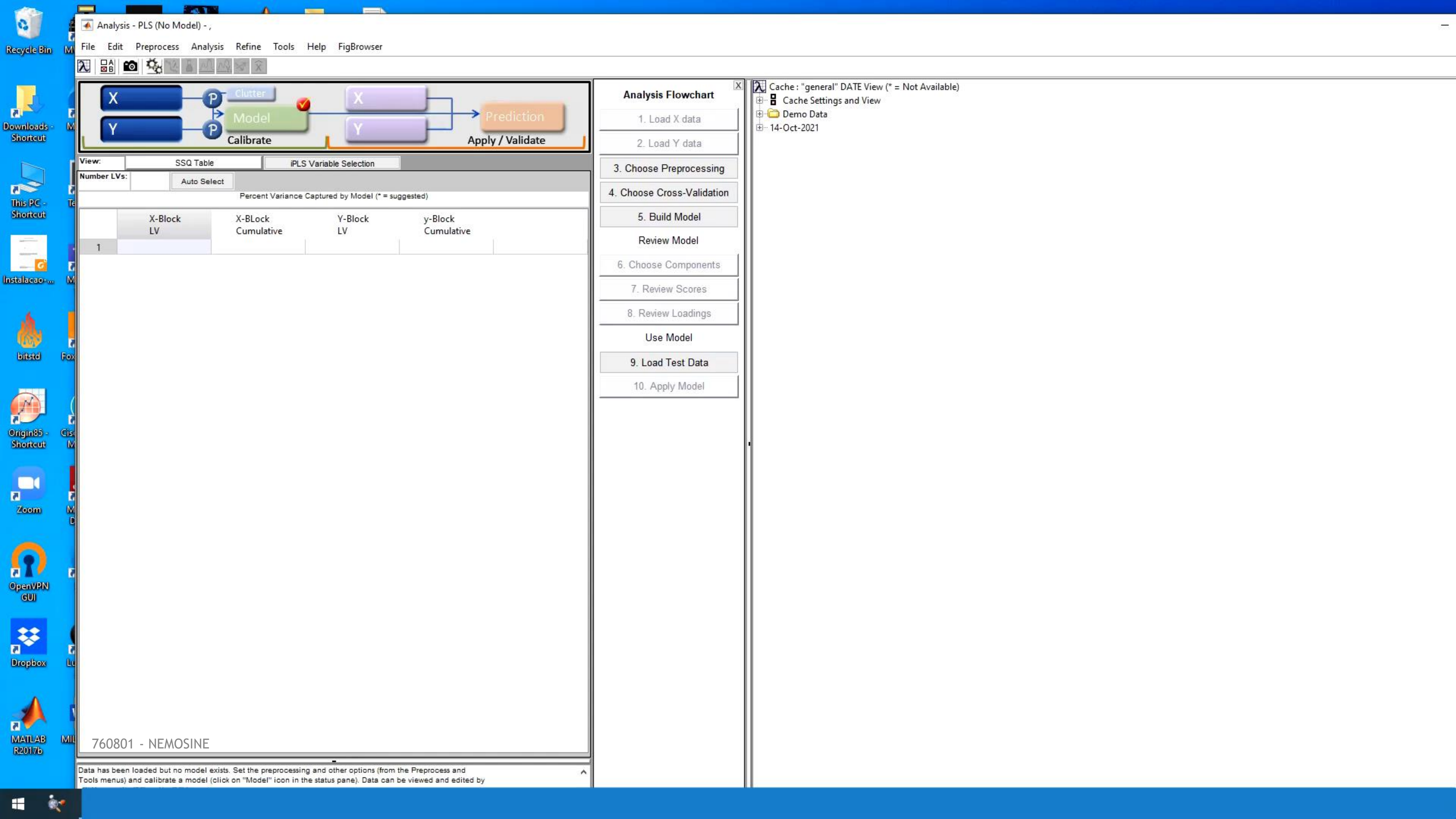




- Cross-validation is splitting the training dataset into groups, each time one group is left out and the model is calibrated based on the remaining groups. The left-out group is then used to predict the dataset in the cross-validation group.
- The RMSEP and RMSECV are indicators of how well a model fits the supplied data and estimates how well it will predict new data.
- Choose the model structure: limited data -> linear models, many degrees of freedom -> partial least square.

