Molasses exhaustion

Zakopane conference, May 2014

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File name: Molasses exhaustion for Zakopane Conference MC 26.03.14.pptx
Responsible: MC
Created by: MC
Version: 2014-03-26
Animation: no
Language: English



1. **Background**
2. Crystal growth models
3. Estimates by 3-step crystal growth model
4. Estimates by 2-step crystal growth model
5. Conclusions

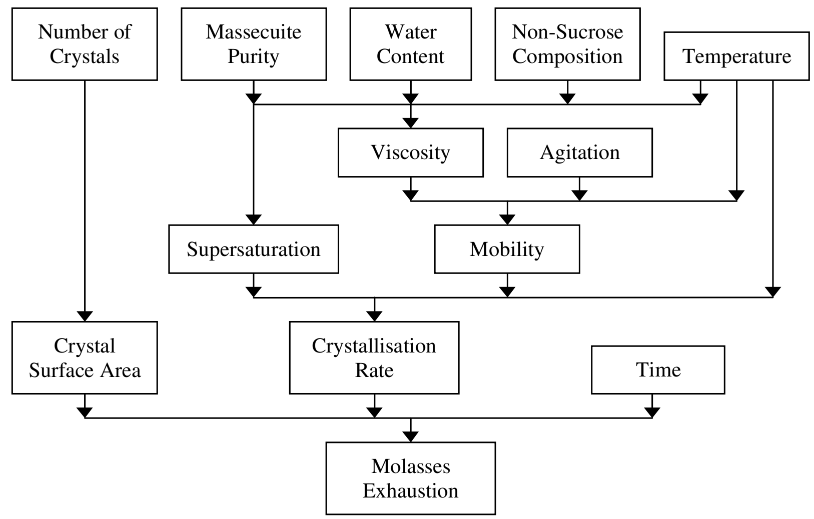
Background

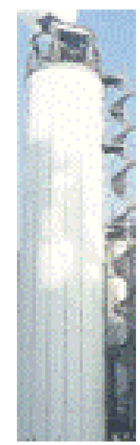
- Cooling crystallizers are used to reduce sugar loss to molasses. The process is complicated by many variables (McGinnis, 1978).

- The many inter-connected variables make molasses exhaustion difficult to accurately predict, which is important when making optimizing & investment decisions.

- To find the crystal growth model for best predicting factory results, data from different cooling crystallization systems at different factories during different campaigns, at different times of the campaign in different North European countries were evaluated.

- The best model was then used to predict the performance of a newly upgraded cooling crystallizer system.





Molasses exhaustion data

A robust data set was used as input to crystal growth calculations made to estimate nutsch purity drops over different factory cooling crystallizer systems.

Calculations were made by a process of iteration from start conditions to the final temperatures & retention times.

Calculated purity drops were compared to measured values and the standard error of estimate (RMSE) then used to evaluate the prediction ability of the model.

$$\sigma_{est} = \sqrt{\frac{\sum (Y - Y')^2}{N}}$$

<u>Data</u> (n=39)

Massecuite pol purities (70-81Q), NS/W (2,6-5,5), crystal sizes (0,20-0,40mm), nutsch purities, residence times (5-77hrs), temperature range (82-42°C), cooling rates (up to 3,8°C/h), raffinose levels (0,9-2,6%rds), invert sugar levels (0,09-0,70%rds) and solubility coefficients.

<u>Different factory schemes & campaigns</u>:

DDS, continental, raw sugar

1996, 1997, 1998, 1999, 2001 & 2003.

<u>Different types of cooling crystallizers</u>:

Horizontal (HCC) & vertical (VCC)

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Crystal growth models

2-step model

1) Bulk diffusion through surface film to crystal surface.
2) Reaction and integration of sucrose molecules into the crystal lattice

$$\frac{dm}{dt}\cdot\frac{1}{A}=\frac{\Delta c_{eff}}{\frac{1}{k_D}+\frac{1}{k_R}} \quad \text{where} \quad \Delta ceff = c_L - c_{L,eq}$$

3-step model

Includes a proposed third step involving surface diffusion along the crystal surface to a suitable integration site (Ekelhof and Schliephake, 1995) and further by Ekelhof (1997).

$$\frac{dm}{dt}\frac{1}{A}=\frac{\Delta ceff}{\frac{1}{k_D}+\frac{1}{k_{ad}}\frac{c_{L,sat}a}{\beta\cdot\Delta ceff}+\frac{1}{k_R}}$$

dm is amount of sucrose crystallized in time dt per unit of crystal surface area *A.*

Δc_{eff} is the effective driving force (kg/m^3).

c_L is concentration of bulk liquid solution.

$c_{L,eq}$ is concentration at equilibrium conditions.

k_D is coefficient for bulk diffusion.

k_{ad} is coefficient for surface diffusion.

k_R is coefficient for the integration reaction.

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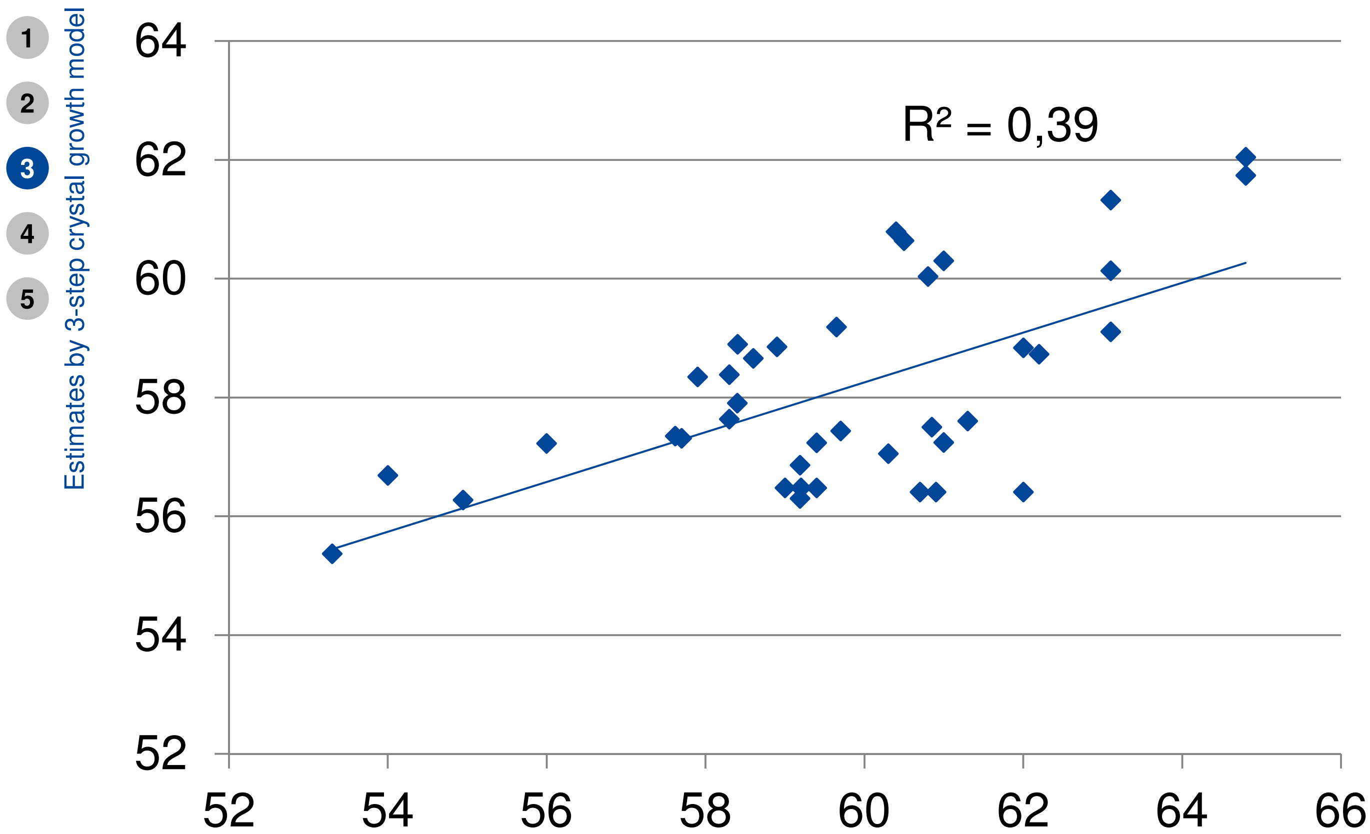
Estimates of nutsch purity by 3-step crystal growth model



