# Purifying biorefinery by-products: A kinetics and thermodynamics approach using solvent-aided layer melt crystallization

Aalto University
School of Chemical Engineering

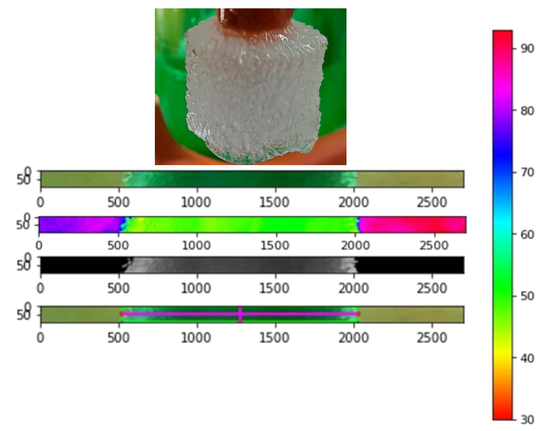
Mitra Ila, Marjatta Louhi-Kultanen, Erik Temmel, Manfred Stepanski, Michael Ginter, Ben McKay, Siu-Ha Soo-Tang, Ed de Jong

## Introduction

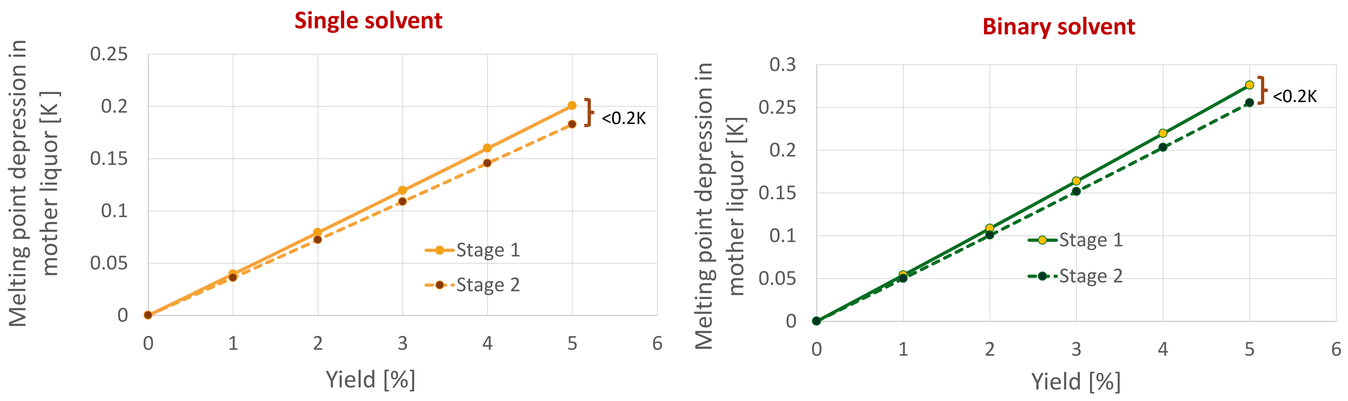
Glycerol is a common industrial by-product produced during various bioprocesses. Reducing waste disposal through reuse of glycerol in different applications relies on its specification and purity level. This work aimed to enhance the effectiveness of the melt crystallization method as a purification technique for bioprocess products to achieve ultimate ultra-pure glycerol at higher crystal growth rates for use in a wide range of applications.

## Methods

- **Method:** Static layer melt crystallization (cold finger)
- **Modifying additives:** single and binary solvent
- **Melting point depression** of the mixtures was predicted by UNIFAC-Dortmund model
- The effect of solvents on **kinetics of crystal growth** measured via image analysis



## Thermodynamic prediction




**Controlling degree of supersaturation (predicted SLE)**
Melting point depression:
Stage 1≈ Stage 2 (less than 0.2 K variation)

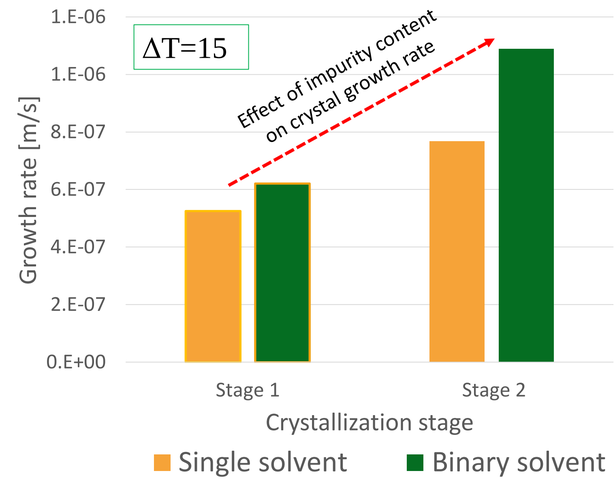
$\Delta T$ (undercooling degree)

