FP7 project - SAM.SSA

Sugar Alcohol based Materials for Seasonal Storage Applications

Workshop and Onsite Demonstration– CiCenergigune

Miñano, Alava, Spain

Sugar alcohols properties and performances

Presented by Alexandre GODIN

Participants:

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- Screening and selection of sugar alcohols (SA) and sugar alcohol blends (SA-blend)
- Key thermodynamics and physical properties of selected SA and SA-blends
- Undercooling, probability of spontaneous nucleation and crystal growth rates

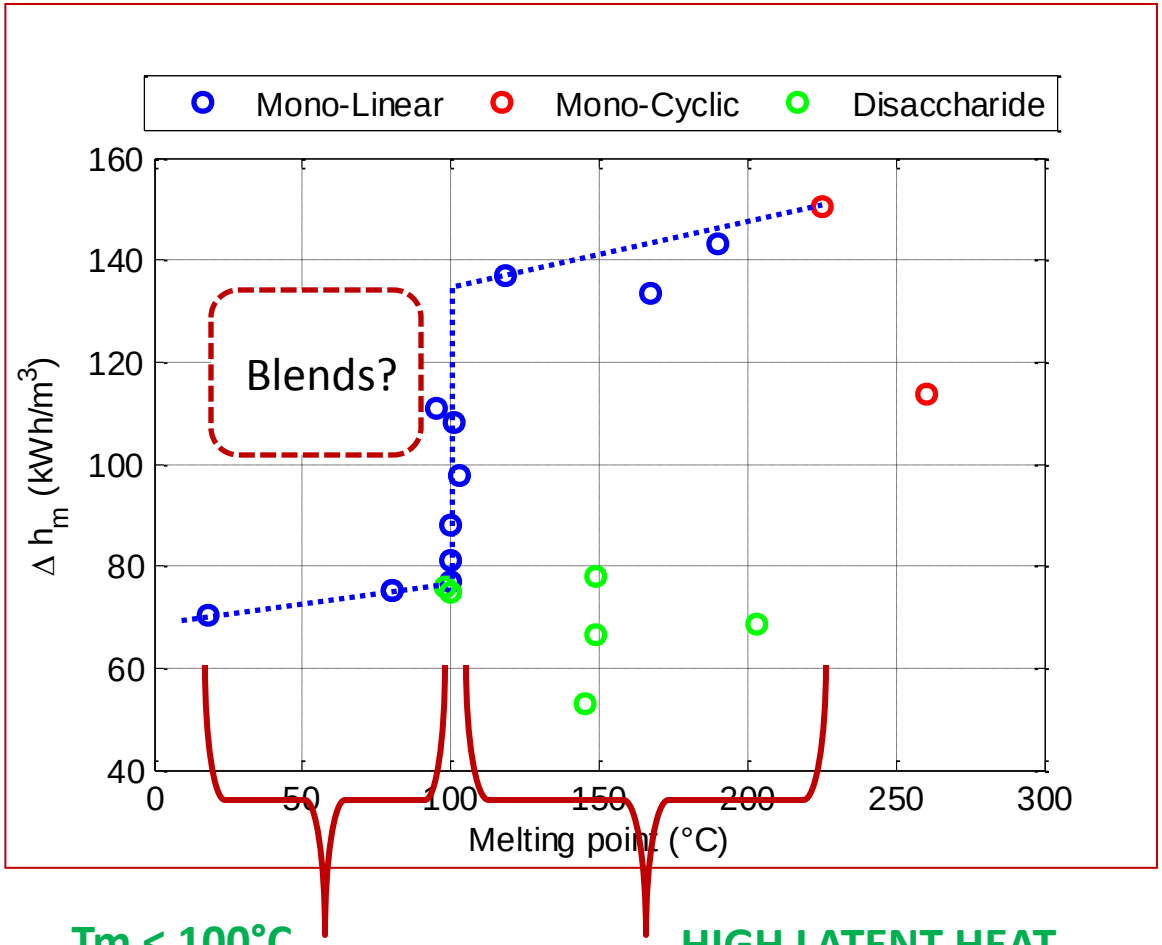
Screening and selection

Starting point
DATA BASE
30 polyols

Mono-, Disaccharide
Linear, ramified, cyclic, mix
C-atoms: 3 – 12

Including most widely used polyols

UPPER LIMIT
Defined by monosaccharide polyols with linear chain



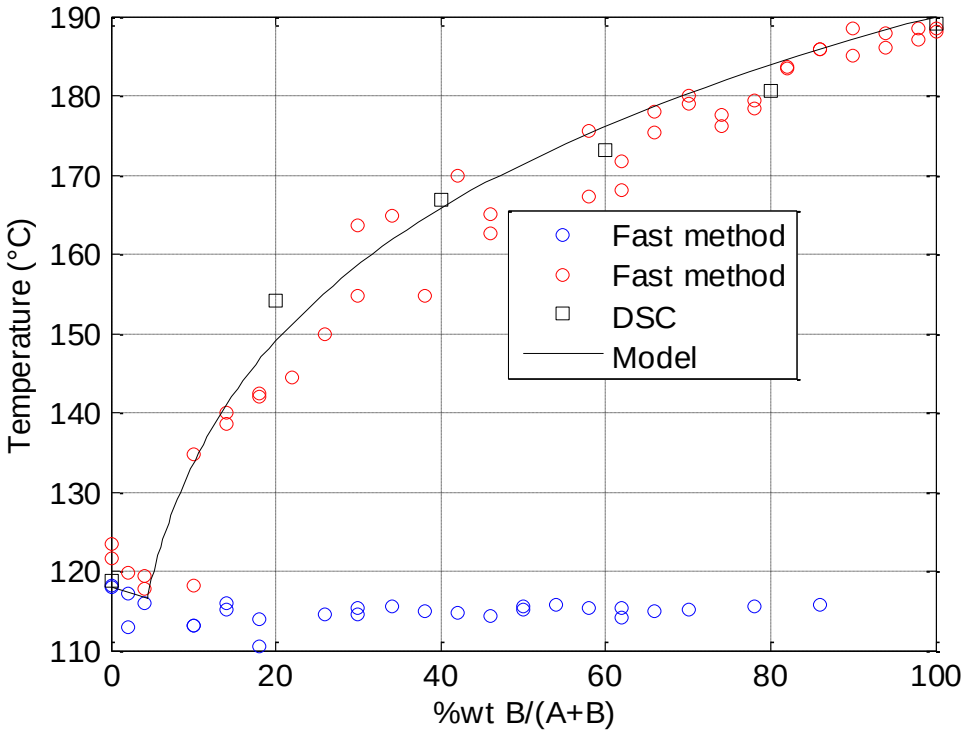
Tm < 100°C
But LOW LATENT HEAT

HIGH LATENT HEAT
But Tm > 100°C

30 SA-based binary systems have been investigated

Looking for either suitable eutectic points or suitable molecular alloys

	High temperature - High energy density components			
	Erythritol	D-Mannitol	Dulcitol	Inositol
D-Mannitol	x			
Dulcitol	x	x		
Inositol	x	x	x	
Glycerol	x	x	x	x
Xylitol	x	x	x	x
Adonitol	x	x	x	x
Sorbitol	x	x	x	x
Arabitol	x	x	x	x
Maltitol	x	x	x	x



Phase diagram determination

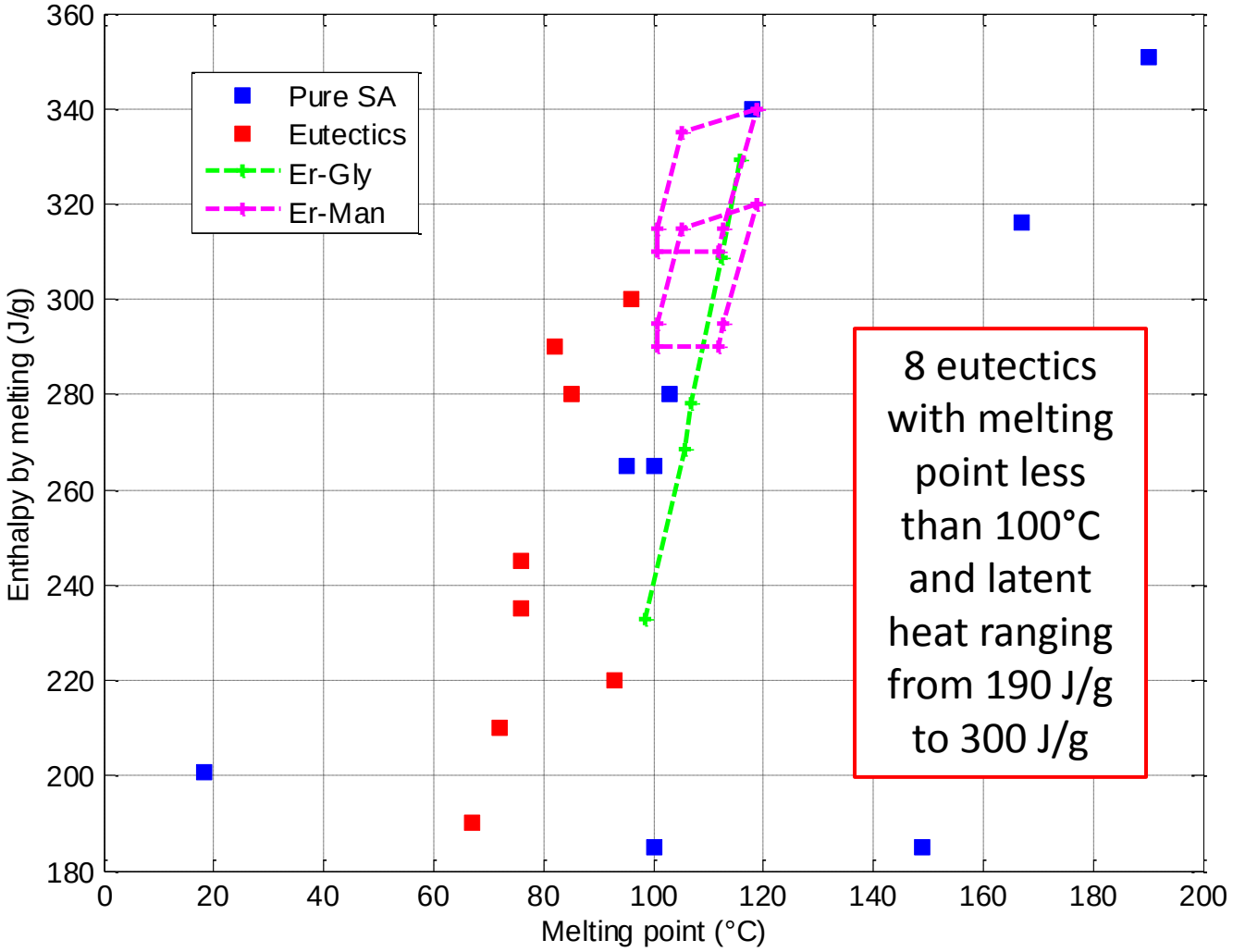
Fast estimation by infrared thermography (new method)