$$\frac{dm}{dt}\frac{1}{A} = \frac{\Delta c_{eff}}{\frac{1}{k_D} + \frac{1}{k_{ad}}\frac{c_{L,sat}a}{\beta \cdot \Delta c_{eff}} + \frac{1}{k_R}}$$

Standard error of estimate (RMSE) = 2,53 purity units.

To understand the reasons for large scatter and model bias cases from the data were evaluated.

Case 1: Nutsch purities measured and estimated by 3-step model at factory using DDS sugarhouse scheme

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Estimates by 3-step crystal growth model

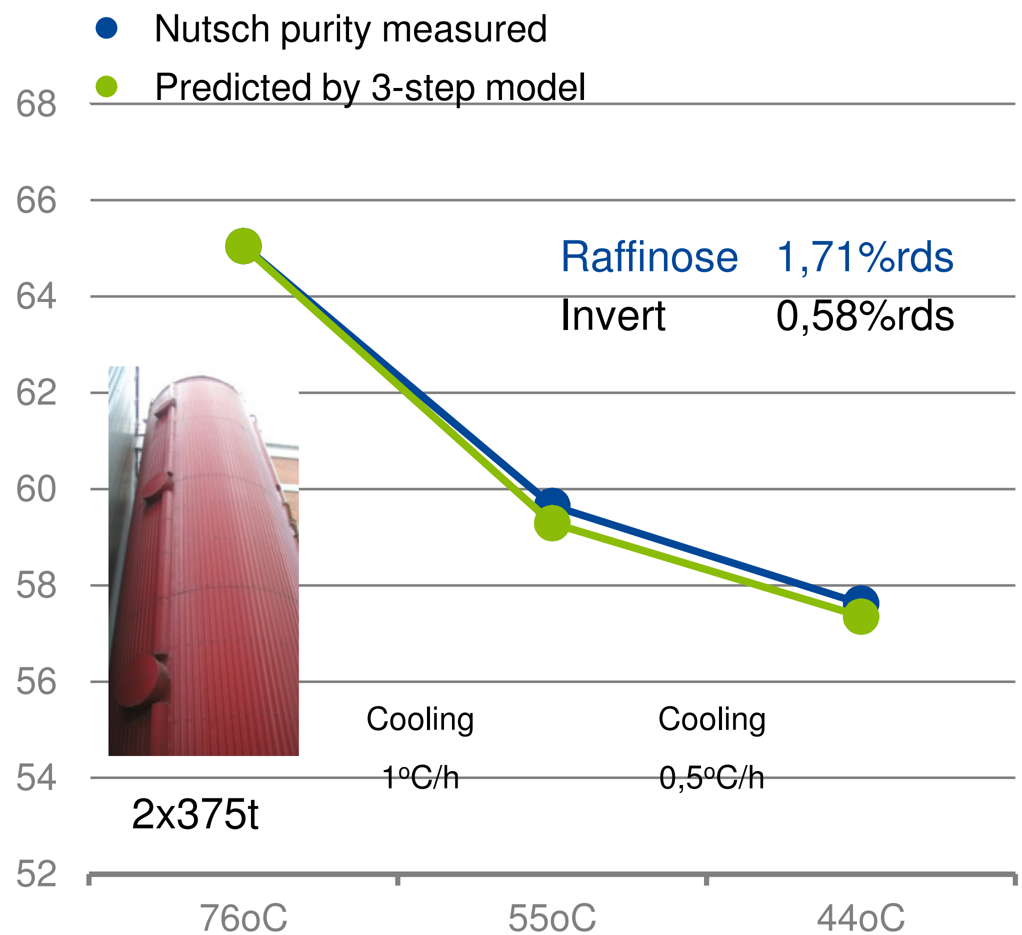
<u>C-massecuite</u>

Pol purity %	80,5
Dry substance %	94,3
NS/W	3,2
Retention hours	40

<u>Nutsch pol purity%</u>

	Measured	Model
VCC2 out	57,6	57,4
Predicted difference		-0,3

Good estimate.



Case 2: Nutsch purities measured and estimated by 3-step model at factory using DDS sugarhouse scheme

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Estimates by 3-step crystal growth model

