ABSORTION OF BIOLUBRICANT OXIDATION PRODUCTS IN NANOPOROUS MATERIAL

B. Coto, A. Marcaide, A. Aranzabe, C. Zubizarreta

Fundación Tekniker, Avda. Otaola 20, Eibar, Spain
bcoto@tekniker.es
www.tekniker.es

Outline

- *Frame of the work*
- *Methodology*
- *Absorption simulations of oxidation products*
- *Molecular Dynamics simulations*
- *Future Work*

Frame of the work

6th Framework Programe. I. P.
Soilcy (*515848*)

To promote the use crude glycerine obtained from used vegetable oil FAME process (biodiesel production) transforming it from a no-value by-product to an added-value renewable raw material.

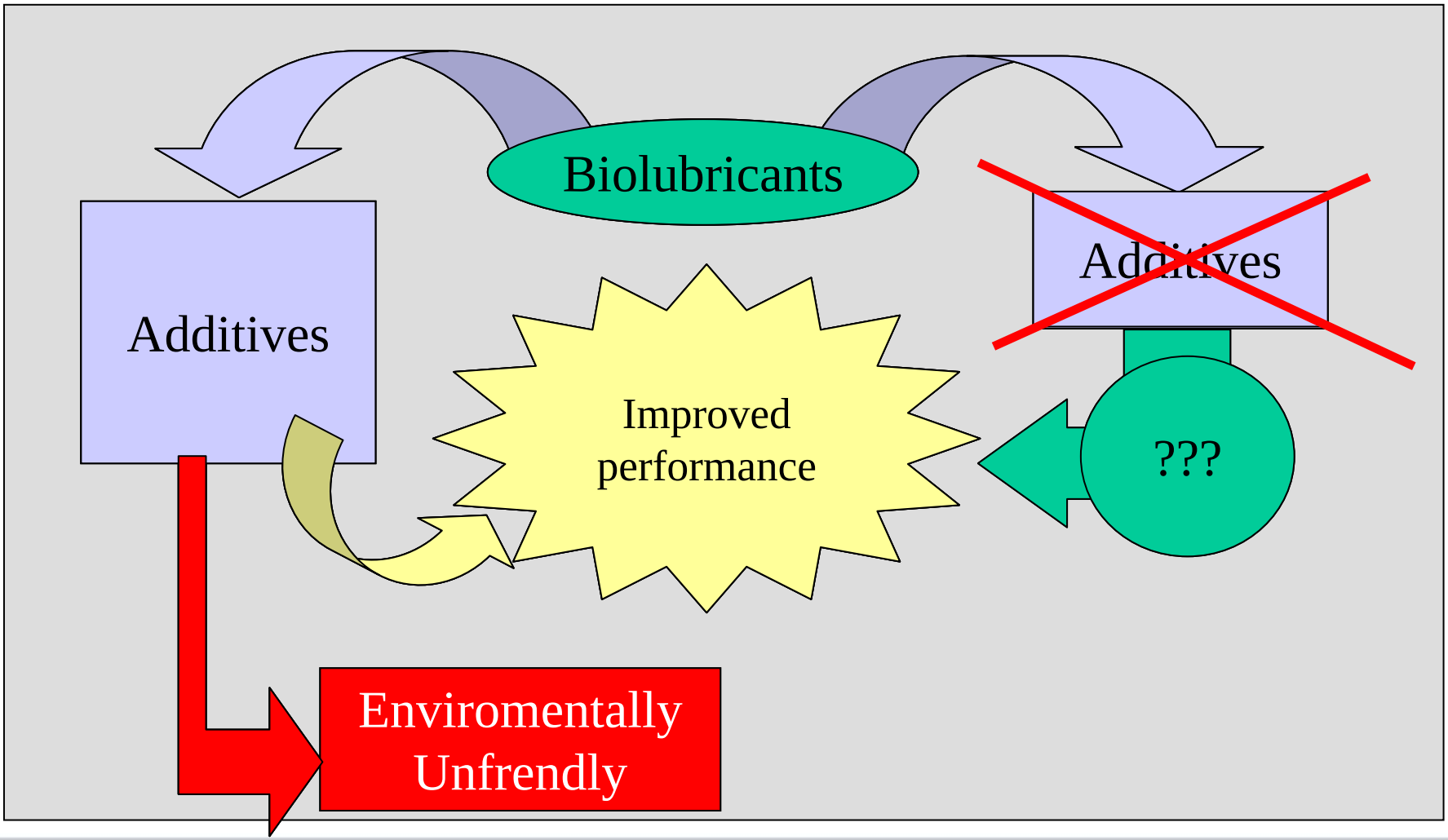
The aim of the project is the optimisation of the new sustainable life cycle of an environmentally friendly and safe compressor oil

To obtain polyglycerol ester derivates from purified crude glycerine for compressor applications