5 Tips on Multivariant Modeling

- Tip1: Include all samples' descriptors/known information.
- Tip2: Autoscale when we have independent set of input variable.
- Tip3: Choose the number of LV with min RMSECV.
- Tip4: Keep an eye on Q-Residuals and Hotelling T^2.
- Tip5: VIP scores to decide on input descriptors.
- Tip6: RMSEP is the real indicator of the performance of the model.


Analysis - PLS (No Model) - ,
File Edit Preprocess Analysis Refine Tools Help FigBrowser
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Y
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Clutter
Model
Calibrate
X
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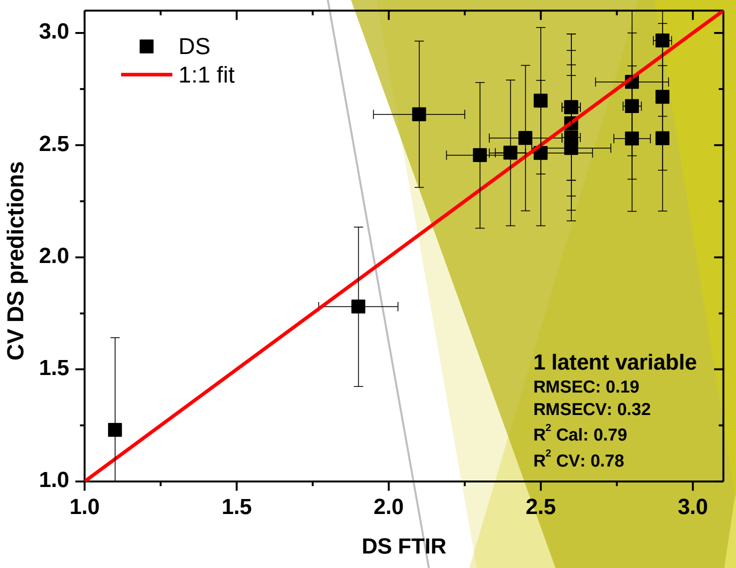
Prediction
Apply / Validate
View:
SSQ Table
iPLS Variable Selection
Number LVs:
Auto Select
Percent Variance Captured by Model (* = suggested)
X-Block LV
X-BLock Cumulative
Y-Block LV
y-Block Cumulative
1
760801 - NEMOSINE
Data has been loaded but no model exists. Set the preprocessing and other options (from the Preprocess and
Tools menus) and calibrate a model (click on "Model" icon in the status pane). Data can be viewed and edited by
Analysis Flowchart
1. Load X data
2. Load Y data
3. Choose Preprocessing
4. Choose Cross-Validation
5. Build Model
Review Model
6. Choose Components
7. Review Scores
8. Review Loadings
Use Model
9. Load Test Data
10. Apply Model
Cache : "general" DATE View (* = Not Available)
Cache Settings and View
Demo Data
14-Oct-2021
Recycle Bin
Downloads - Shortcut
This PC - Shortcut
Instalacao-...
bitstd
Origin85 - Shortcut
Zoom
OpenVPN GUI
Dropbox
MATLAB R2017b