C-massecuite

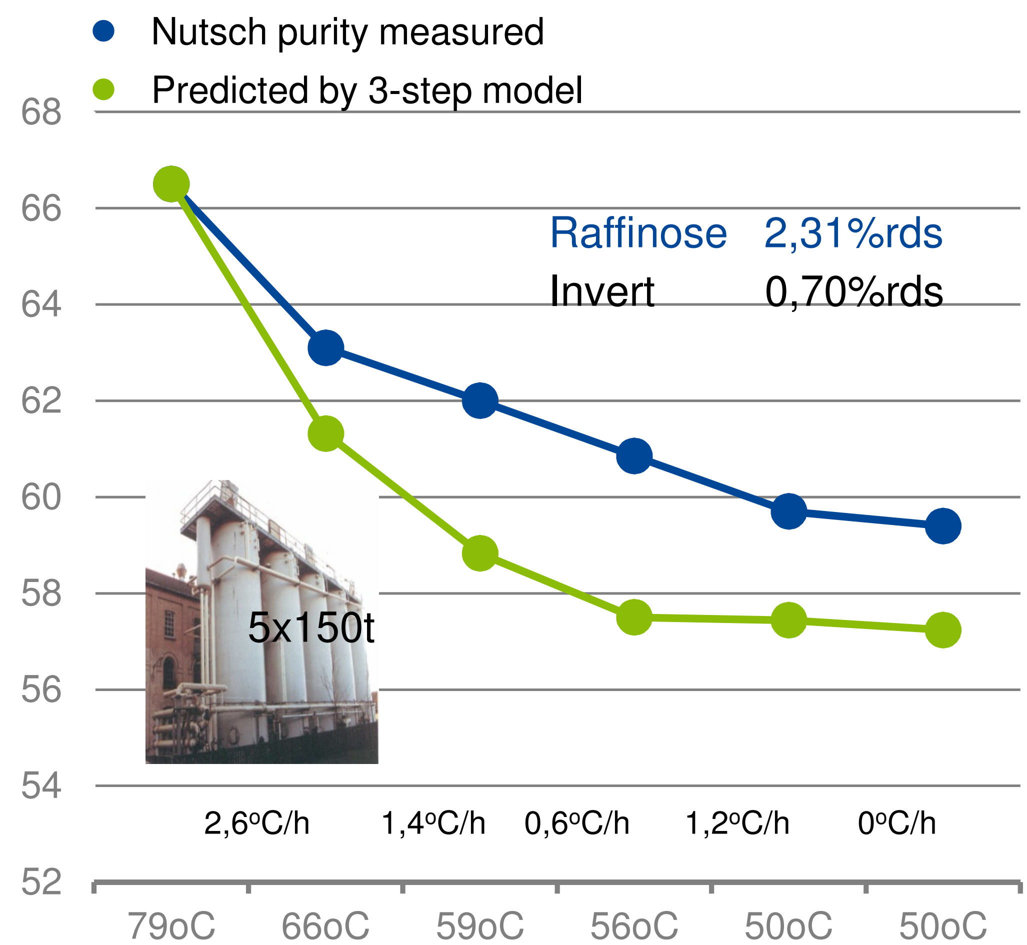
Pol purity %	79,7
Dry substance %	93,3
NS/W	2,8
Retention hours	25

Nutsch pol purity%

	Measured	Model
VCC5 out	59,4	57,2
Predicted difference		-2,2

Over-estimate.

Due to higher raffinose level?



Case 3: Nutsch purity measured and estimated by 3-step model at factory making 100% raw beet sugar

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Estimates by 3-step crystal growth model

<u>C-massecuite</u>

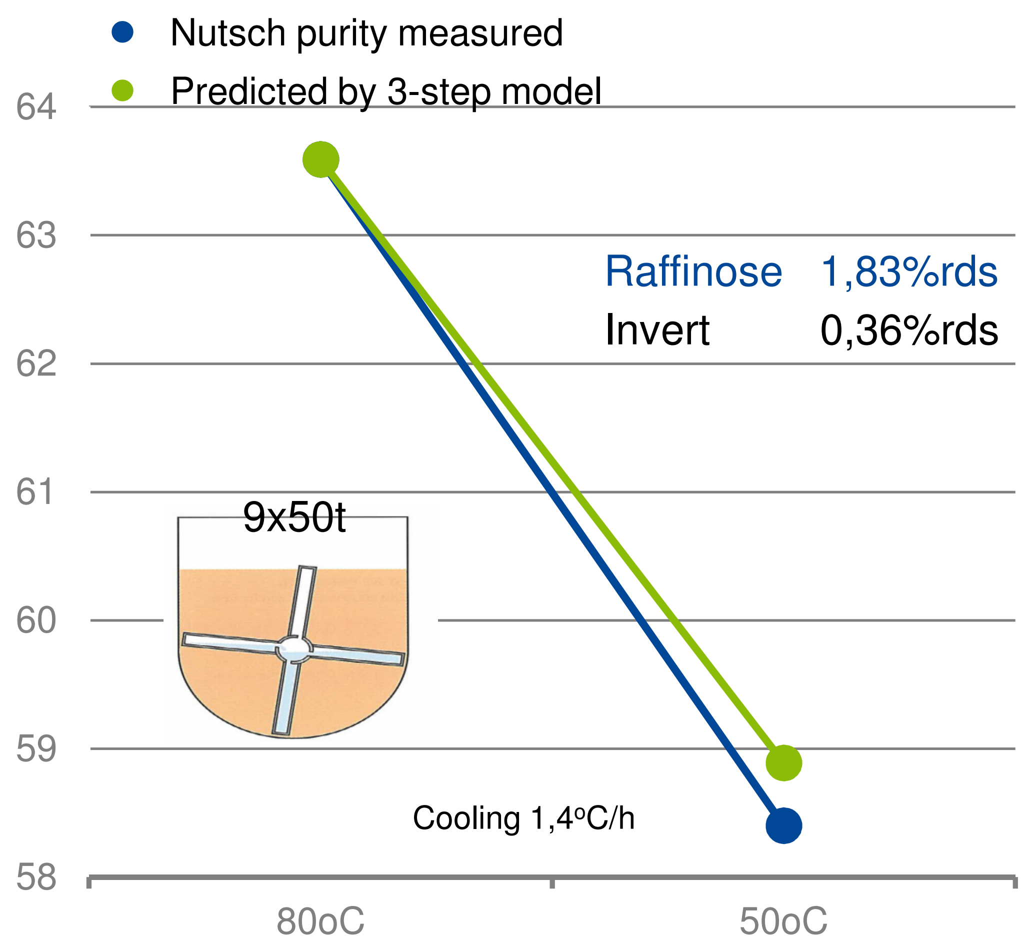
Pol purity %	71,8
Dry substance %	94,7
NS/W	5,0
Retention hours	21

<u>Nutsch pol purity%</u>

	Measured	Model
HCC9 out	58,4	58,9
Predicted difference		+0,5

Better estimate.

Due to lower raffinose level?