Differential Scanning Calorimeter (DSC)

Thermodynamic modeling

Most of the systems show eutectic points

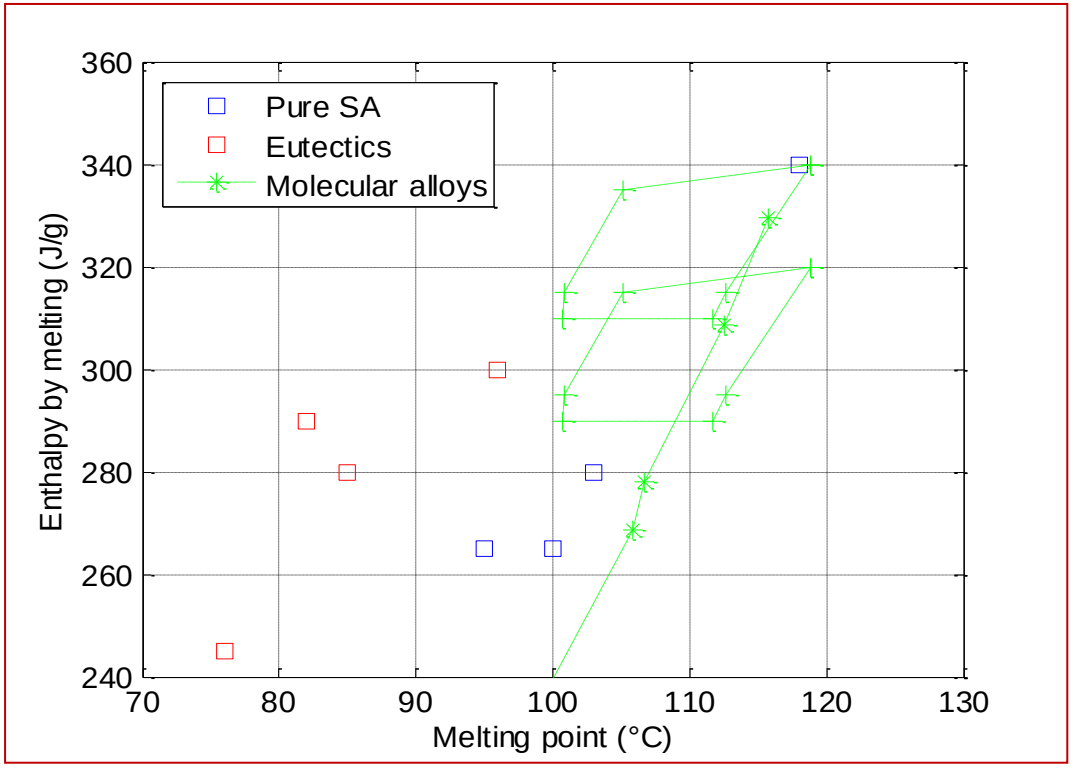
Those with melting point bellow 100°C have been considered



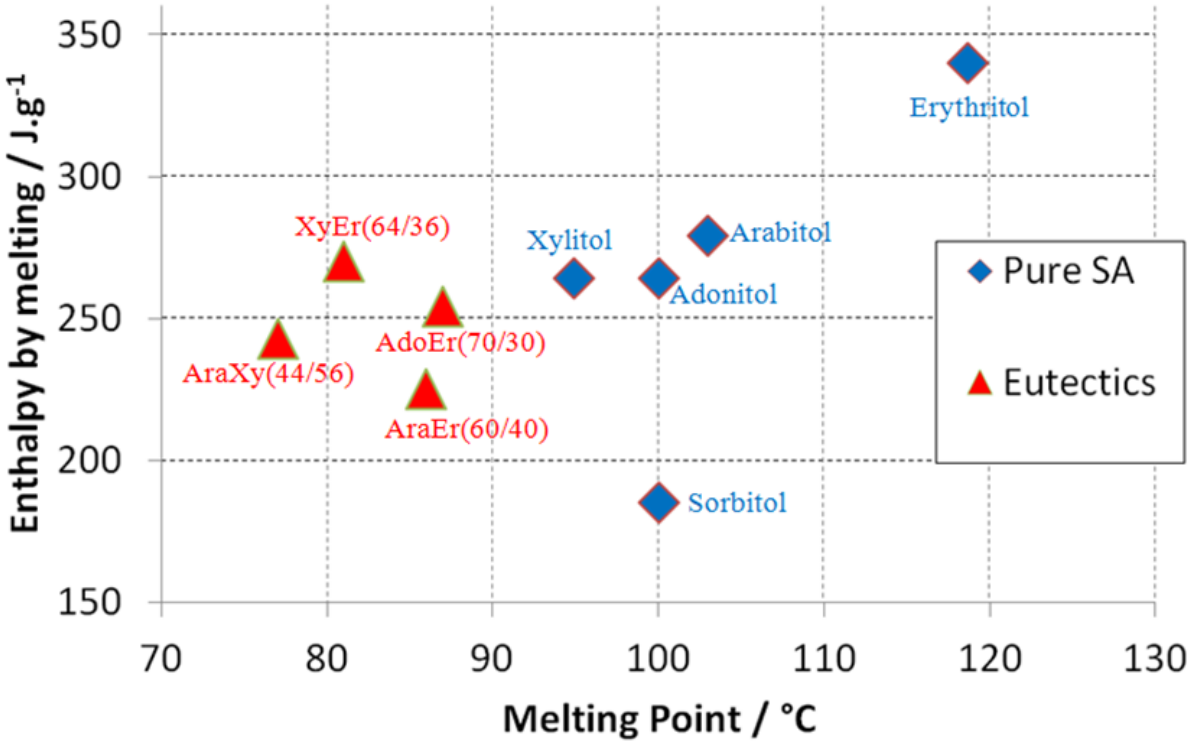
SELECTED PRODUCTS FOR FURTHER ANALYSIS

Tm : 75°C - 120°C
Potential to achieved total energy density by melting around 120 kWh/m3 – 200 kWh/m3

Erythritol
Xylitol
Adonitol
L-Arabitol
+
Four eutectics
Er/Xy (36/64)
Ar/Xy (44/56)
Ad/Er (70/30)
Ar/Er (60/40)