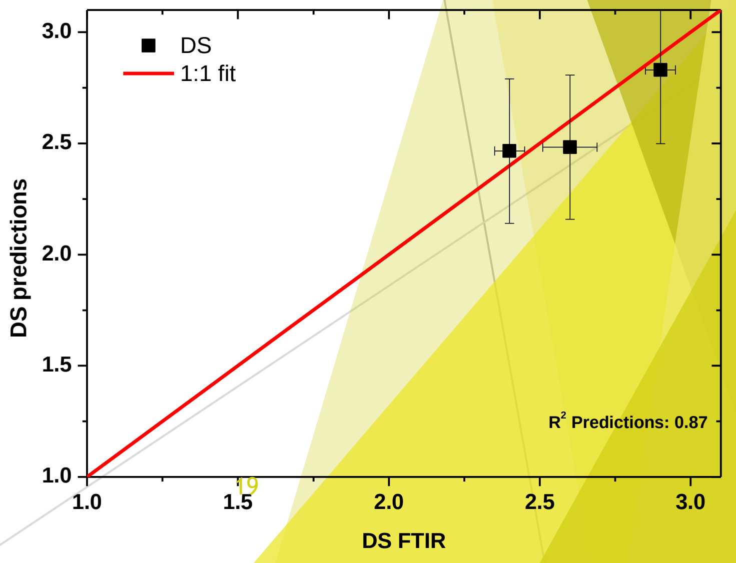
Results: CM-DS

- Collaboration with three archives:
  - Phonogrammarchiv of the Austria Academy of Sciences (OEAW, Vienna, Austria)
  - Institut Valencià de Cultura (IVC, Valencia, Spain)
  - Deutsches Filminstitut & Filmmuseum (DFF, Frankfurt, Germany).
- A chemometric model was developed to determine the current degree of degradation quantified by the current degree of substitution (how many acetyl groups per cellulose ring).
- Model input: gas data (provided by partner BIOSENSOR), AD-strip value and fabrication date, model output DS.
- To develop/train the model DS is quantified by FTIR (performed by partner NOVA)
- The model provides predictions with 87% accuracy.