**Driving force for crystallization**: stage 1≈ Stage 2 (yield<5%)

The crystal growth rate was measured at a crystallization yield of less than 5% before the formation of two liquid phases in solvent-aided systems

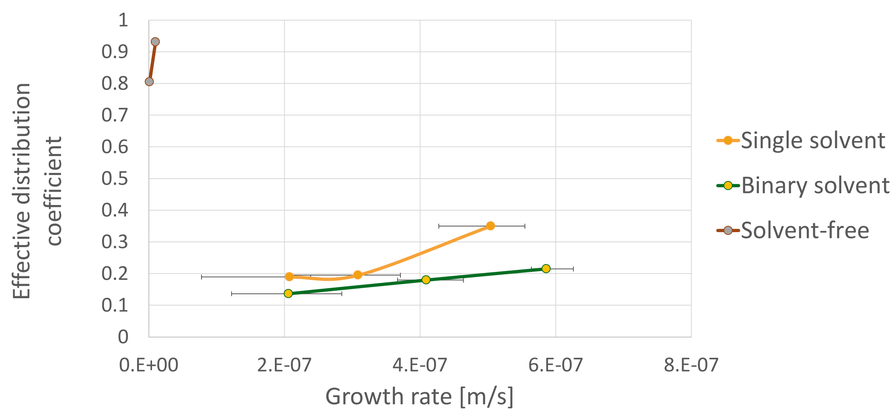
## Kinetics of crystal growth

- The addition of **binary solvent enhanced the crystal growth rate** in both crystallization stages.
- **The higher impurity content** in the first crystallization stage **decreased the crystal growth rate** compared to the second stage at the same degree of supersaturation.




## Purification efficiency

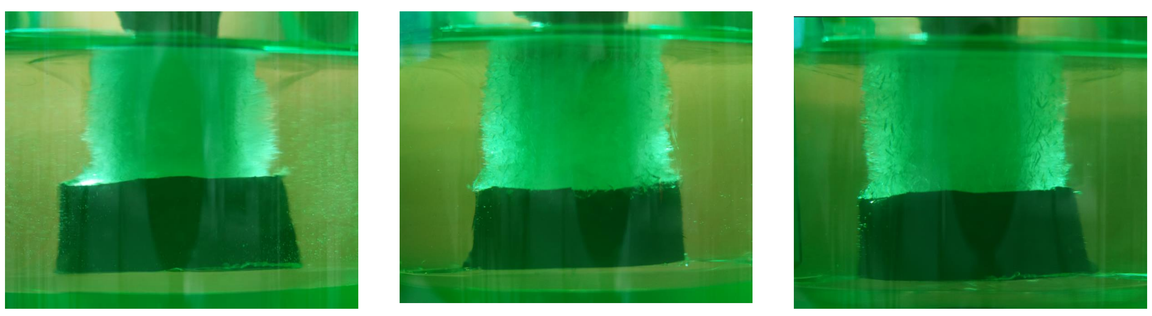
High impurity content in the crystalline product obtained from solvent-free system with slow crystal growth rate compared to the solvent-aided system.




- Crystal growth rate versus final product purity was measured for solvent-free and solvent-aided systems at **ΔT (UNIFAC-DMD) = 5, 10, 15**

## The effect of assisting solvents on the uniform growth of the crystal layer

The crystalline layer in the solvent-free system grew unevenly during the progressing crystallization. Addition of single and binary solvent led to uniform crystal growth at different degrees of subcooling.



Solvent-free system (ΔT=15) | Solvent-aided system (single solvent, ΔT=15) | Solvent-aided system (Binary solvent, ΔT=15)

## Conclusions

- Purification of glycerol via solvent-free layer crystallization showed poor purification at a relatively slow crystal growth rate.
- Addition of solvents increase product purity at higher crystal growth rates. A higher rate of crystal growth is preferred due to the shorter residence time required for crystallization.
- Employing binary solvent enhances both crystal growth rate and purity compared to the single solvent.
- An increase in the crystal growth rate in the second stage of crystallization with lower impurity content may indicate the role of the surface kinetics in the crystal growth rate.

## Acknowledgment

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