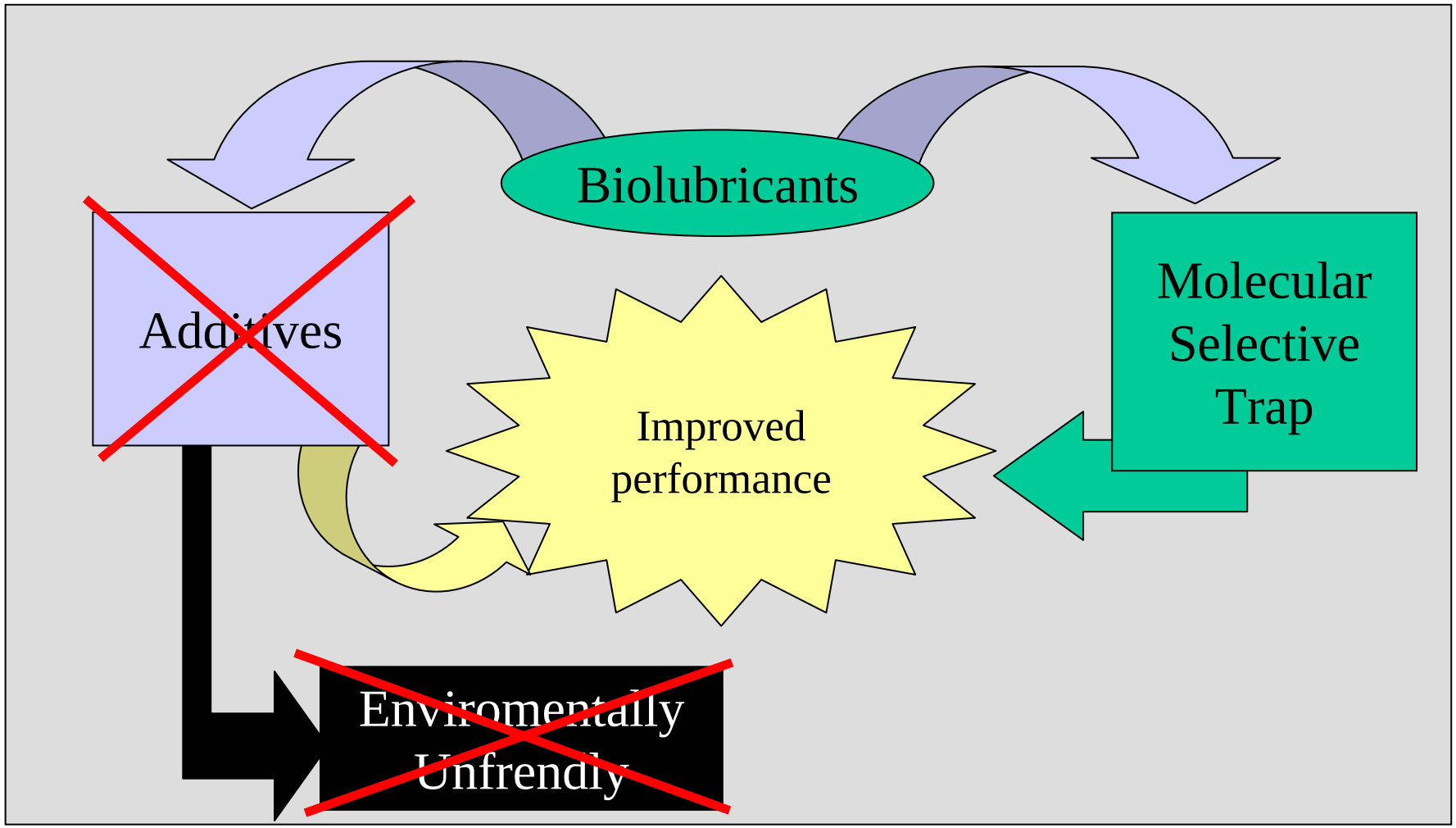
To replace harmful antiox… compressor oil additives by means the design of a new compressor device based on a molecular sieve for a selective trapping of oxidation products

To develop an eco-indicator based on biodegradability and toxicity measurements to fill the gap for a reliable environmental impact evaluation of lubricants

Biolubricants



Molecular Sieve

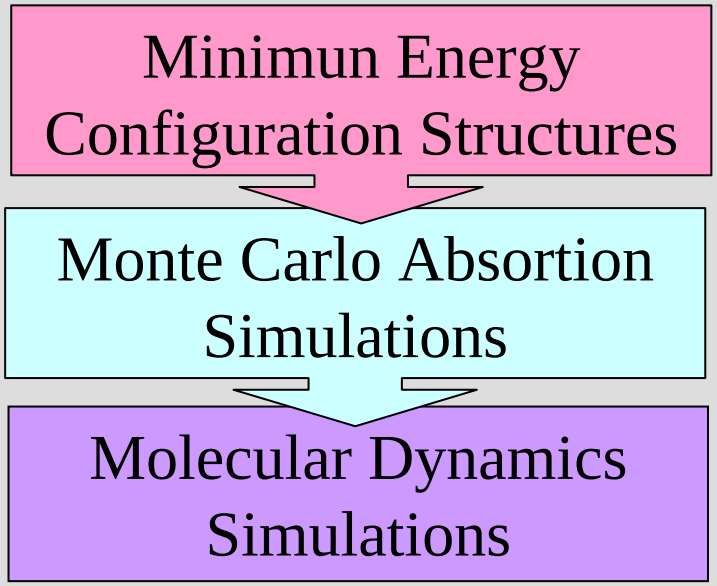


Compressor oil application

- *Modelling can help to select proper materials*
- *Sorptive behaviour of the oxidation products from a a trimethylolpropane (TMP) ester base oil inside a nanoporous material*
- *Compressor working conditions of pressure and temperature*

Computational methods

- *Atomistic modelling aproach*
- *Forcefield based calcultions*
  - *Each atom has a potential energy associated to surrounding atoms*
  - *Forcefields contains parameters for the energy expresions*



Materials Studio and Compass Forcefield

- Materials Studio 4.2
- COMPASS Forcefield
  - Widely Validated
  - 13 Terms
  - Bond and non bonding interactions

$$E_{pot} = \sum_b \left[K_2 (b - b_0)^2 + K_3 (b - b_0)^3 + K_4 (b - b_0)^4\right] \quad (1)$$

$$+ \sum_\theta H_2 (\theta - \theta_0)^2 + H_3 (\theta - \theta_0)^3 + H_4 (\theta - \theta_0)^4 \quad (2)$$

$$+ \sum_\phi \left[V_1 \left[1 - \cos\left(\phi - \phi_1^0\right)\right] + V_2 \left[1 - \cos\left(2\phi - \phi_2^0\right)\right] + V_3 \left[1 - \cos\left(3\phi - \right.\right.\right. \quad (3)$$

$$+ \sum_\chi K_\chi \chi^2 + \sum_b \sum_{b'} F_{bb'} (b - b_0) (b' - b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0) (\theta' - \quad (4)\ (5)\ (6)$$