Training dataset



Validation dataset

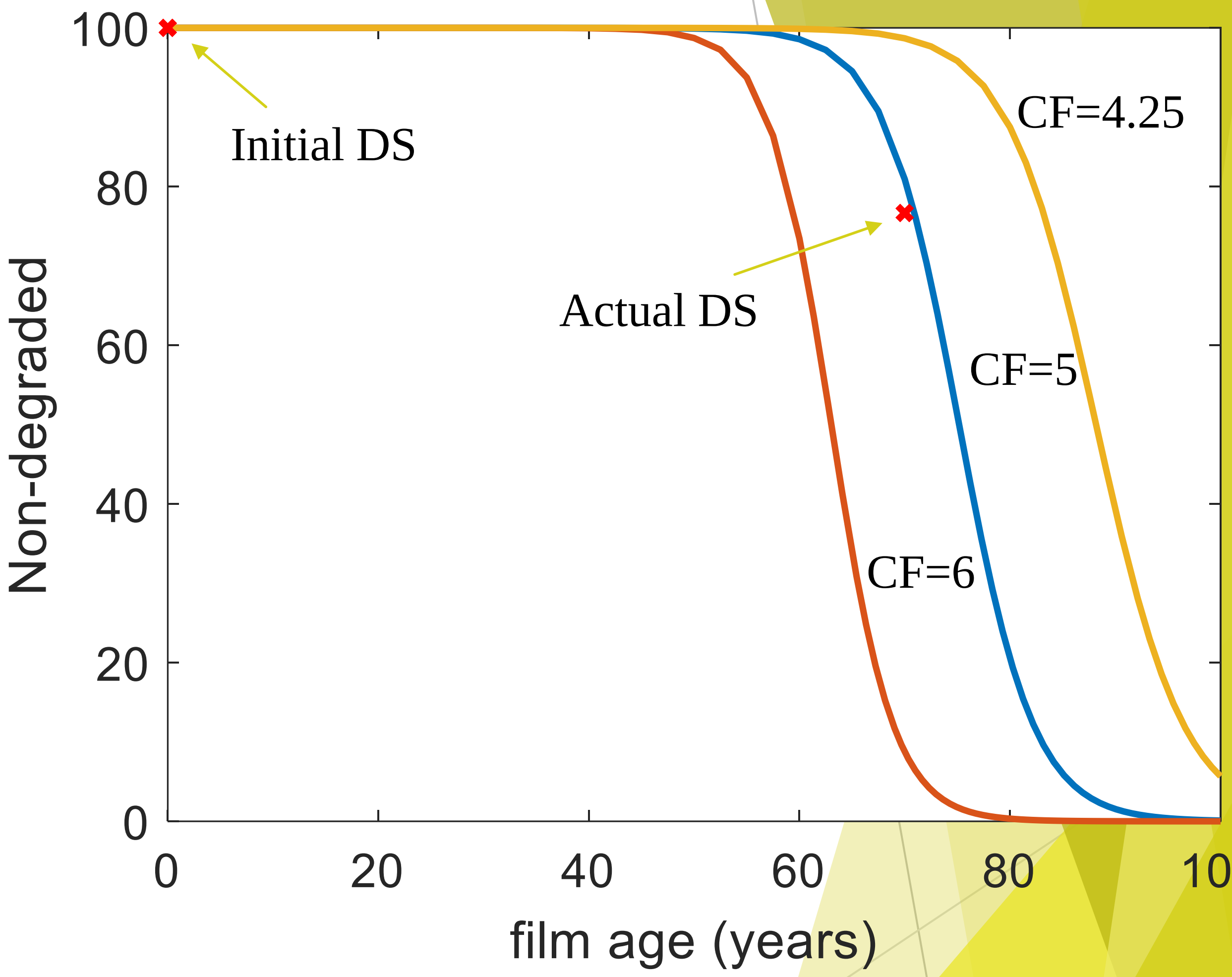


CF determination:

- The kinetic curve obtained from the MM, upon using the storage conditions (T, RH, V, m), is after accelerated by multiplying for a CF value that describes the experimental data of the real film.

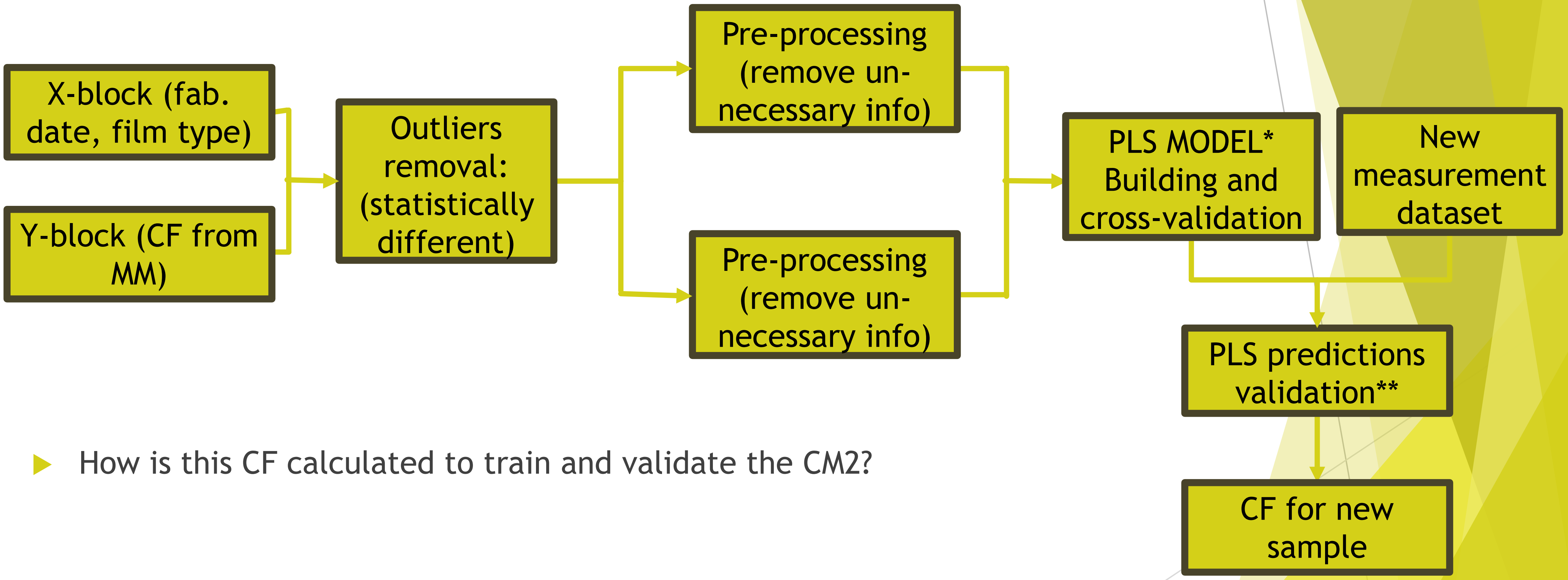
$$\frac{dC_A}{dt} = -(CF)\frac{K_B T}{\mathrm{h}}\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)\frac{C_A C_B}{C_0}$$