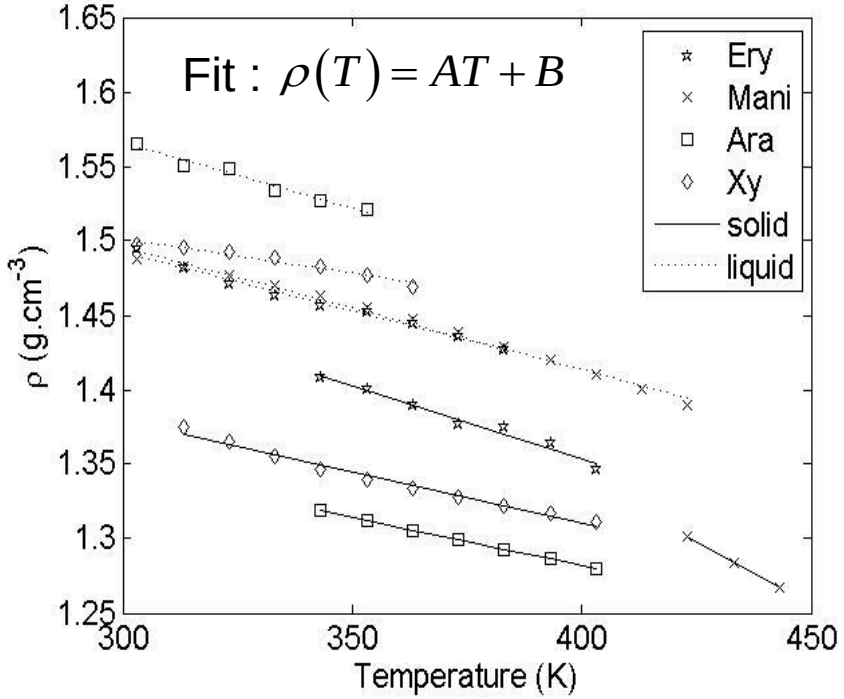
Full Characterization



Melting point & Latent heat

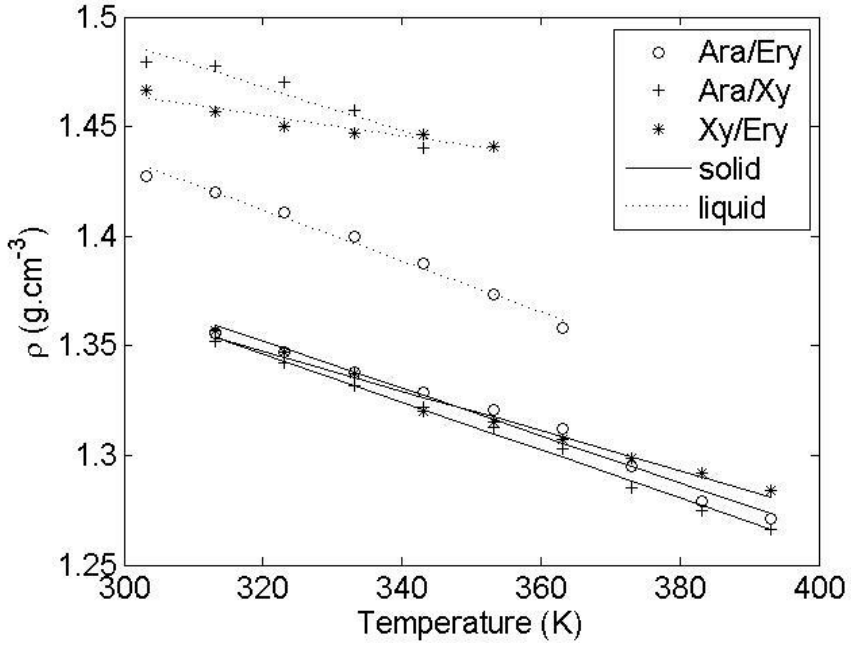
LATENT HEAT as high as that of salt hydrates
BUT with no problems of separation, segregation and corrosion

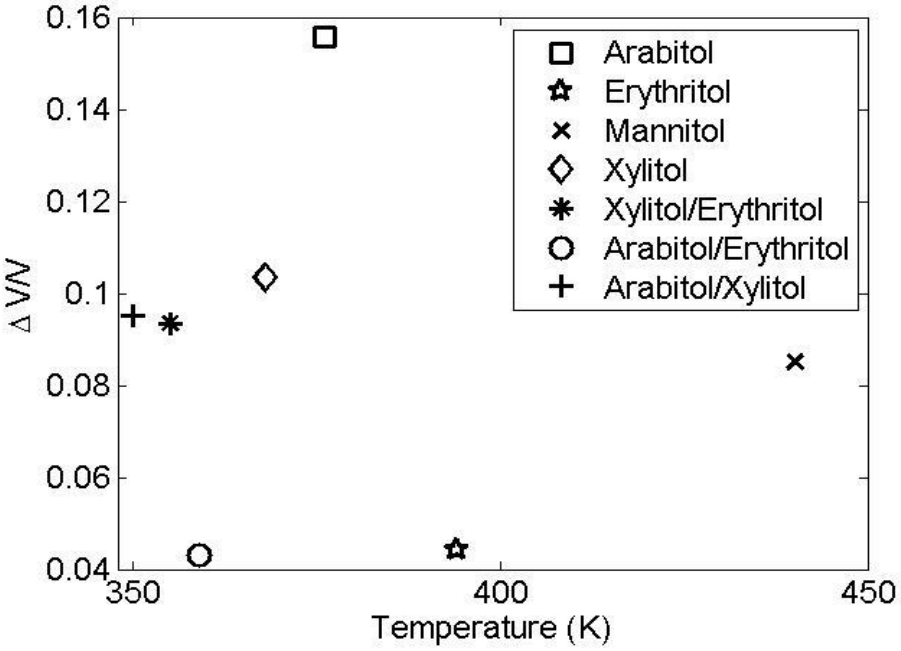
Density and volume expansion



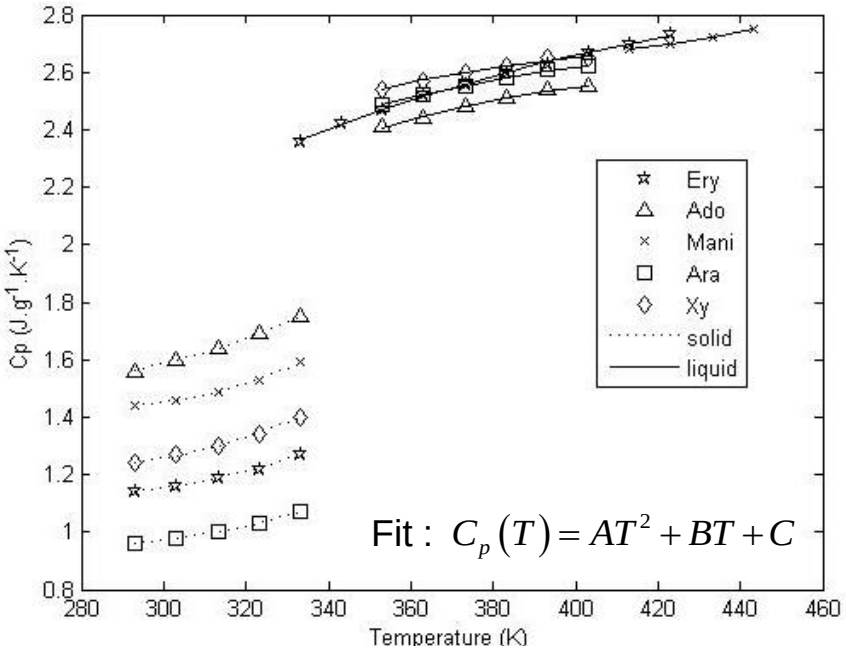
Very high density values
compared to most organic PCMs
ρ_{liq} ~ 1250-1500 kg/m3

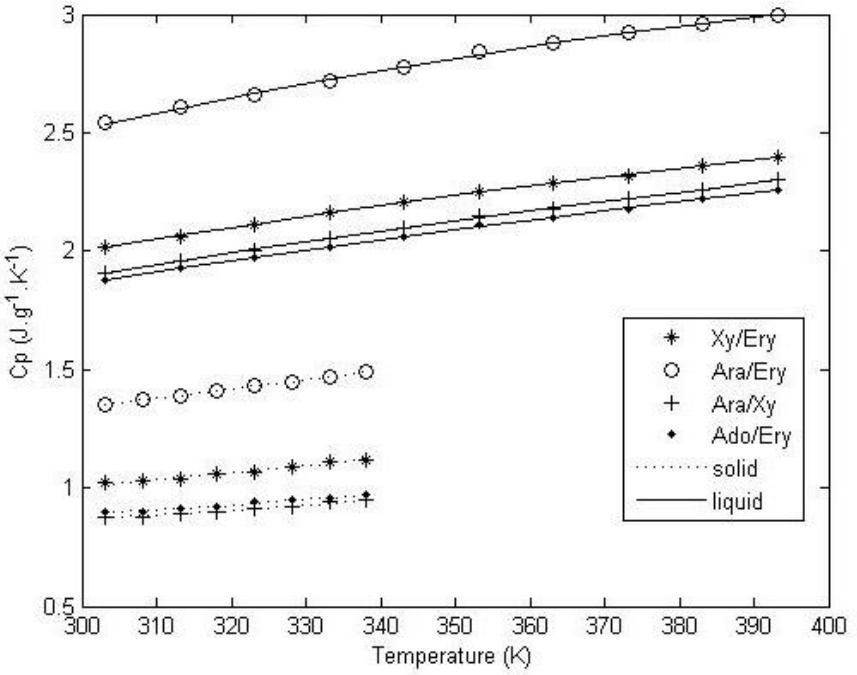
Moderate-to-Low volume
expansion for most of them
$\Delta V/V < 10\%$