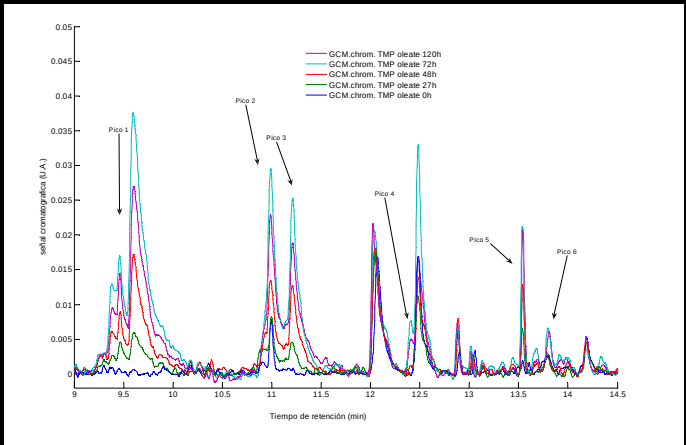
$$+ \sum_b \sum_\theta F_{b\theta} (b - b_0) (\theta - \theta_0) + \sum_b \sum_\phi (b - b_0) \left[V_1 \cos\phi + V_2 \cos 2\phi + \right. \quad (7)\ (8)$$

$$+ \sum_{b'} \sum_\phi (b' - b'_0) \left[V_1 \cos\phi + V_2 \cos 2\phi + V_3 \cos 3\phi\right] \quad (9)$$

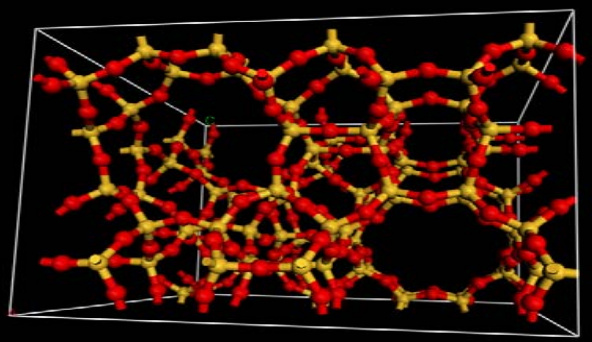
$$+ \sum_\theta \sum_\phi (\theta - \theta_0) \left[V_1 \cos\phi + V_2 \cos 2\phi + V_3 \cos 3\phi\right] \quad (10)$$

$$+ \sum_\phi \sum_\theta \sum_{\theta'} K_{\phi\theta\theta'} \cos\phi (\theta - \theta_0) (\theta' - \theta'_0) + \sum_{i>j} \frac{q_i q_j}{\varepsilon r_{ij}} + \sum_{i>j} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6}\right] \quad (11)\ (12)\ (13)$$