- For each film the CF is determined upon obtaining the degradation curve resulting from the MM that best fits visually the initial and actual DS.
- To obtain the degradation curves, the storage conditions (T, RH, storage box volume) over the lifespan of the films must be provided to the mechanistic model.
- The temperature is found to be the most critical parameter.



The CF interval in this case [4.25, 6] corresponding to temperature interval 20 ± 1°C. Note that in this figure all curves are simulated at T=20 ºC the only changing parameter is the CF.

Chemometric model: CF determination

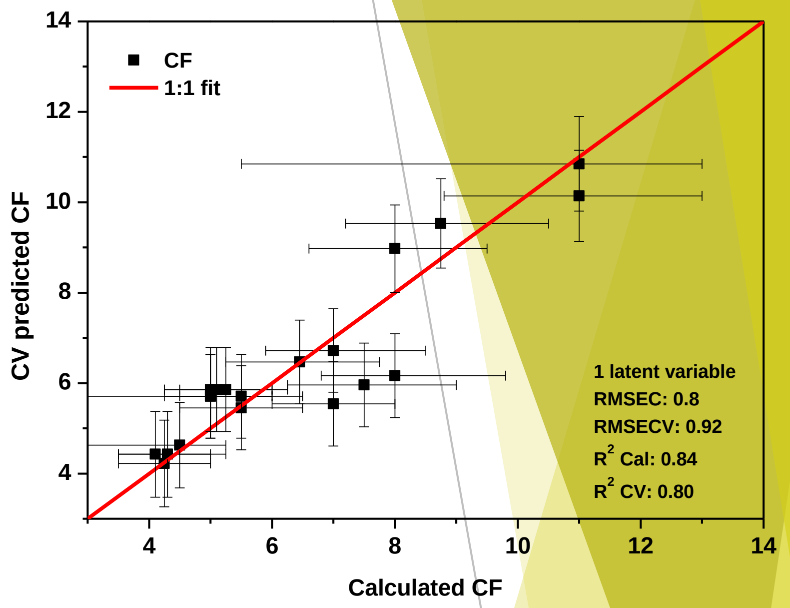


- How is this CF calculated to train and validate the CM2?