Specific heat capacity





SA
Solid: 1 – 1.8 J/g/K
Liquid: 2.3 – 2.8 J/g/K

x 0.45 - 0.67

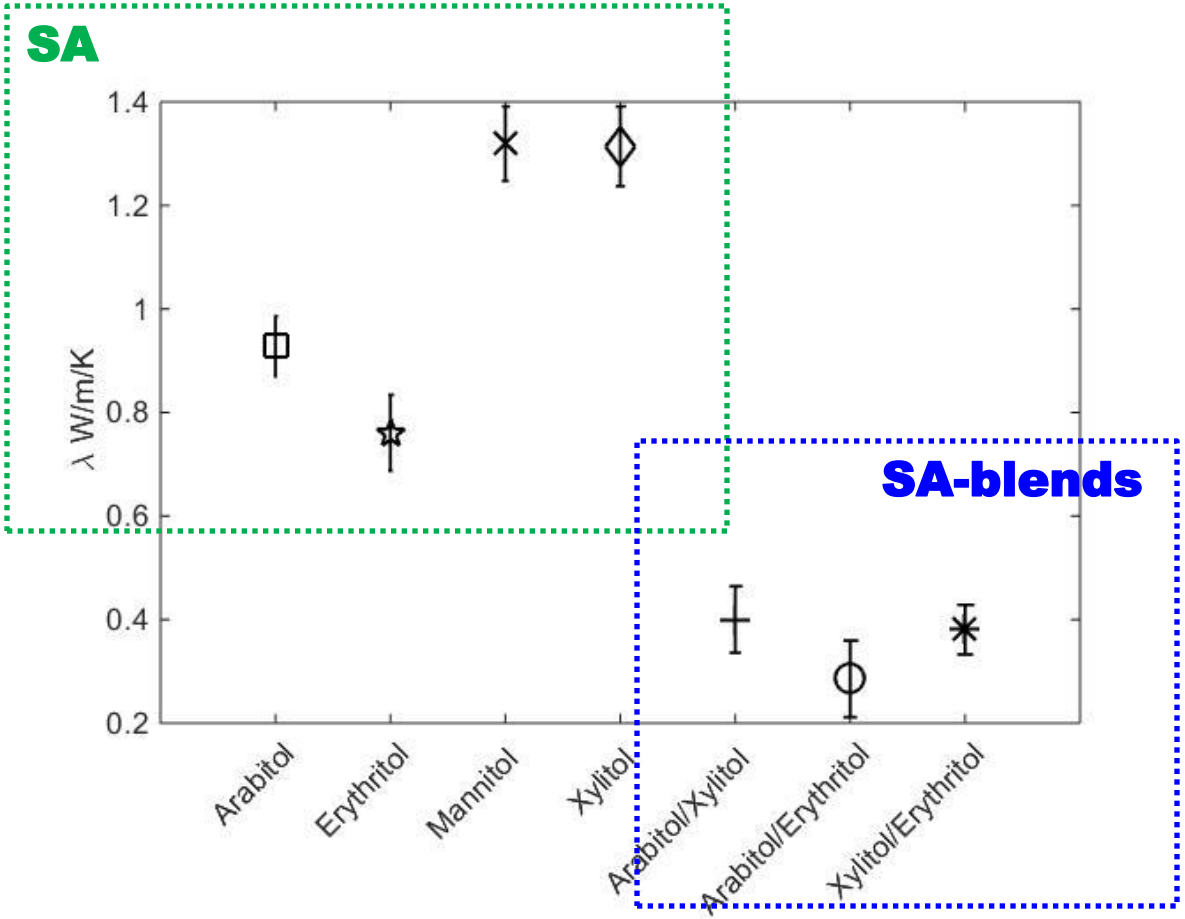
Water
4.19 J/g/K

x 0.43 - 0.71

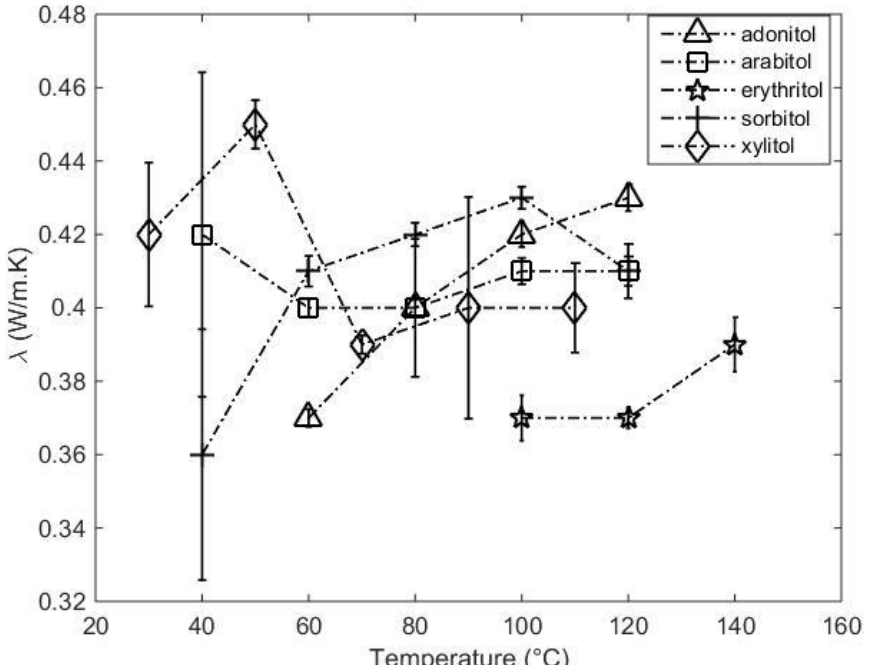
SA-blends
Solid: 0.8 – 1.5 J/g/K
Liquid: 1.8 – 3.0 J/g/K

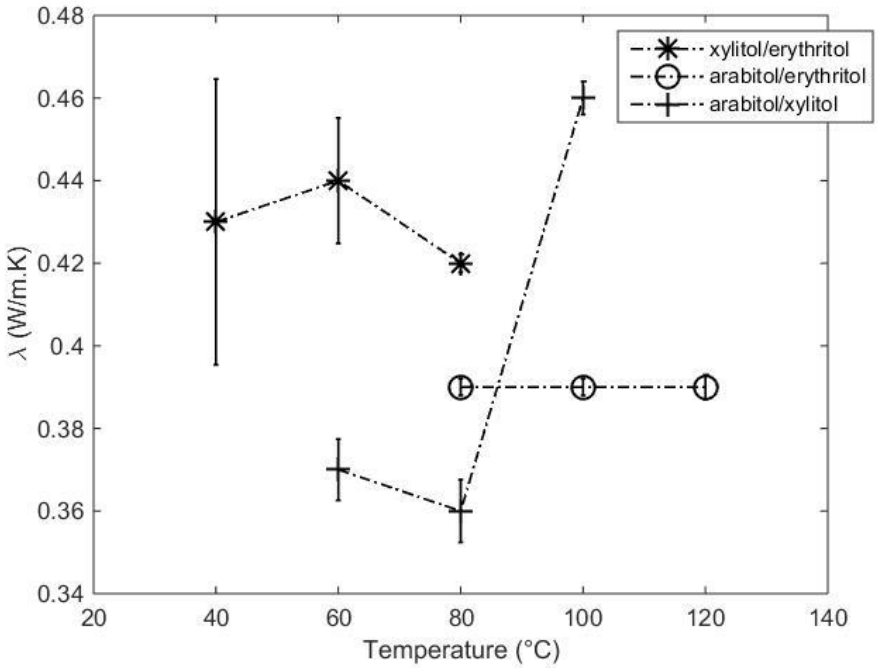
Thermal conductivity (solid phase)

In the same range than salt hydrates



Most organic PCMs
< 0.2 W/m/K





Thermal conductivity (liquid phase)