Kinetic minimum super-saturation, $\Delta q_{S/Wmin}$

1 2 3 4 5

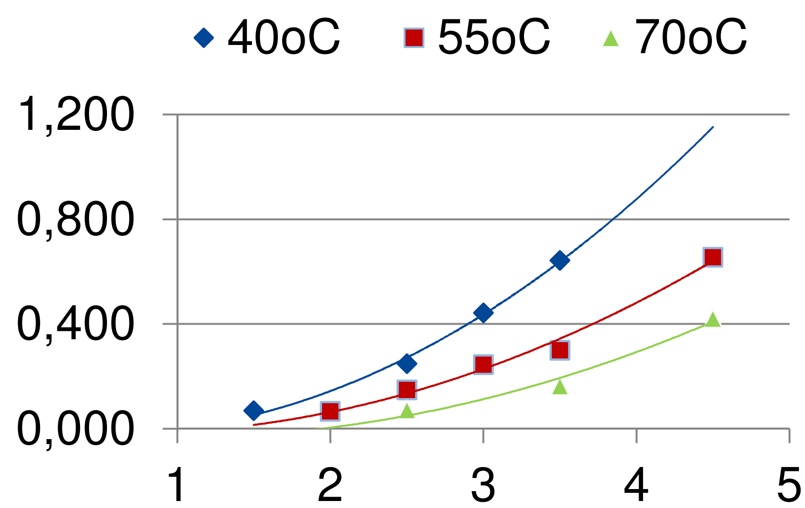
Estimates by 3-step crystal growth model

The kinetic minimum super-saturation $\Delta q_{S/Wmin}$ determines the crystallization end point $q_{S/We}$

$$q_{S/W,e} = q_{S/W,sat} + \Delta q_{S/W,\min} \quad \approx \quad c_{L,eq} \text{ kg/m3}$$

$$\Delta c_{eff} = c_L - c_{L,eq}$$

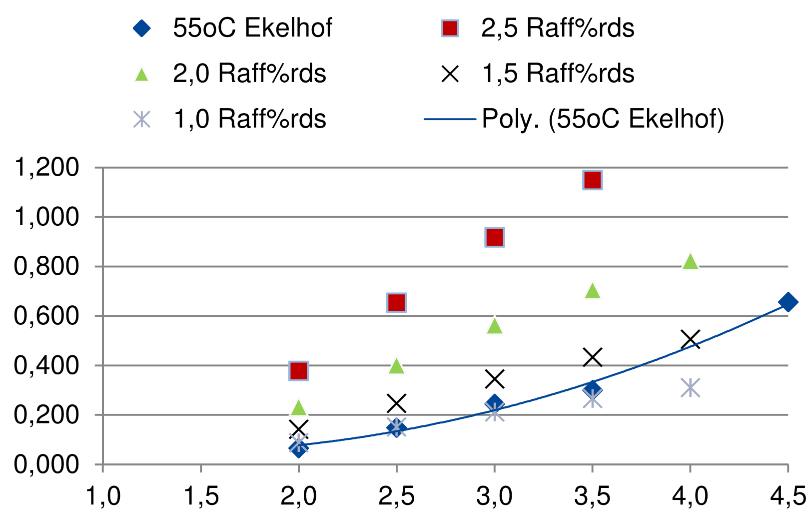
$\Delta q_{S/Wmin}$ as function of temperature and non-sugar water ratio for 3-step crystal growth model. (Ekelhof and Schliephake, 1995).

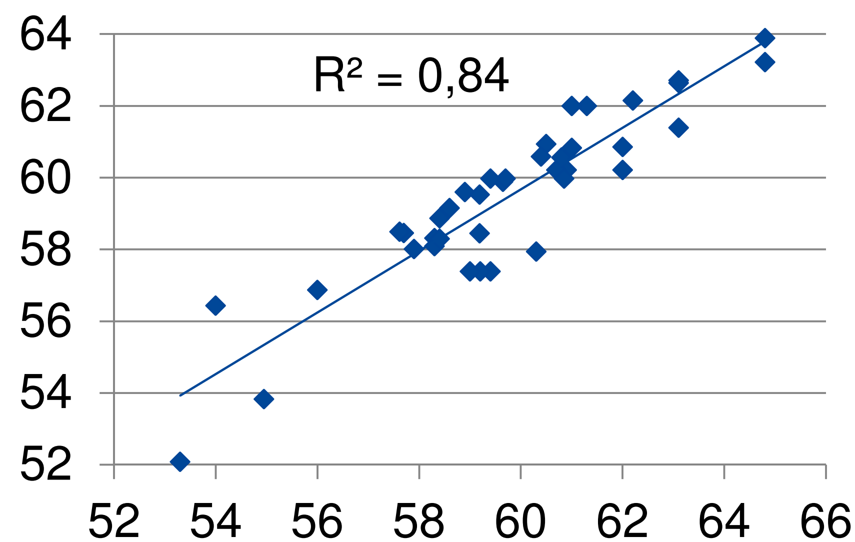


Raffinose is well known to slow crystallization rates in beet juice. Levels varied a lot from 0,9 to 2,6%rds.

Raffinose and invert levels were measured in all data sets enabling their influence on crystal growth rate through $\Delta q_{S/Wmin}$ to be evaluated.

Better estimate by 3-step model when accounting for the influence of raffinose on the kinetic minimum super-saturation, $\Delta q_{S/Wmin}$





Left chart shows raffinose to have a significant influence on the kinetic minimum super-saturation .

Right chart shows when accounting for the influence of raffinose on the kinetic minimum super-saturation the standard error of estimate (RMSE) to decline significantly from 2,53 to 1,06 purity units.

Variations in invert sugar levels showed no influence on the standard error at 95% confidence.



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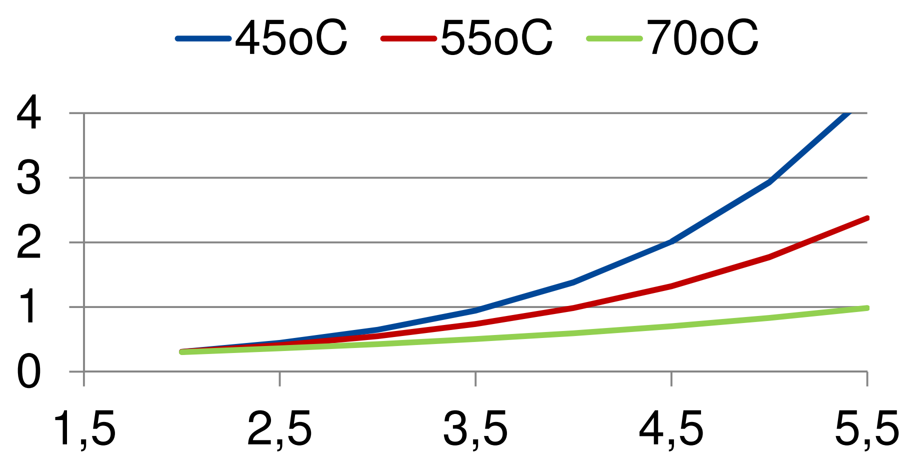
Kinetic minimum super-saturations, $\Delta q_{S/Wmin}$, for 2-step model