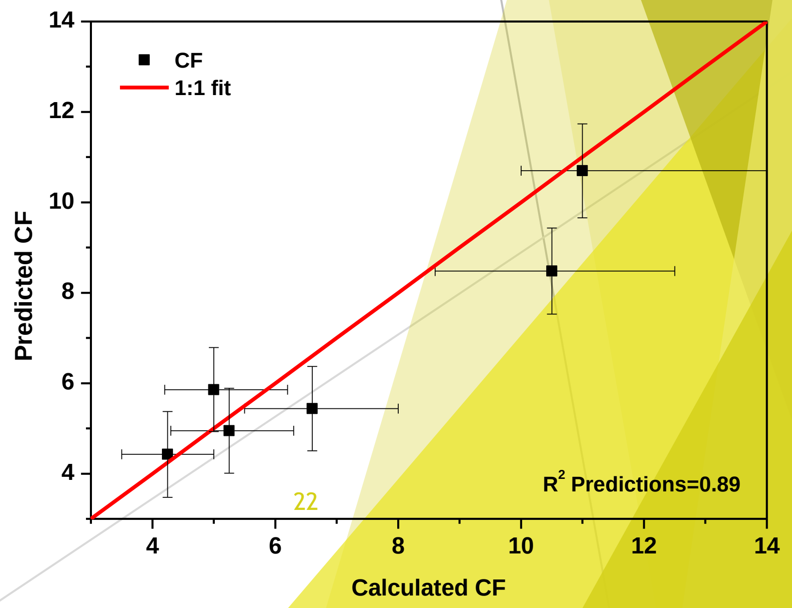
Results: CM-CF

- Films were provided by partners: OEAW, IVC and DFF.
- A chemometric model was developed to how much faster (kinetics is multiplied by a correction factor (CF)) each historical film is degrading than the pure polymer.
- Model input: film type (Black/white, sound, color) and fabrication date, model output is the CF.
- To develop/train the model CF is quantified by accelerating the mechanistic model to fit two point the initial DS and the actual DS of each film.
- The model provides predictions with 89%.