Less important than the thermal conductivity in solid

0.36 – 0.46 W/m/K

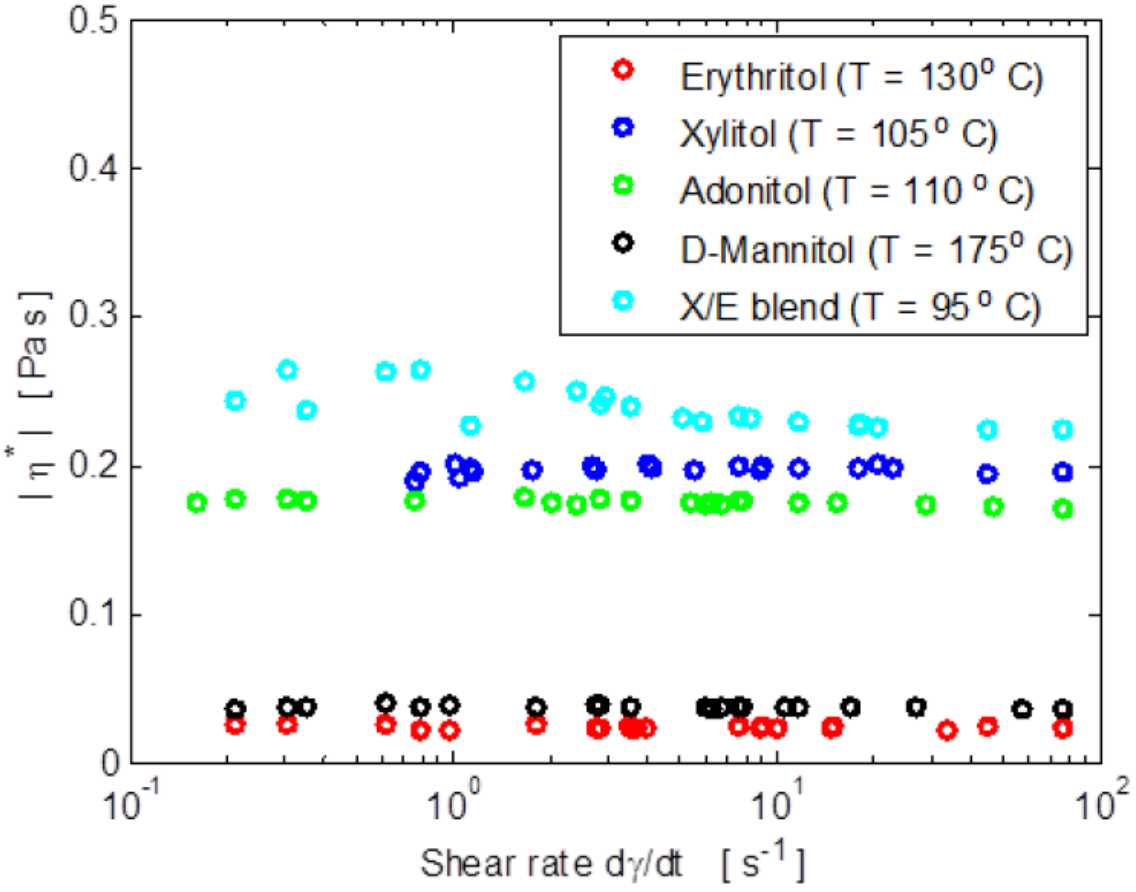
Comparable to salt hydrates

No significant differences between SA et SA-blends

No significant variation with temperature

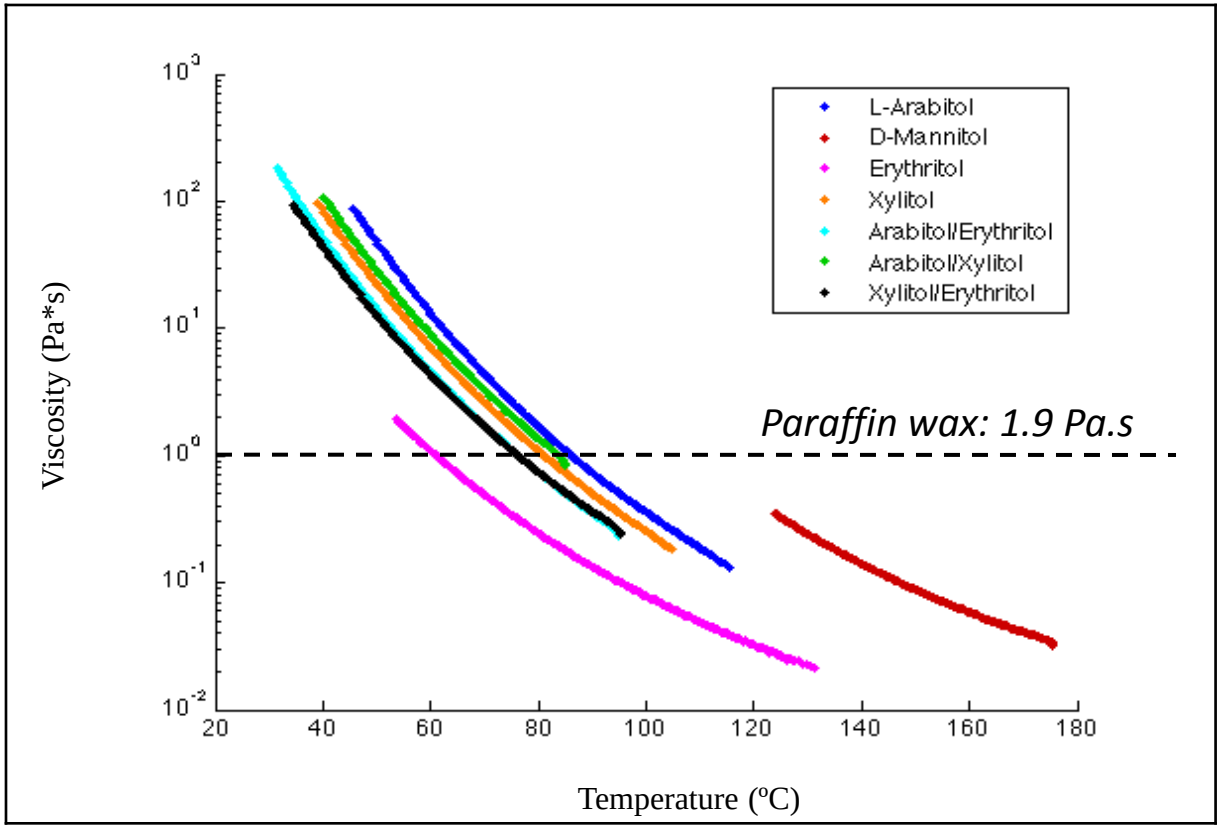
Rheology - Viscosity

Dynamical Mechanical Analysis



At low shear rates, the SA and SA-blends behave as **Newtonian fluids**

Measurements at constant shear rate



Erythritol
D-Mannitol
Arrhenius Model

$$\eta(T) = \eta_\infty e^{-\frac{E_a}{RT}}$$

For the other ones

$$\eta(T) = e^{AT^3+BT^2+CT+D}$$

The viscosity increases rapidly when decreasing temperature and becomes very high in highly undercooled melts

Atoms mobility in the liquid → Nucleation rates & crystal growth kinetics

Probability of Spontaneous Nucleation

Within classical nucleation theory
For diffusion-limited crystallization
The **nucleation rate** under steady-state conditions is governed by 2 exponential terms

activation energy regarding the atomic diffusion process

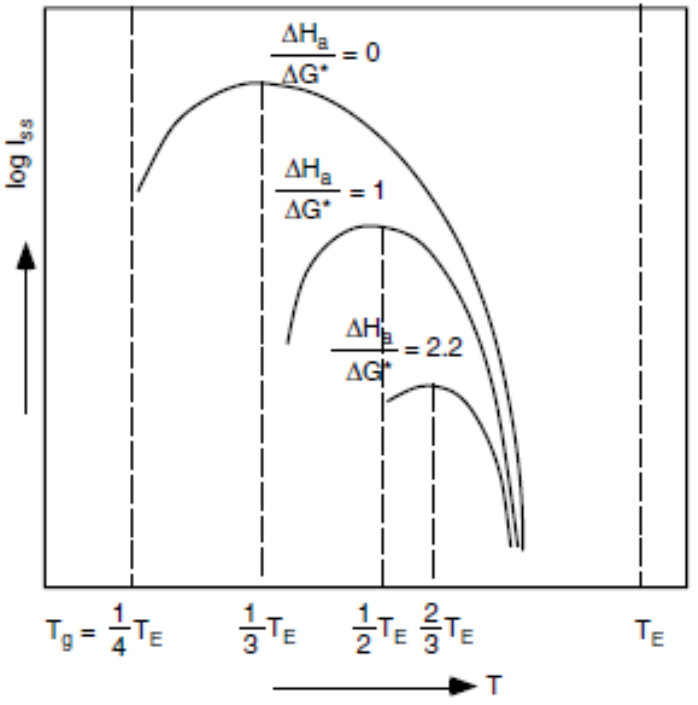
activation energy for the formation of critical nuclei

$$I_{ss}(T) = C \exp\left(+\frac{\Delta G_a(T)}{k_B T}\right) \exp\left(-\frac{\Delta G^*(T)}{k_B T}\right)$$

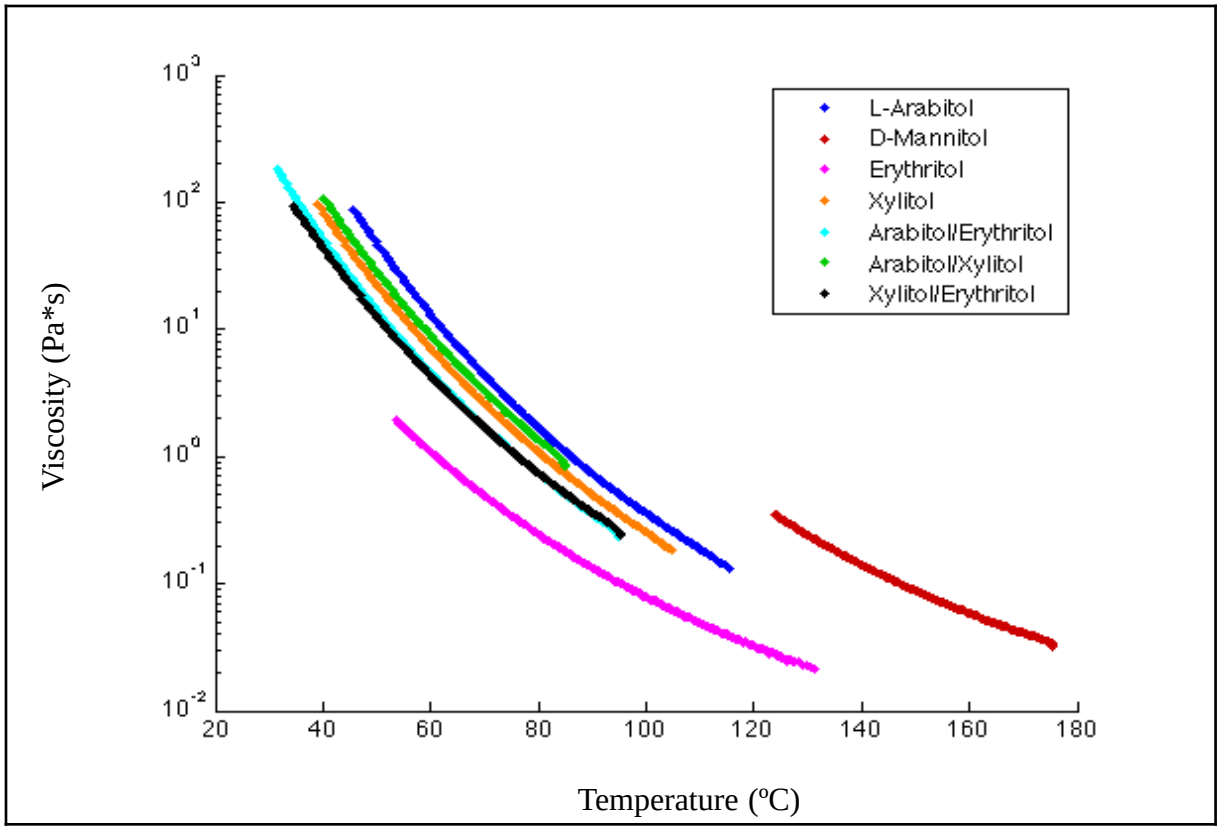
At high undercooling, this term controls the nucleation

At small undercooling, this term dominates

With increasing undercooling, the nucleation rate first increases until a maximum value and then it decreases



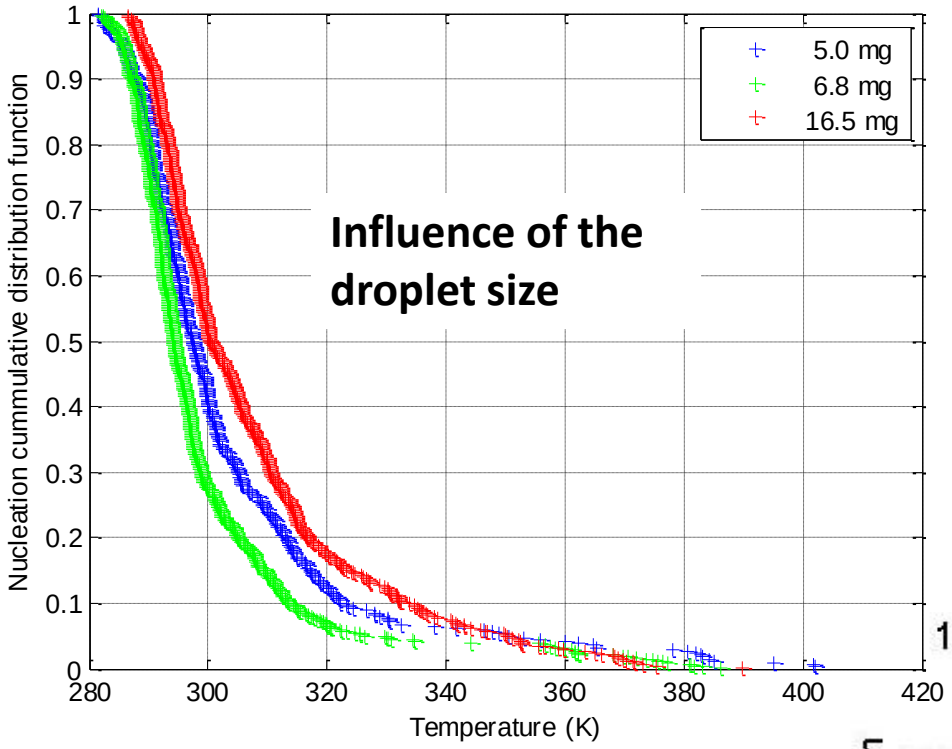
MOREOVER, with increasing influence of the T-dependence of the diffusion term, the maximum value of the nucleation rate is shifted to higher T and it is lower