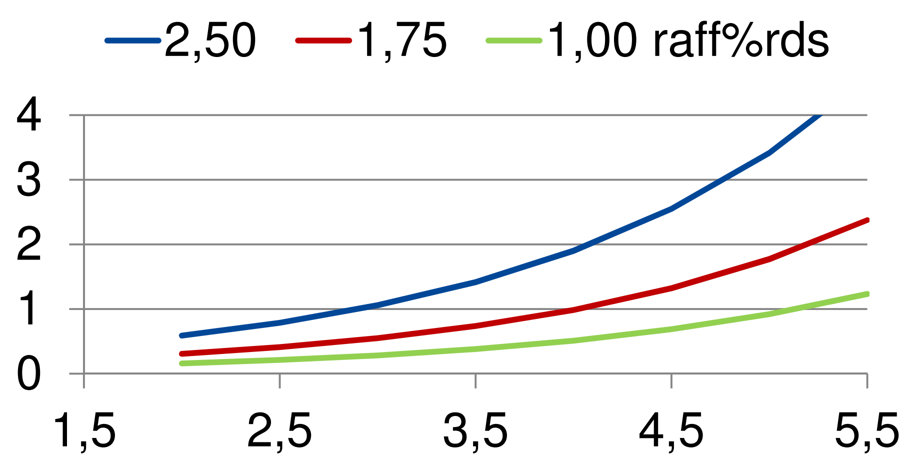
1 2 3 4 5 Estimates by 2-step crystal growth model

Simpler 2-step crystal growth model is known to give a good estimate of experimental data for pure sucrose solutions.

What about for impure sucrose solutions when accounting for influences of non-sugars and temperature on $\Delta q_{S/Wmin}$ as indicated by the measured data?



Data also showed significant influence of raffinose on the kinetic minimum super-saturation, see for 55°C.



How do these influences affect the prediction ability of the 2-step crystal growth model?

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Estimates of nutsch purity by 2-step model when accounting for influence of temperature and non/sugar water ratio on $\Delta q_{S/Wmin}$

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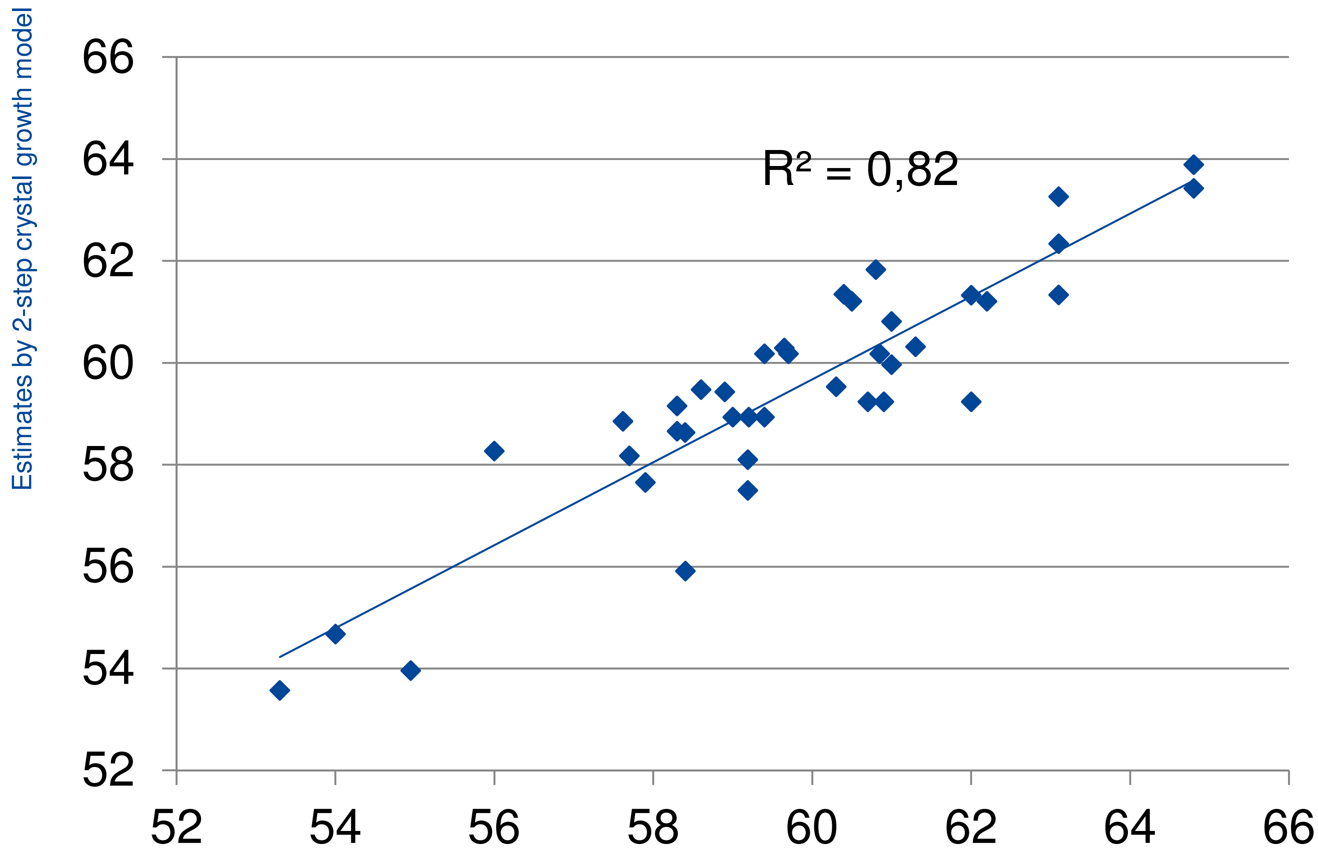

$$\frac{dm}{dt}\cdot\frac{1}{A}=\frac{\Delta c_{eff}}{\frac{1}{k_D}+\frac{1}{k_R}}$$

Standard error was 1,11 purity units compared to 2,53 units for 3-step model, when unadjusted for the influence of raffinose. Prediction correlation also much improved. Could error and bias be further reduced by accounting for influence of raffinose on $\Delta q_{S/Wmin}$?