Molecules and Sorbent

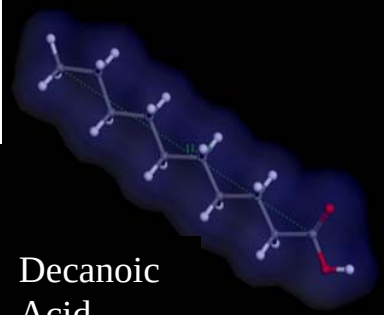


Cromatographic Analysis

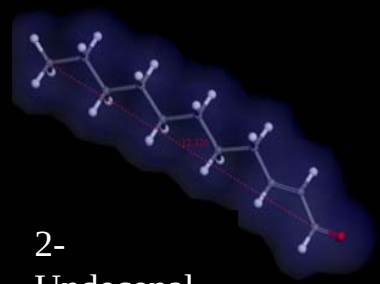


Nanoporous Material

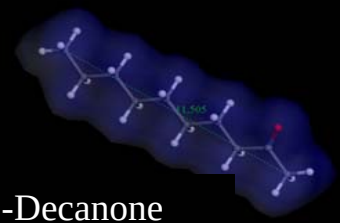
Oxidation Products Molecules



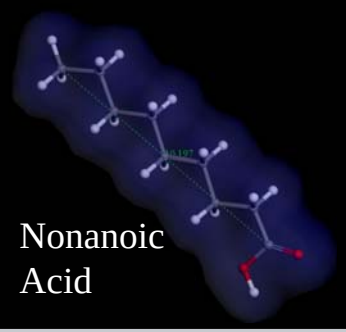
Decanoic Acid



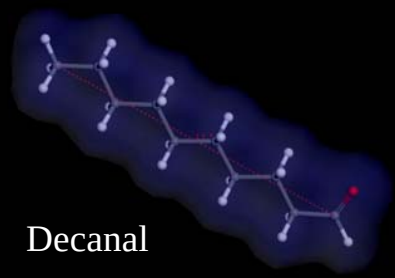
2-Undecenal



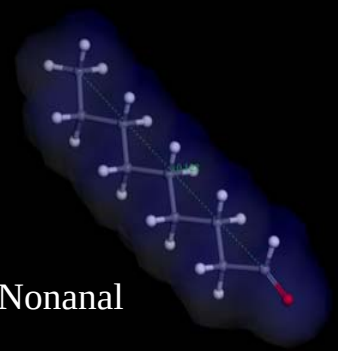
2-Decanone



Nonanoic Acid



Decanal



Nonanal

Energy minimization

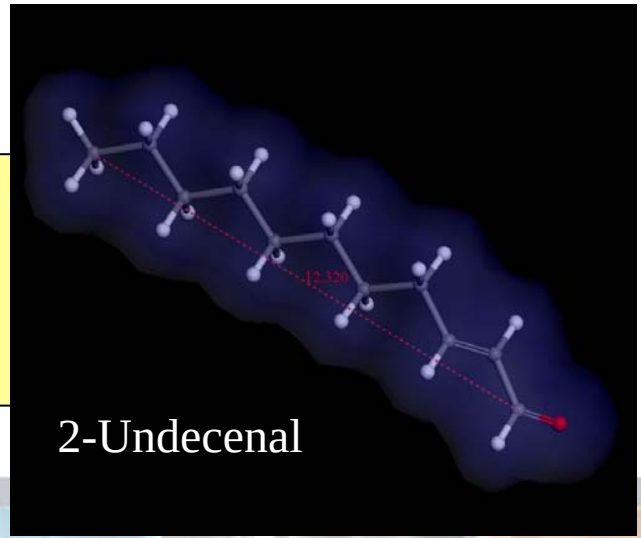
Energy Minimization

·Steepest Descents
·Conjugated Gradient

Geometry optimization

Molecule	Length (Å)	Occupied Volume (Å^3)	Surface Area (Å^2)
Nonanal	10,122	175,660	208,330
Nonanoic Acid	10,197	183,470	215,570
2-Decanone	11,505	193,500	226,800
Decanal	11,546	194,090	227,430
2-Undecenal	12,320	205,120	241,840
Decanoic Acid	11,510	209,810	242,810

Connolly Surfaces: Occupied Volume and Surface Area



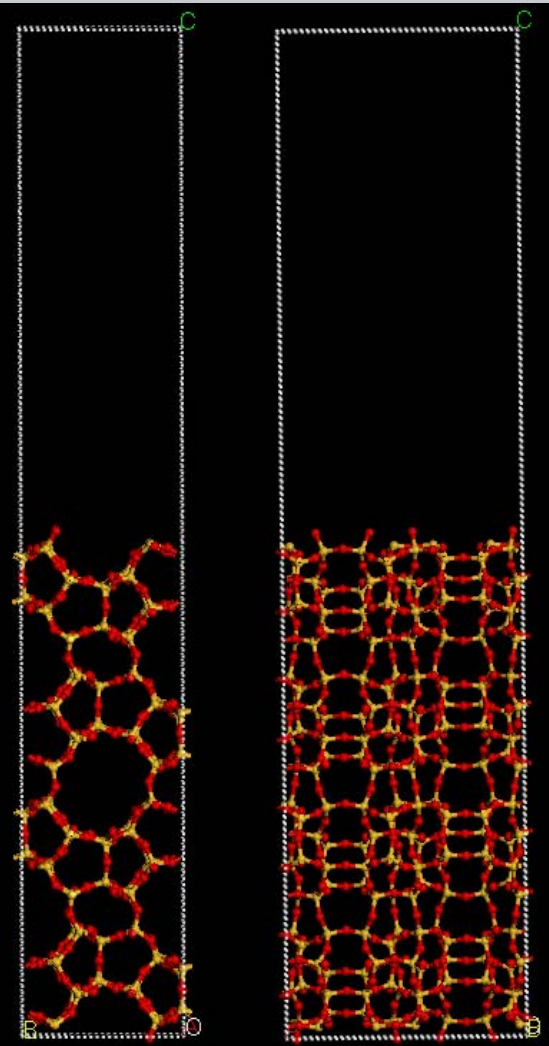
2-Undecenal

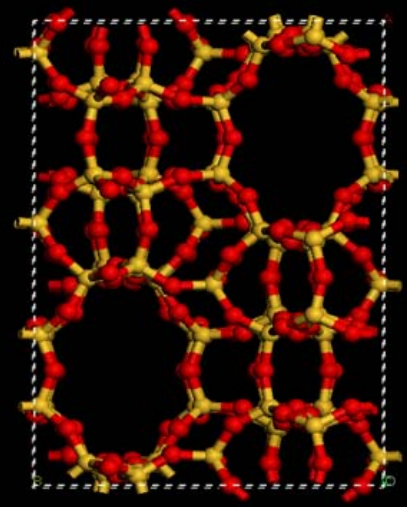
Computational Unit Cell

- (100) Surface
- Vacuum Slab: 2D Boundary Condition
- Computational Cell:

a = 2 nm; b = 1.33 nm; c = 8 nm

- Geometry optimization
- Connolly Surfaces
  - Occupied Volume = 7.23 nm^3
  - Surface area = 2.89 nm^3
  - Free Volume = 14.05 nm^3





Free Pore Volume:

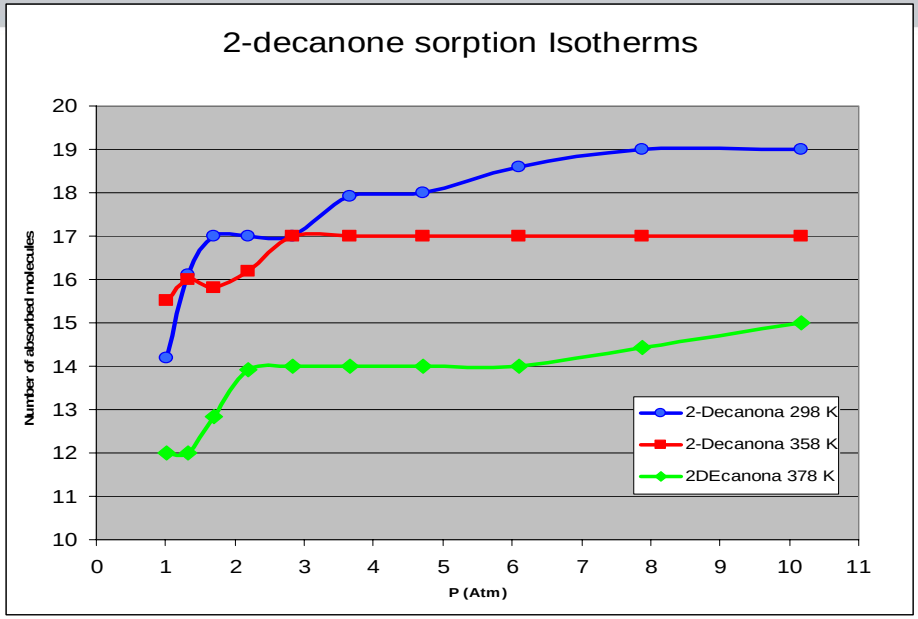
3.4 nm^3

Monte Carlo Methods

- *Grand Canonical ensamble*
  - *System can exchange energy and particles with a surrounding reservoir*
  - *Resorvoir is described by temperature and fugacities so it is not necessary to simulate it in a explicit way*
- *Monte Carlo Biased Method*
  - *Fixed pressure simulations*
  - *Trial configurations are generated with a probability*
  - *Acceptance probability depends on the energy of the system congiguration generated*
  - *Torsional degrees of freedom are taken into account*

Absorption Isotherms

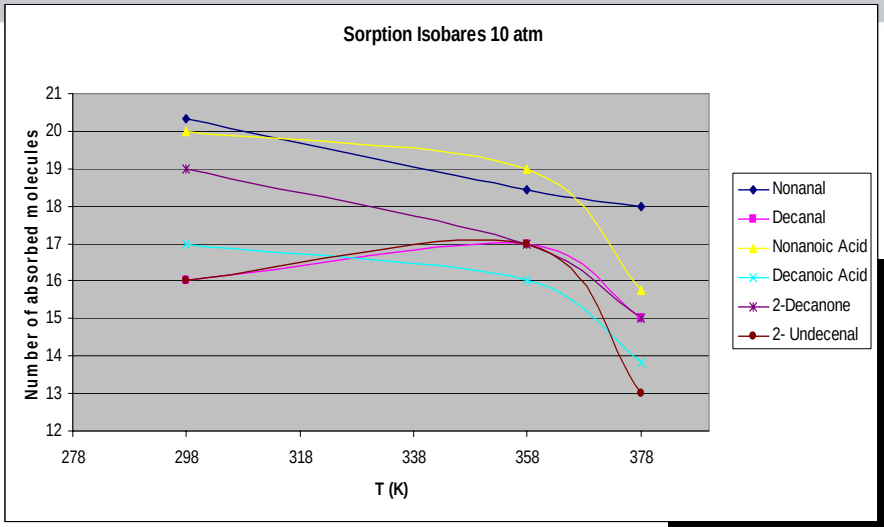
- Sorption was studied for T and P from room conditions up to the working conditions of a compressor for each molecule
- Sorption Isotherms were calculated