Erythritol
Xylitol
Adonitol
L-Arabitol
Er/Xy (36/64)
Ar/Xy (44/56)
Ad/Er (70/30)
Ar/Er (60/40)

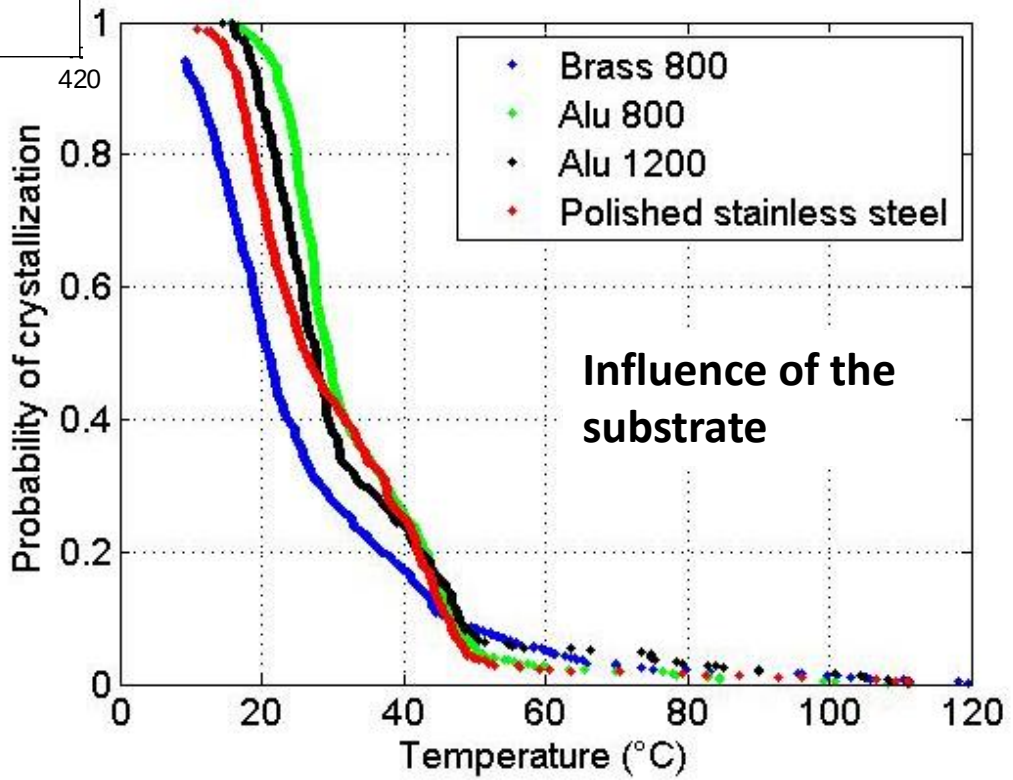
For all the products
(except Erythritol)

The energy barrier for atomic diffusion and conformation changes is so high that the nucleation rate is almost zero. The induction time tends to infinity. The PROBABILITY OF SPONTANEOUS NUCLEATION is negligible.



Test carried out at constant cooling with droplets of different size deposited on an Al-substrate

Test carried out at constant cooling with droplets of 10 mg deposited on different substrates



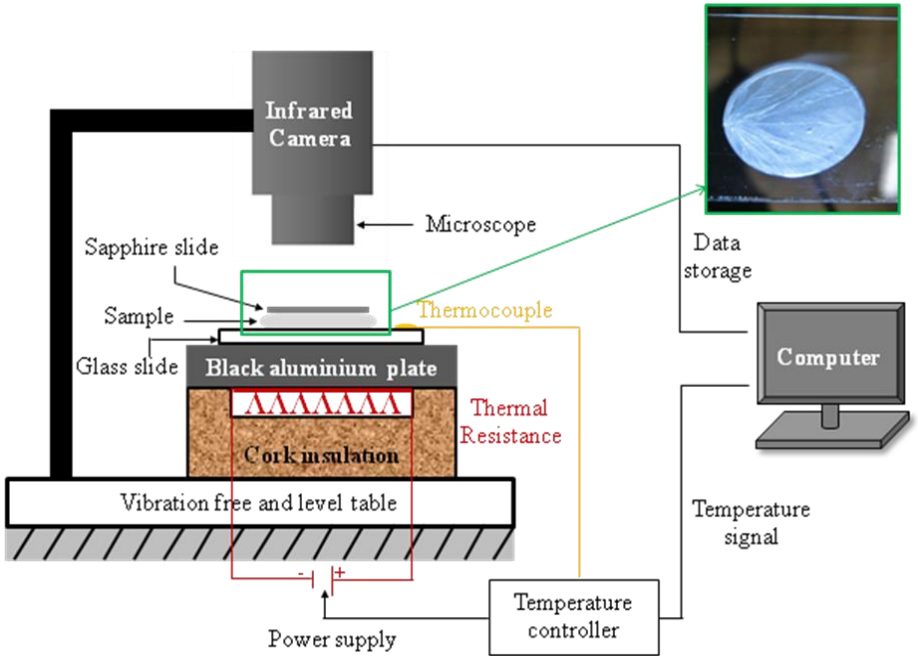
Erythritol

The probability of spontaneous nucleation start to be higher than 1% at temperatures below 96°C