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Estimates of nutsch purity by 2-step model when accounting also for influence of raffinose on the kinetic minimum super-saturation, $\Delta q_{S/Wmin}$

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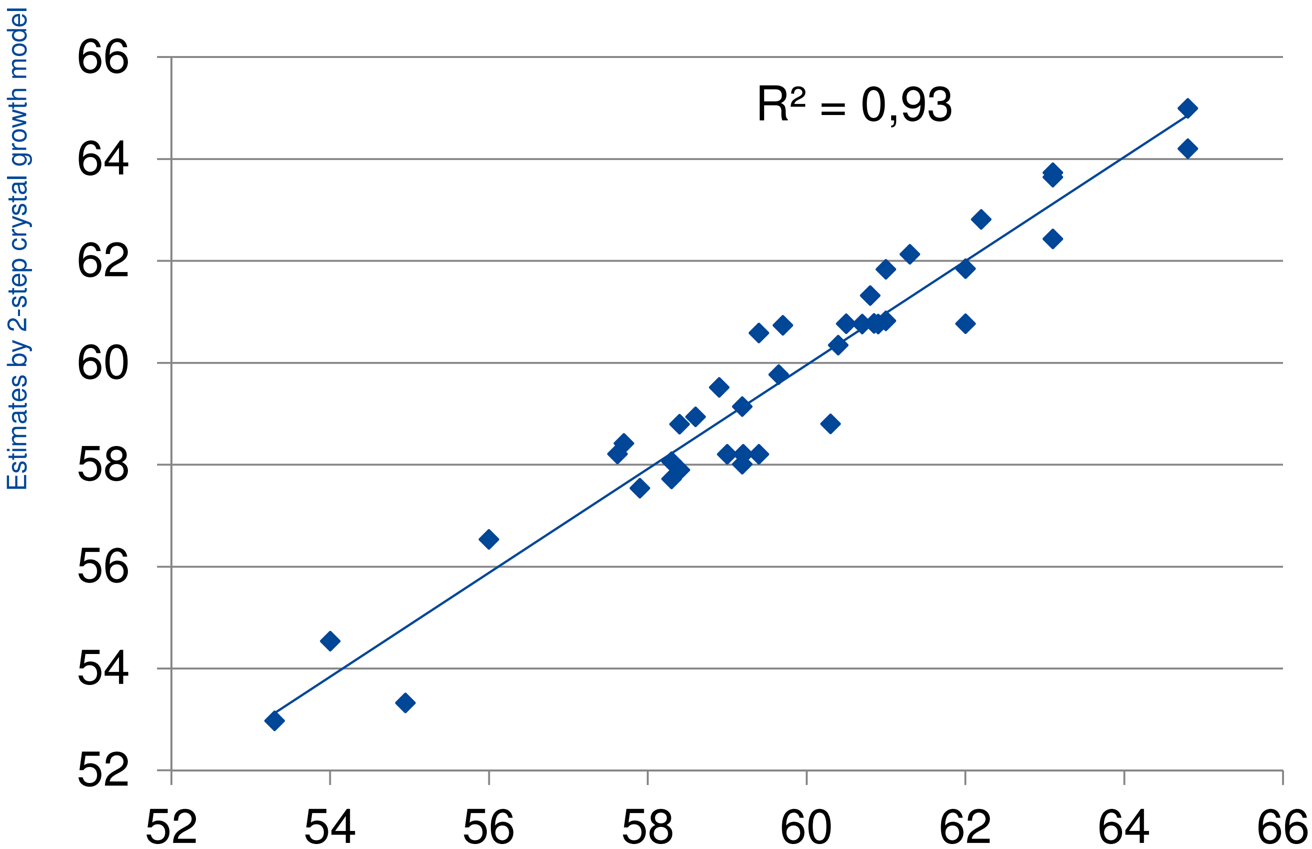

$$\frac{dm}{dt} \cdot \frac{1}{A} = \frac{\Delta c_{eff}}{\frac{1}{k_D} + \frac{1}{k_R}}$$

Standard error declined from1,11 to 0,72 purity units. Prediction correlation improved. Regression line shows model bias to have been eliminated!

Could error be further reduced by accounting for variations of invert sugar on $\Delta q_{S/Wmin}$?

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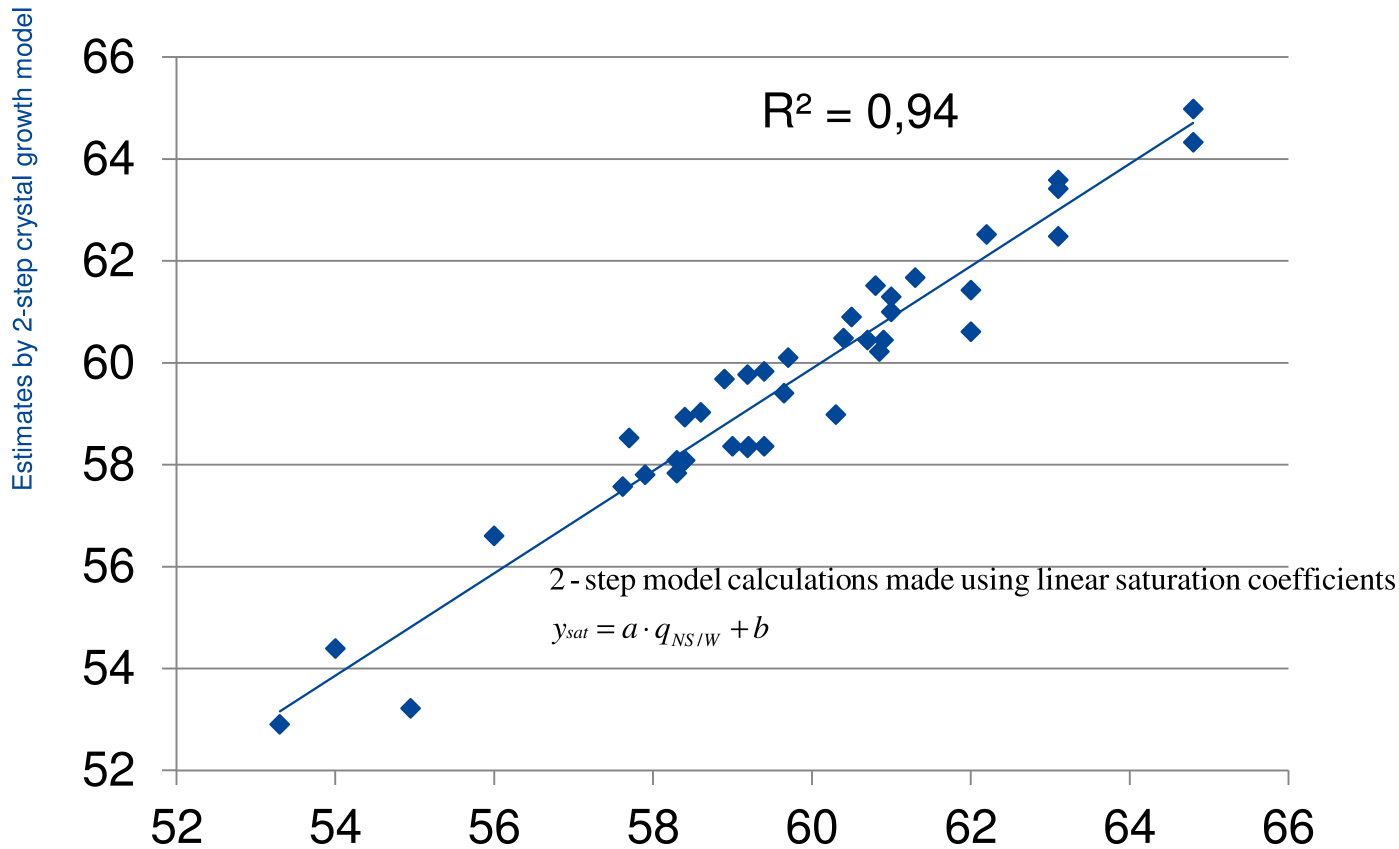
Estimate of nutsch purity by 2-step model when accounting for influences of both raffinose & invert on kinetic minimum super-saturation, $\Delta q_{S/Wmin}$