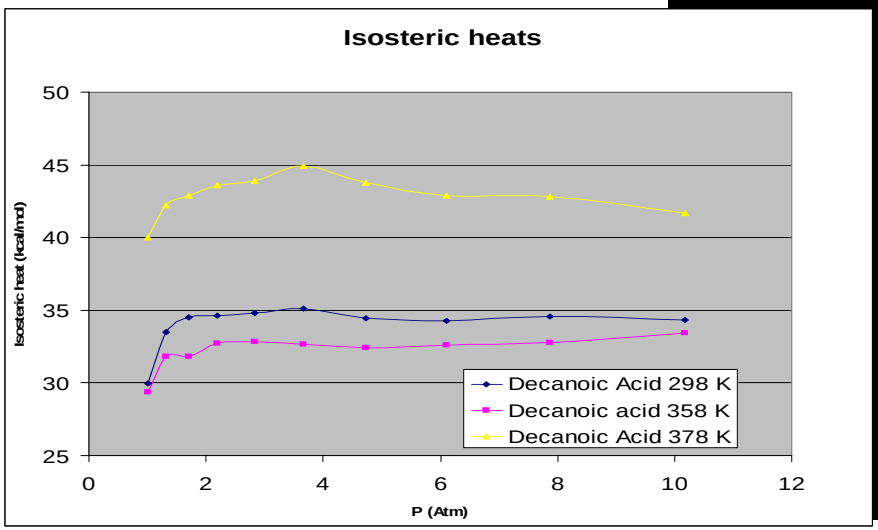


298 K
1 Atm

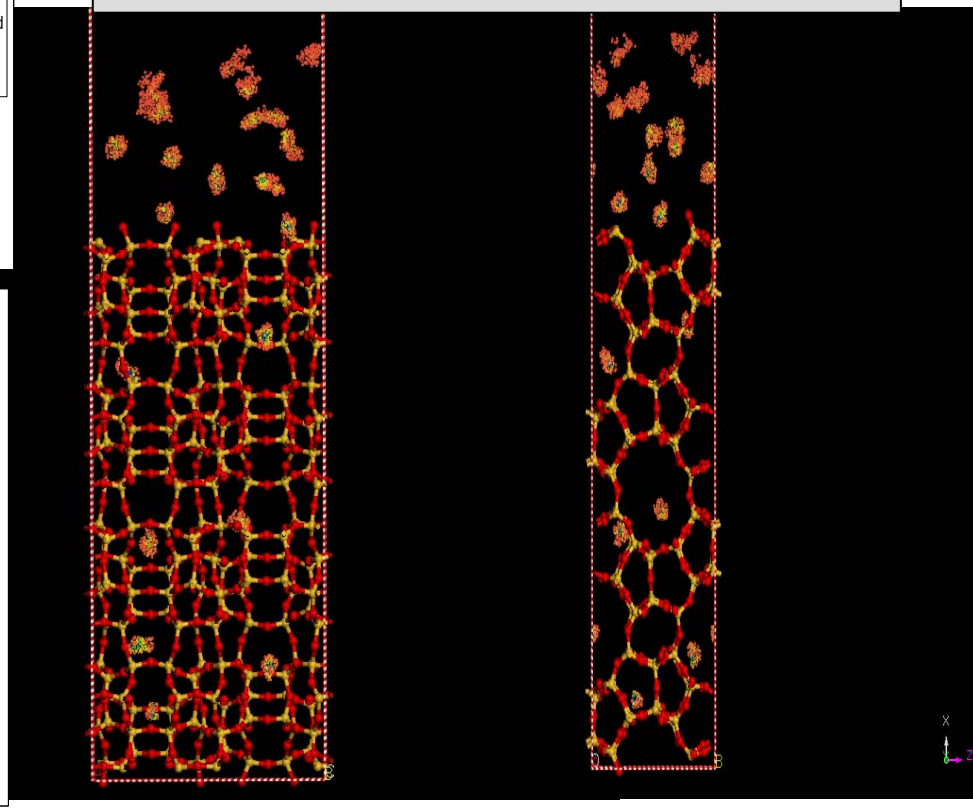
Molecule	Maximun Load	Average Load	Average Energy (kcal/mol)	Maximun Density (molecules/nm^3)
2-Undecenal	14,000	13,048	-973,825	0,889
2-Decanona	16,000	14,527	-591,868	0,990
Decanoic Acid	15,000	14,655	-988,189	0,998
Nonanoic Acid	17,000	15,641	-1005,992	1,066
Decanal	17,000	15,744	-545,818	1,073
Nonanal	18,000	17,215	-525,937	1,173