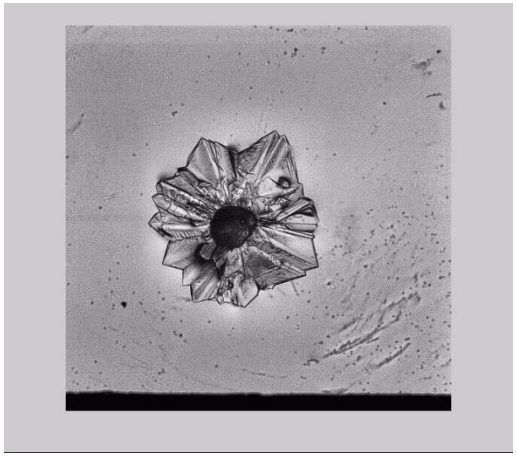
Crystal Growth Rates

In situ experimental analysis by microscopic imaging techniques

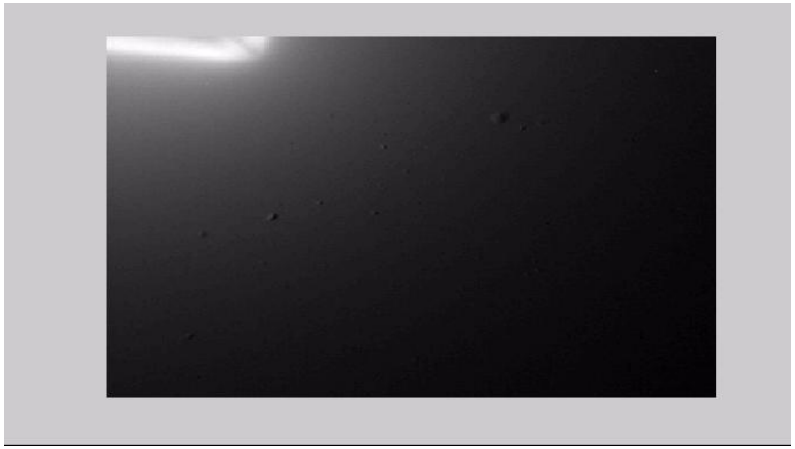
Isothermal conditions



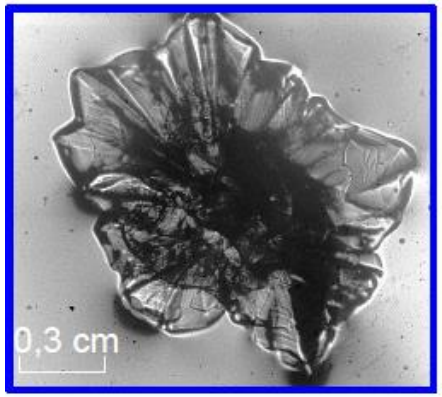
OPTICAL MICROSCOPY



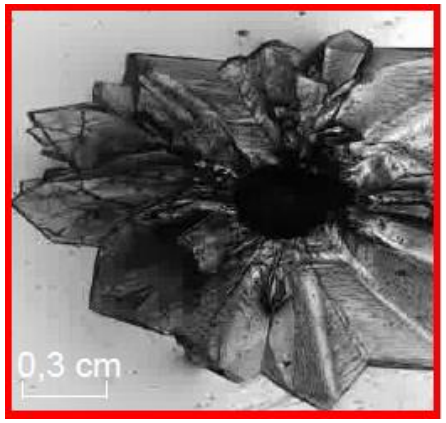
MICROSCOPIC IR-THERMOGRAPHY



FACETED DENDRITIC GROWTH

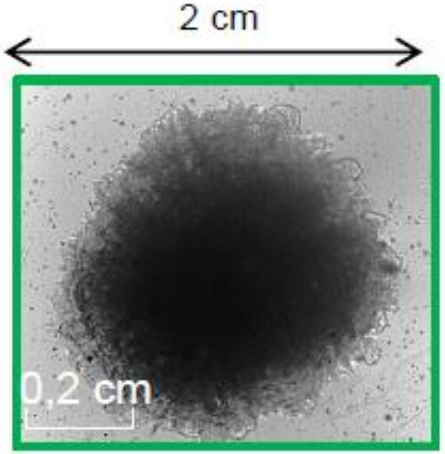


Xylitol

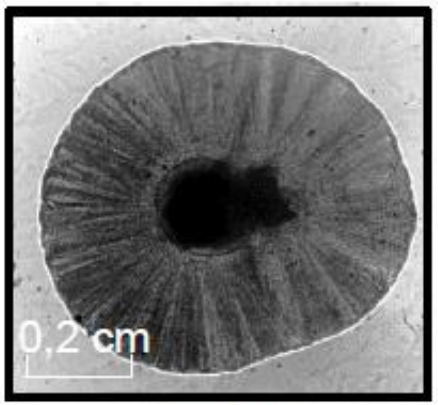


Erythritol

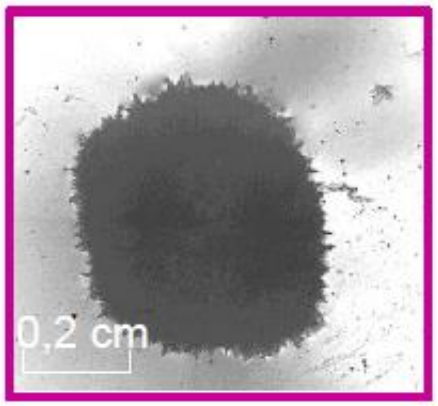
DENSE-BRANCHING MORPHOLOGY



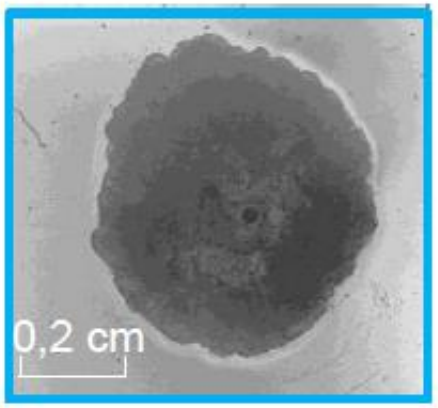
Adonitol



Arabitol



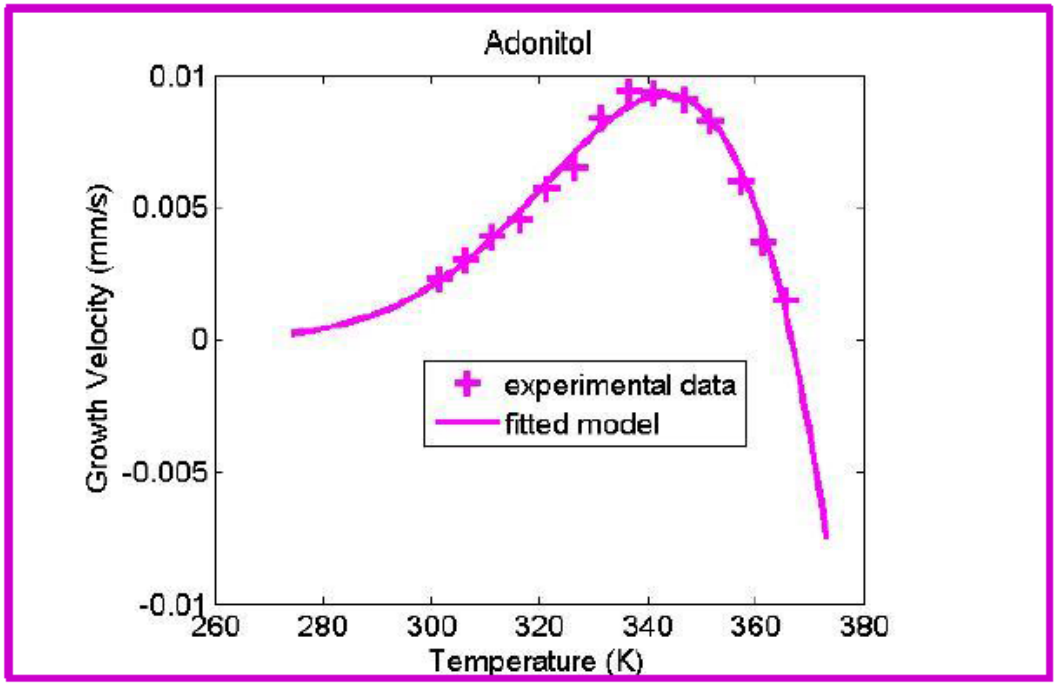
60% Arabitol
+ 40% Erythritol



64 % Xylitol
+ 36 % Erythritol

CRYSTAL GROWTH KINETICS

- Growth is controlled by rearrangement processes only at the liquid-solid interface and is therefore interface-controlled
- The rearrangement process involves a diffusive jump (diffusion-limited kinetics) as well as conformation changes for some SA
- The modern form of the Wilson-Frenkel model represents adequately observed crystal growth rates



fraction of interface sites that are active growth sites

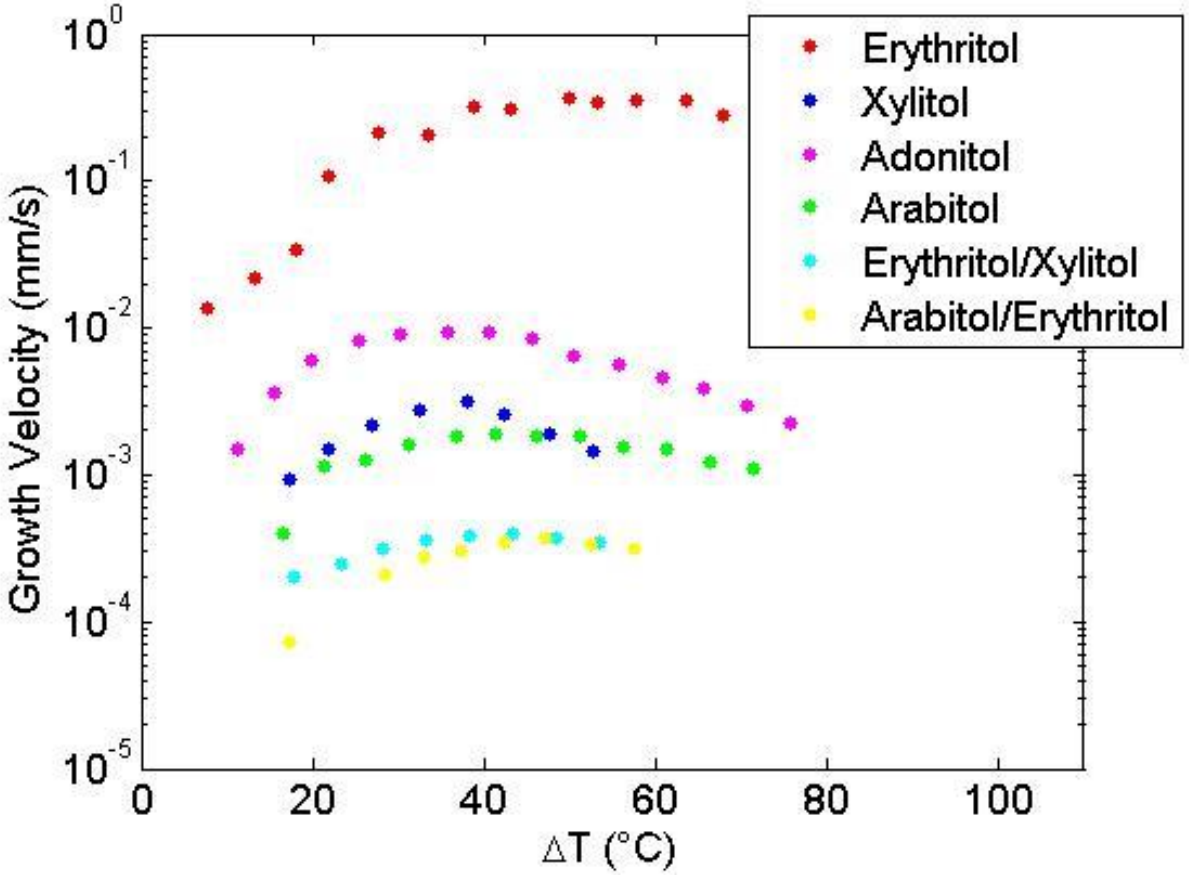
activation energy for atomic rearrangements

chemical potential difference between the two phases

$$v = a_o f v' \exp\left(-\frac{\Delta G_a}{RT}\right)\left[1-\exp\left(-\frac{\Delta G_{ls}}{RT}\right)\right]$$

Wilson-Frenkel model

$$v = \frac{a_o f}{l^2}\sqrt{\frac{3k_B T}{m}}\exp\left(-\frac{\Delta S_a}{R}\right)\left[1-\exp\left(-\frac{\Delta G_{ls}}{RT}\right)\right]$$