$y_{sat} = a \cdot q_{NS/W} + b$

$$\frac{dm}{dt} \cdot \frac{1}{A} = \frac{\Delta c_{eff}}{\frac{1}{k_D} + \frac{1}{k_R}}$$

$$F = \frac{\left(\frac{RSS_1 - RSS_2}{p_2 - p_1}\right)}{\left(\frac{RSS_2}{n - p_2}\right)}$$

Standard error decreased further from 0,72 to 0,64 purity units when also accounting for the influence of invert on $\Delta q_{S/Wmin}$. F-test shows a statistically better model at 95% confidence.

Other errors?

What about errors when extrapolating the saturation curve?

An accurate estimate of super-saturation is essential for a good prediction of crystal growth rate. The saturation coefficients used to calculate super-saturation are measured at $q_{NS/W}$ below 3,0.

Grut's solubility data, $q_{NS/W}$ <3,0, can be described by the following equation, Vavrinecz (1965).

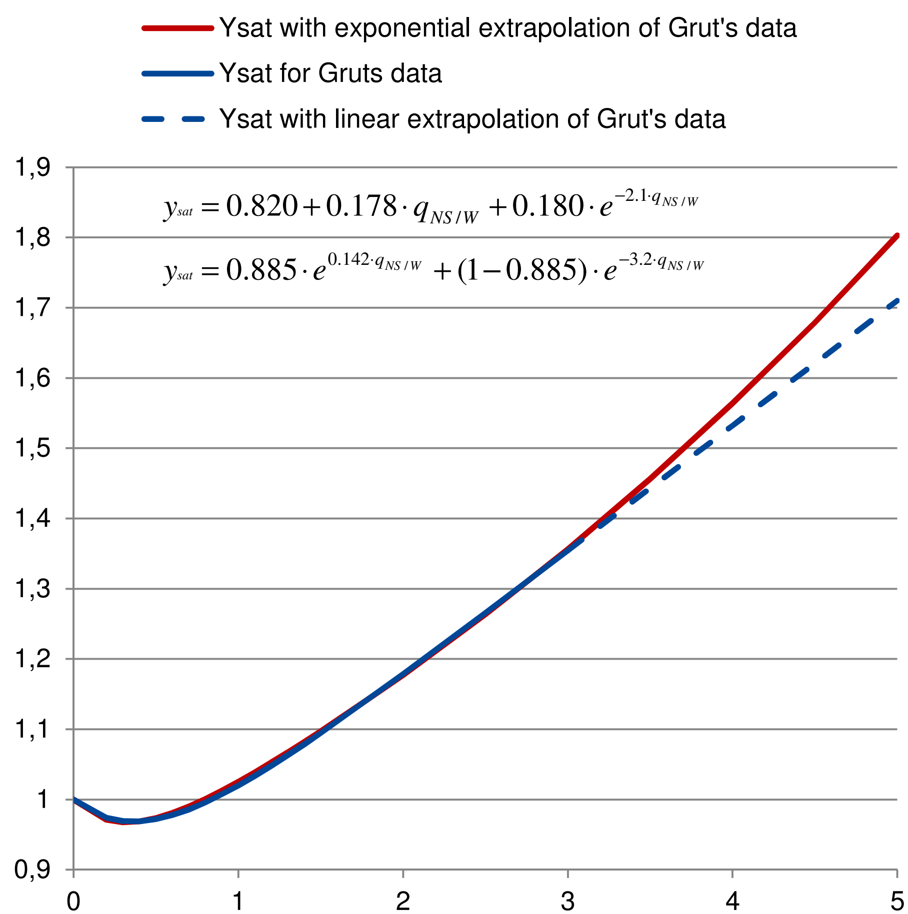
$$y_{sat} = 0.820 + 0.178 \cdot q_{NS/W} + 0.180 \cdot e^{-2.1 \cdot q_{NS/W}}$$

The saturation line has been found to show curvature above a $q_{NS/W}$ of 3,0, Carter (2003) .

$$y_{sat} = 0.885 \cdot e^{0.142 \cdot q_{NS/W}} + (1 - 0.885) \cdot e^{-3.2 \cdot q_{NS/W}}$$

The difference between linear and exponential extrapolation of Grut's data is shown in the Chart.

How does this curvature affect model error for factories operating at $q_{NS/W}$ above 3,0?



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Estimates of nutsch purity by 2-step crystal growth model when using exponential saturation coefficients, y_{sat}

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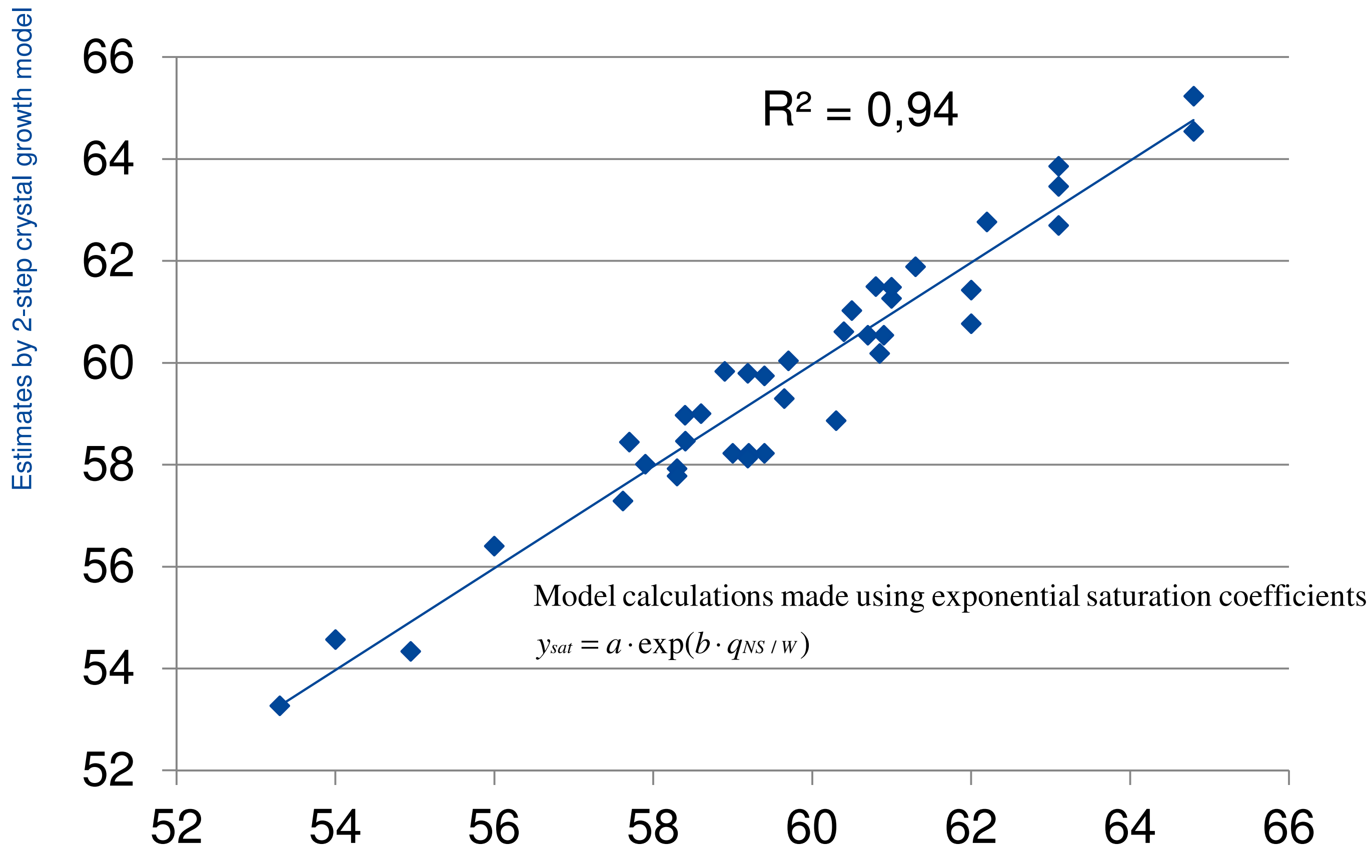