Training dataset



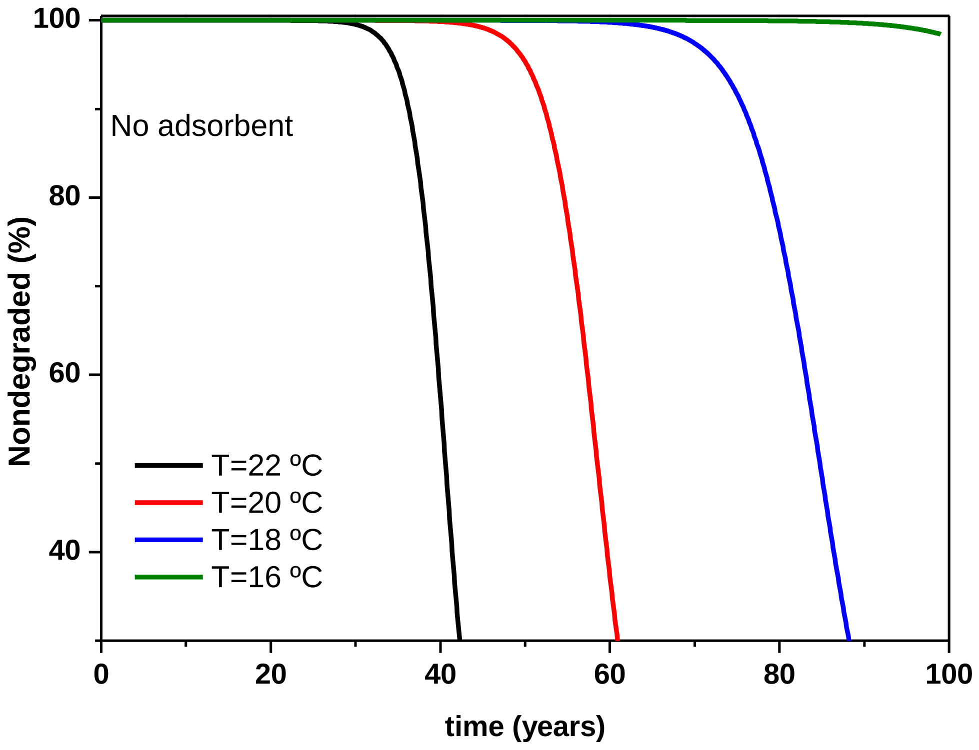
Validation dataset

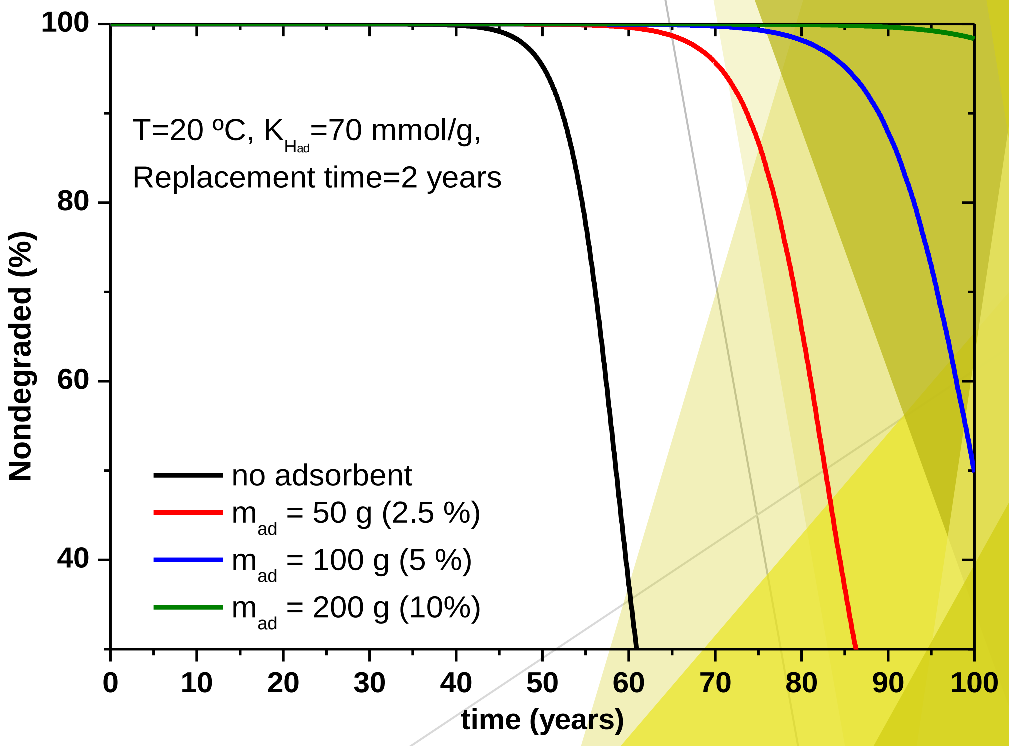


Effect of adsorbent

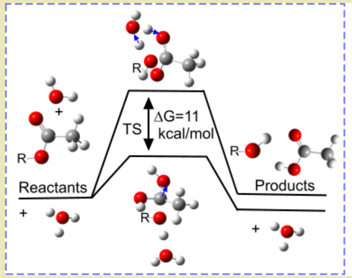
- Using the mass balance equation with the adsorbent and the film in the box

$$V(C_0 - C_{out}) = m(Q_{in} - Q_0) + m_{ad}(Q_{in_{ad}} - Q_{0_{ad}}).$$

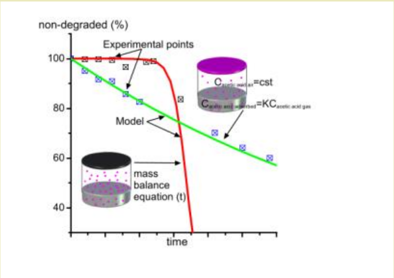




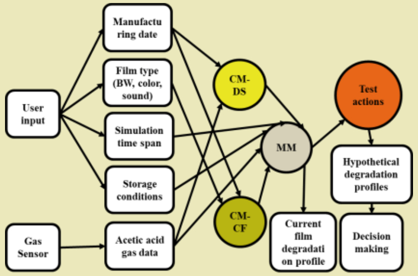
Conclusions



DFT calculation of Gibbs free energy of activation is an important step in the first-principles model. The first-principles model It gives deep understanding of the degradation kinetics and clear idea about the role of acetic acid as a reactant and reaction catalyser.



Mass-balance equation was used to account for the acetic acid volatility. Also it was used to add the functionality of accounting for the presence of an adsorbent. The transition state theory was used to determine the long-life kinetics. The model gives quantitate information about the quantitates of AA released and the amount of adsorbent to use.



The mechanistic model is adapted to the case of historical films via two data-based models. The developed solution enables the user of simulating several storage scenarios and thus choose a personalized preservation plan.

NEMOSINE Consortium

Questions?

Thanks for your attention

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For more info →

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Twitter: https://twitter.com/nemosineproject

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