Sorption isobares, Isosteric heats and preferred absorption sites



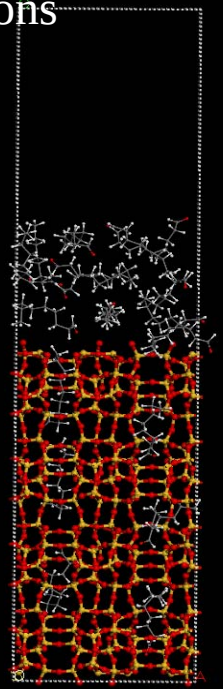


Density of absorption profiles of nonanal at 358 K 10 atm

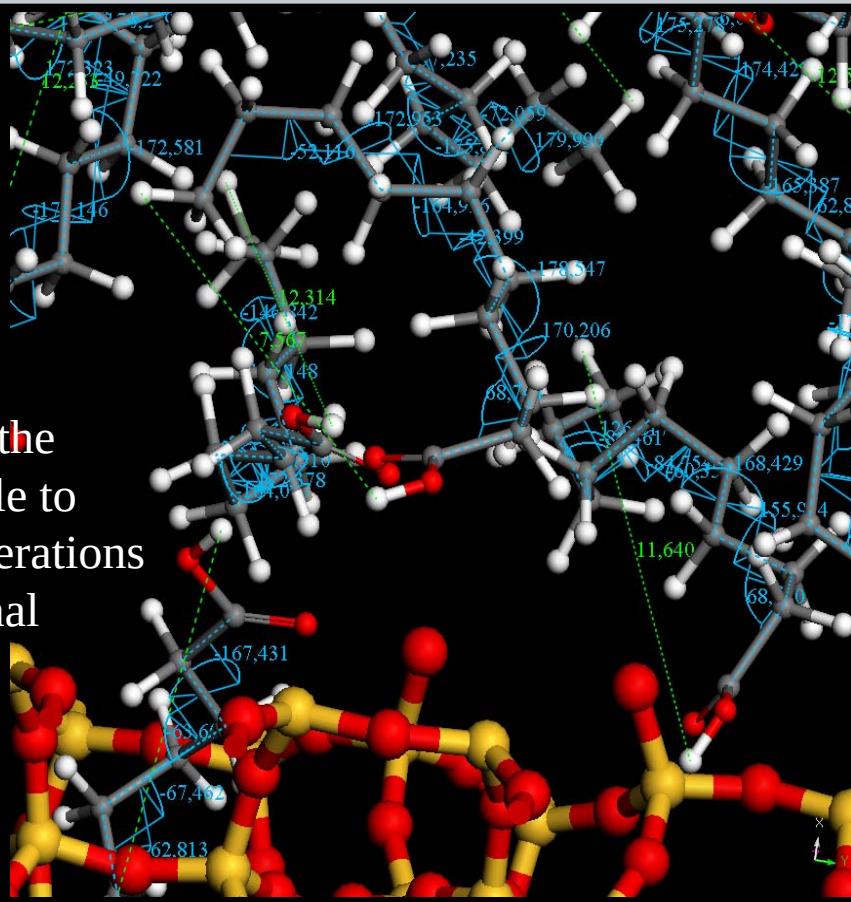


Fixed Pressure Calculations

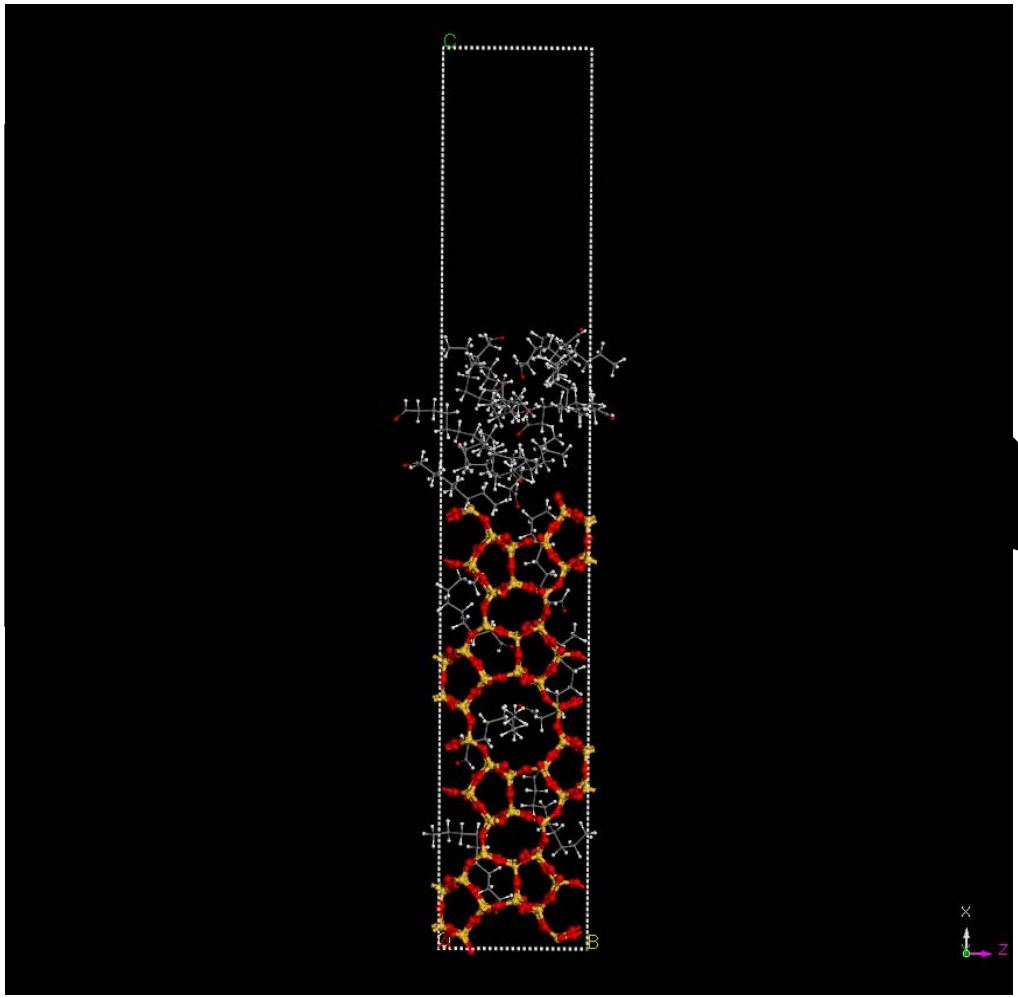
- Fixed Pressure calculations allow to obtain the minimun energy configurations for given conditions



- Detailed view of the system is available to study specific interations and conformational analysis



Molecular Dynamics Simulations



Minimun Energy Configuration Structures

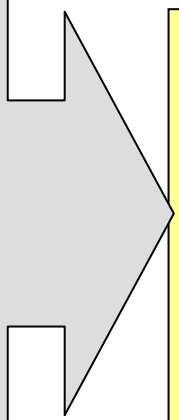
Monte Carlo Absortion Simulations

Minimun Energy Configuration Structures

Molecular Dynamics Simulations

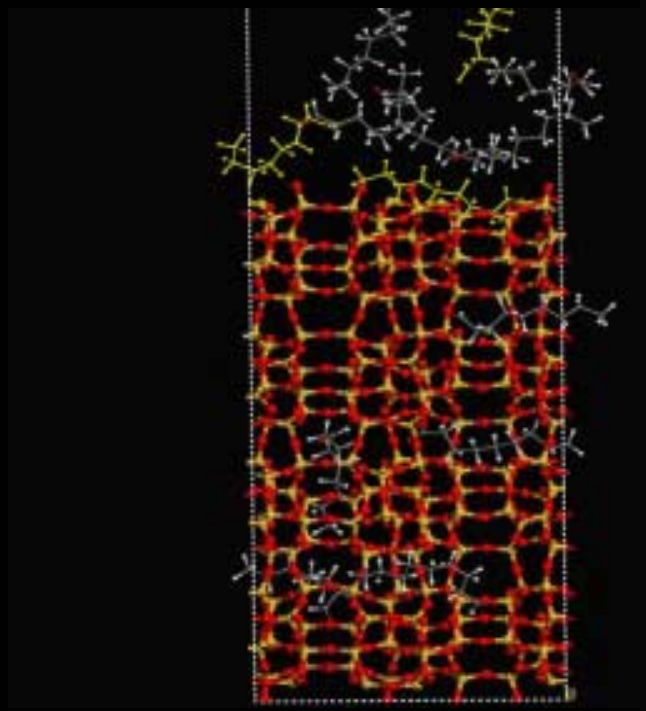
Molecular Dynamics

- *Newton's equation is solved for a given potential (COMPASS)*
- *Verlet integration*
  - *1.5 ns simulations*
  - *Step 2 fs.*
- *NPT Ensemble*
  - *Berendsen Thermostat*
  - *Berendsen Barostat*