$$\frac{dm}{dt} \cdot \frac{1}{A} = \frac{\Delta c_{eff}}{\frac{1}{k_D} + \frac{1}{k_R}}$$

Standard error decreased from 0,64 units to 0,63 purity units when using exponential y_{sat}.
Error was halved from 0,83 to 0,40 purity units for five data sets at high $q_{NS/W}$ >4,0.

Estimate of nutsch purities measured over newly upgraded cooling crystallizer system in 2012 by developed 2-step model

<u>C-massecuite</u>

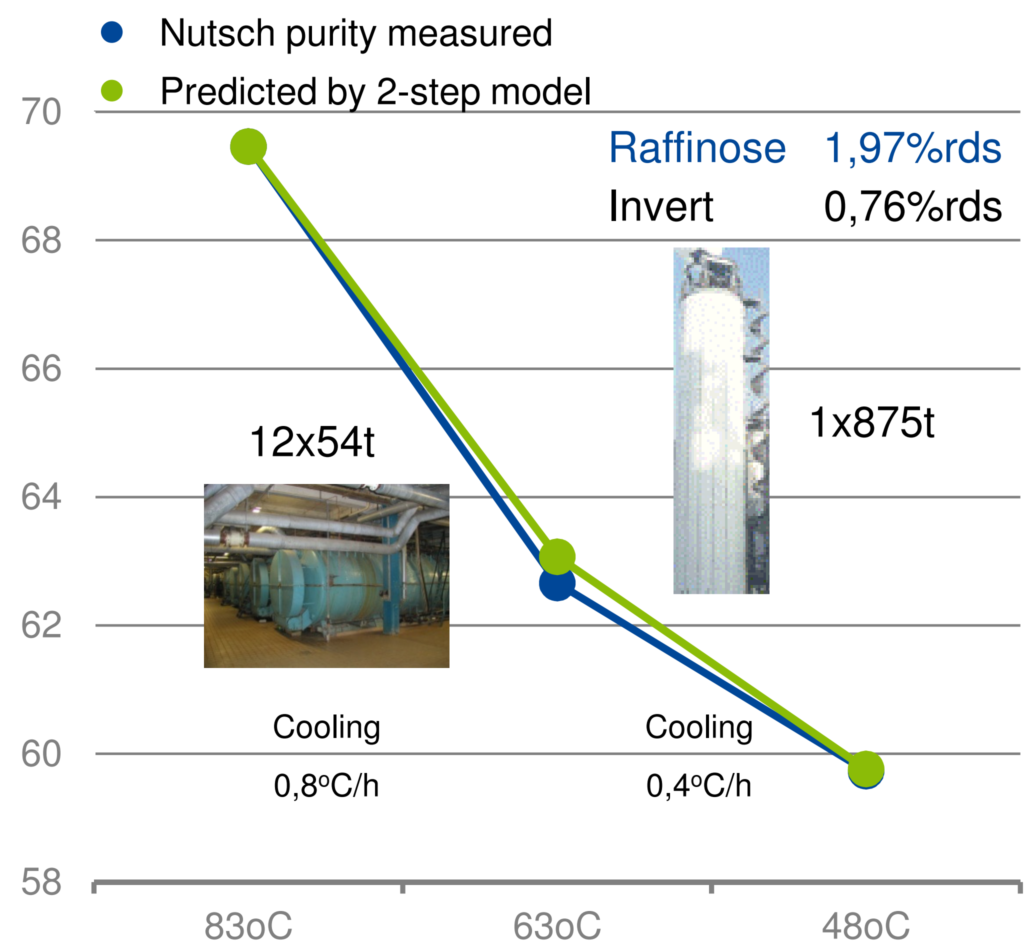
Pol purity %	81,5
Dry substance %	93,2
NS/W	2,6
Retention hours	62

<u>Nutsch pol purity%</u>

	Measured	Model
HCC out	62,7	63,1
VCC out	59,7	59,8
Predicted difference		+0,1

Good model estimate.

Good investment decision.





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Conclusions

- The cooling crystallization process is complicated by many important and inter-connected variables, which makes molasses exhaustion difficult to predict accurately .

- A robust set of data (n=39) from different cooling crystallizer systems, countries, campaign years & periods was evaluated to find the crystal growth model best able to predict factory results for molasses exhaustion.

- A 2-step model gave the lowest standard error of 0,63 purity units, the highest prediction correlation (R^2=0,94) and no bias when accounting for the influences of non-sugars, temperature and also raffinose and invert sugar levels on the effective concentration difference Δc_{eff}.

$$\frac{dm}{dt} \cdot \frac{1}{A} = \frac{\Delta ceff}{\frac{1}{k_D} + \frac{1}{k_R}}$$

- This model was validated by giving a good estimate of total purity drop (+0,1 units) measured over a newly upgraded cooling crystallizer system.

- The ability to accurately predict molasses exhaustion makes it possible to make good investment decisions to increase sugar yield.

Thank You

for Your Attention!