Order of magnitude for crystal growth

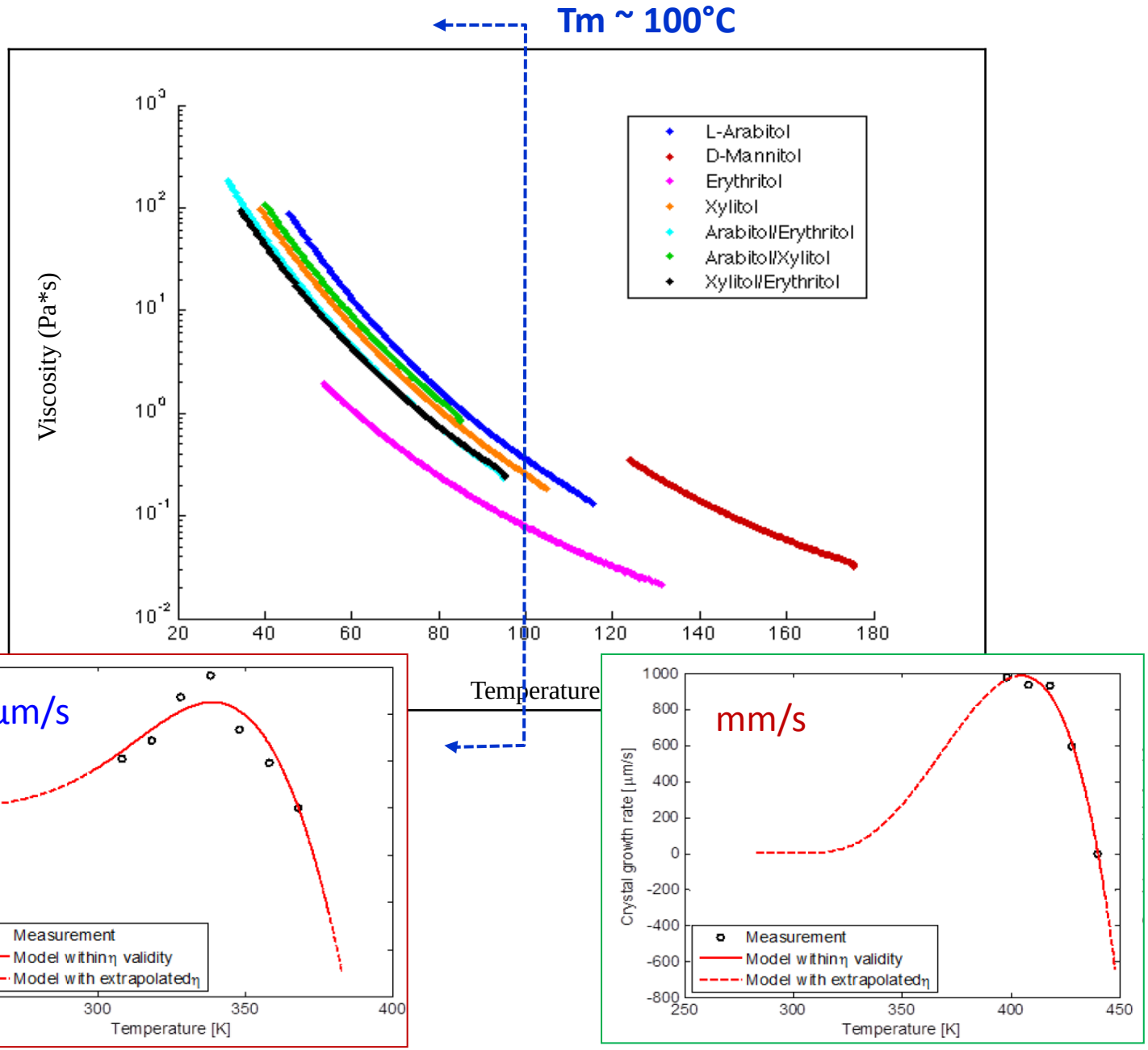
Erythritol — mm/s

Xylitol
Adonitol
L-Arabitol
Er/Xy (36/64)
Ar/Xy (44/56)
Ad/Er (70/30)
Ar/Er (60/40)

— µm/s

The undercooled melts are highly viscous

Conformational changes in the molecules are required to go from liquid to solid



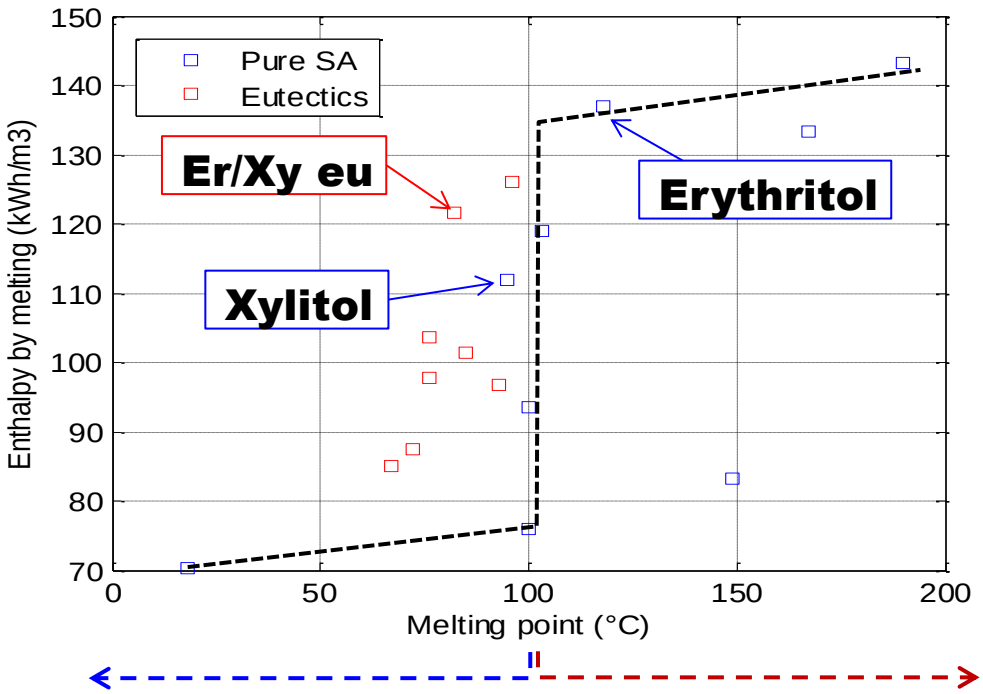
FINAL SELECTION

Melting point

Latent heat

Availability in the market

Cost



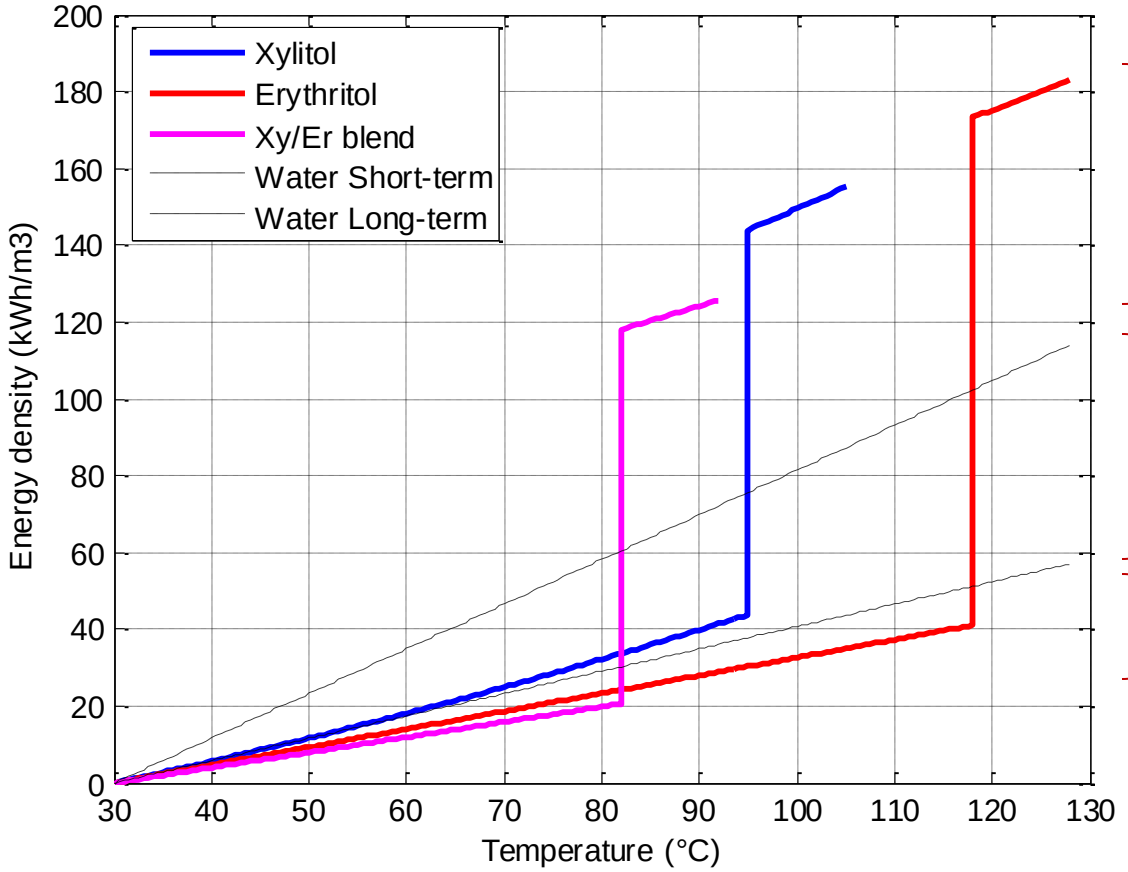
Very high undercooling with very low probability of spontaneous nucleation

The activation of the crystallization will be difficult
Lower crystal growth rates

Lower undercooling & higher probability of spontaneous nucleation

Crystallization can be easily activated
Higher crystal growth rates

COMPARED TO WATER



Sugar alcohols
120 – 190 kWh/m3

Water in a short-term basis
60 – 100 kWh/m3

Water in a long-term basis
30 – 50 kWh/m3

For seasonal storage applications, SA can provide total energy density 4-6 times higher than that of water

Thank you for your attention