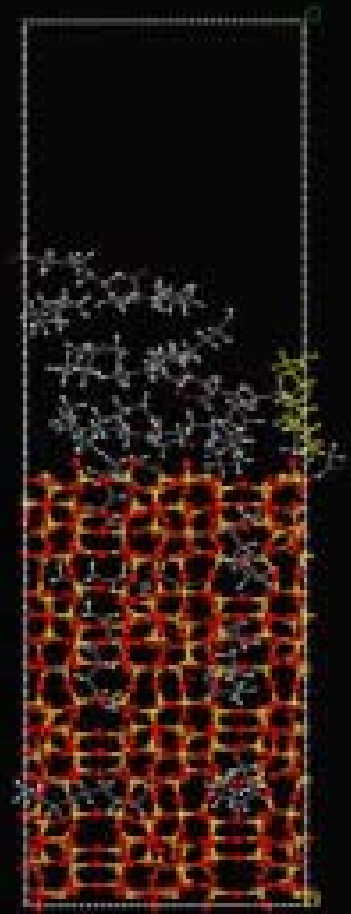


- Atomic Trajectories
- Dinamical Behaviour

Molecular Dynamics

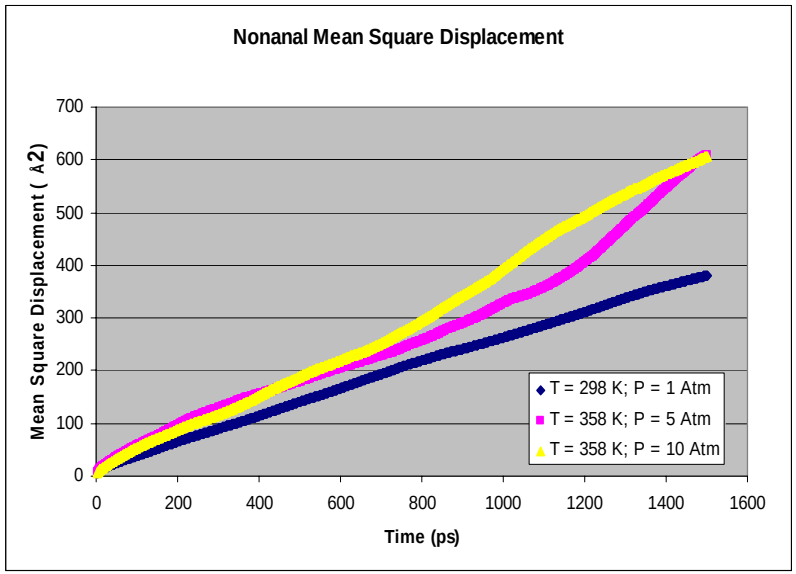


Nonanal 298 K 1 atm

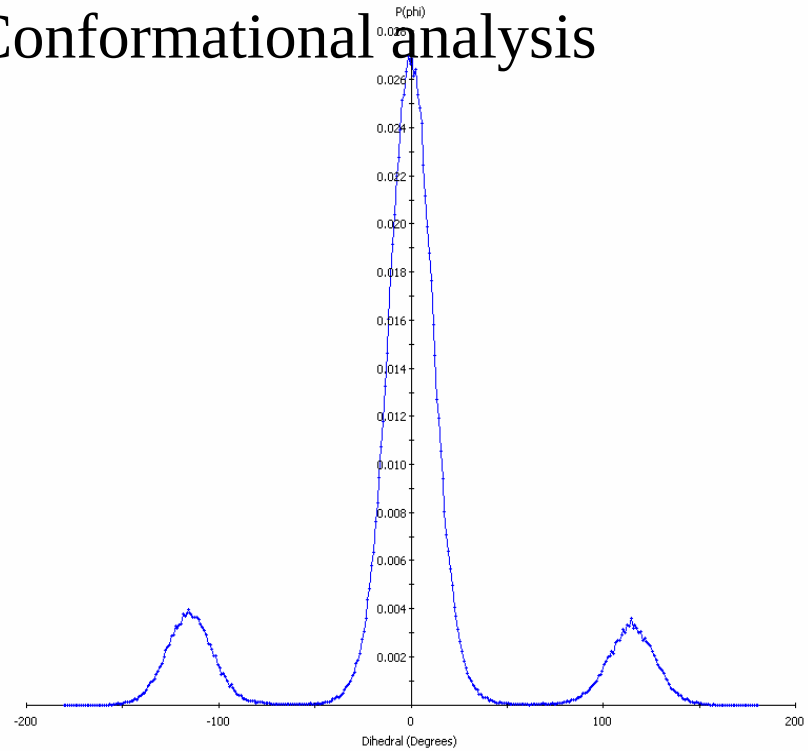


Nonanal 358 K 10 atm

Trajectories Analysis



Conformational analysis



Diffusion Coefficient

Nonanal	T=298 K; P=1atm	T=358 K; P=5atm	T=358K; P=10atm
Diffusivity(nm2 s-1)	4,12·10-4	5,84·10-4	6,79·10-4

Work in Progress & Future Work

- *Molecular Dynamics Simulations*
- *Future Work*
  - *Absortion simulations with mixtures of molecules*
  - *Different materials*
  - *Compare with experiments*
  - *Functionalization and/or doping of the nanopororus materials*

Summary

- *Molecular Modelling simulations have been carried out to study the absortion of oxidation producs of an TMP ester oil in a porous nanomaterial for compressor applications*
- *Geometry optimization was done to obtain lengths and volumes for the modelled system*
- *MC simulations were performed to study the sorption behaviour of the oxidation products*
- *MD calculations were performed in order to study the dynamic behaviour of the system*
- *Next steps will involve other sorbent nanomaterials and comparison with experimental results*

Acknowledgements

- U.E. - 6th FP – IP Soilcy (Contract 515848)
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THANK YOU FOR YOUR ATTENTION