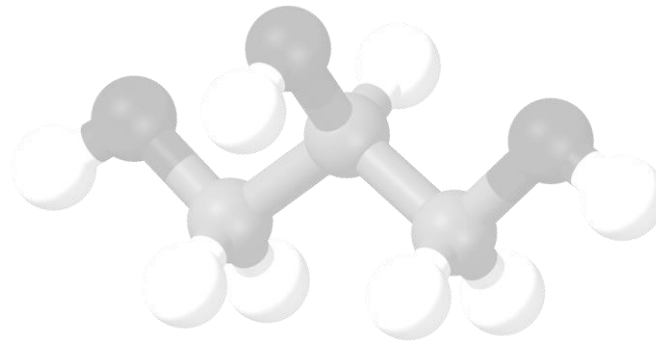


# Glycerol hydrochlorination: a process intensification approach using reactive distillation.

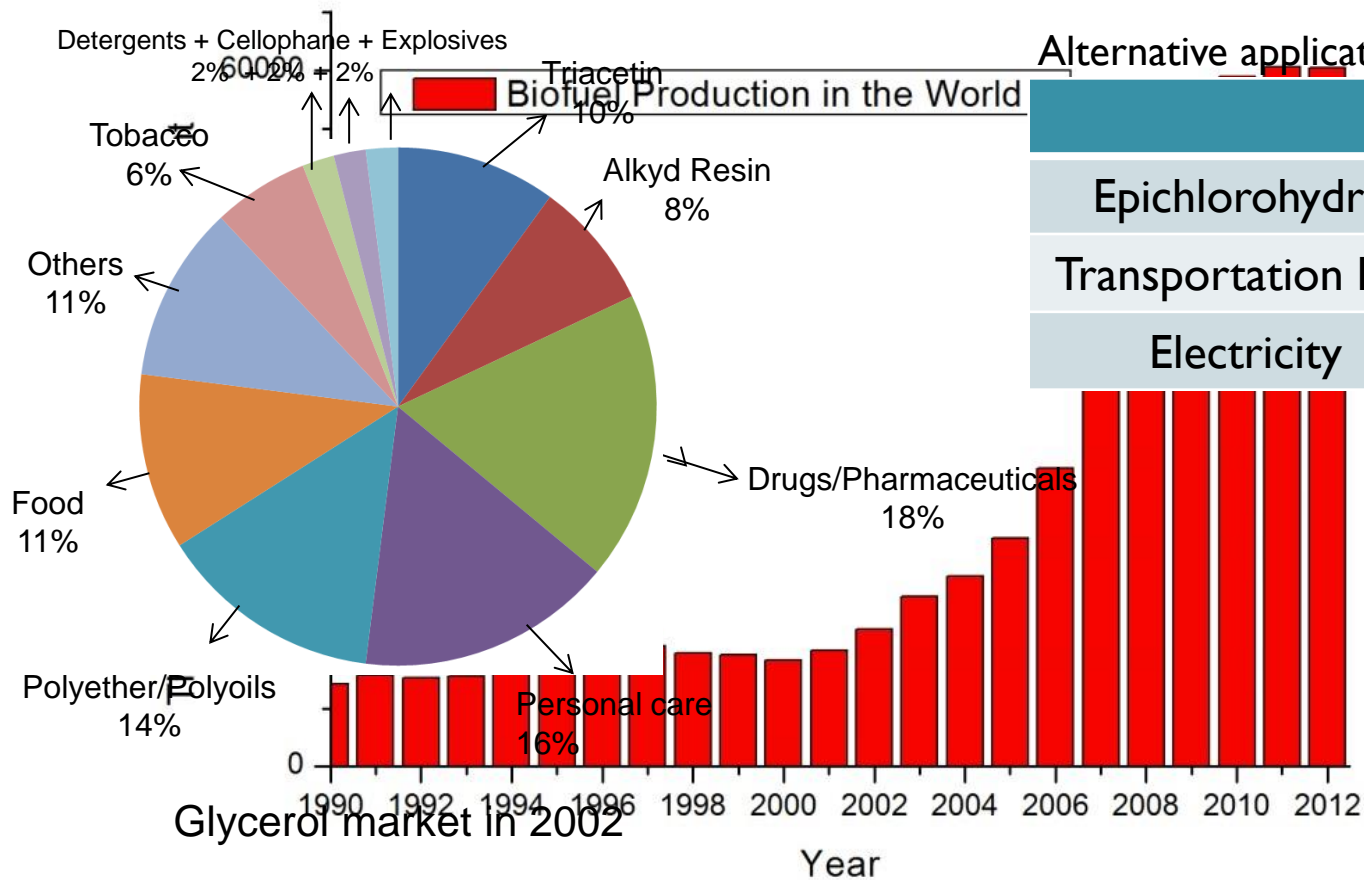


Cesar Araujo

Supervisors: Jyri-Pekka Mikkola and Tapio Salmi

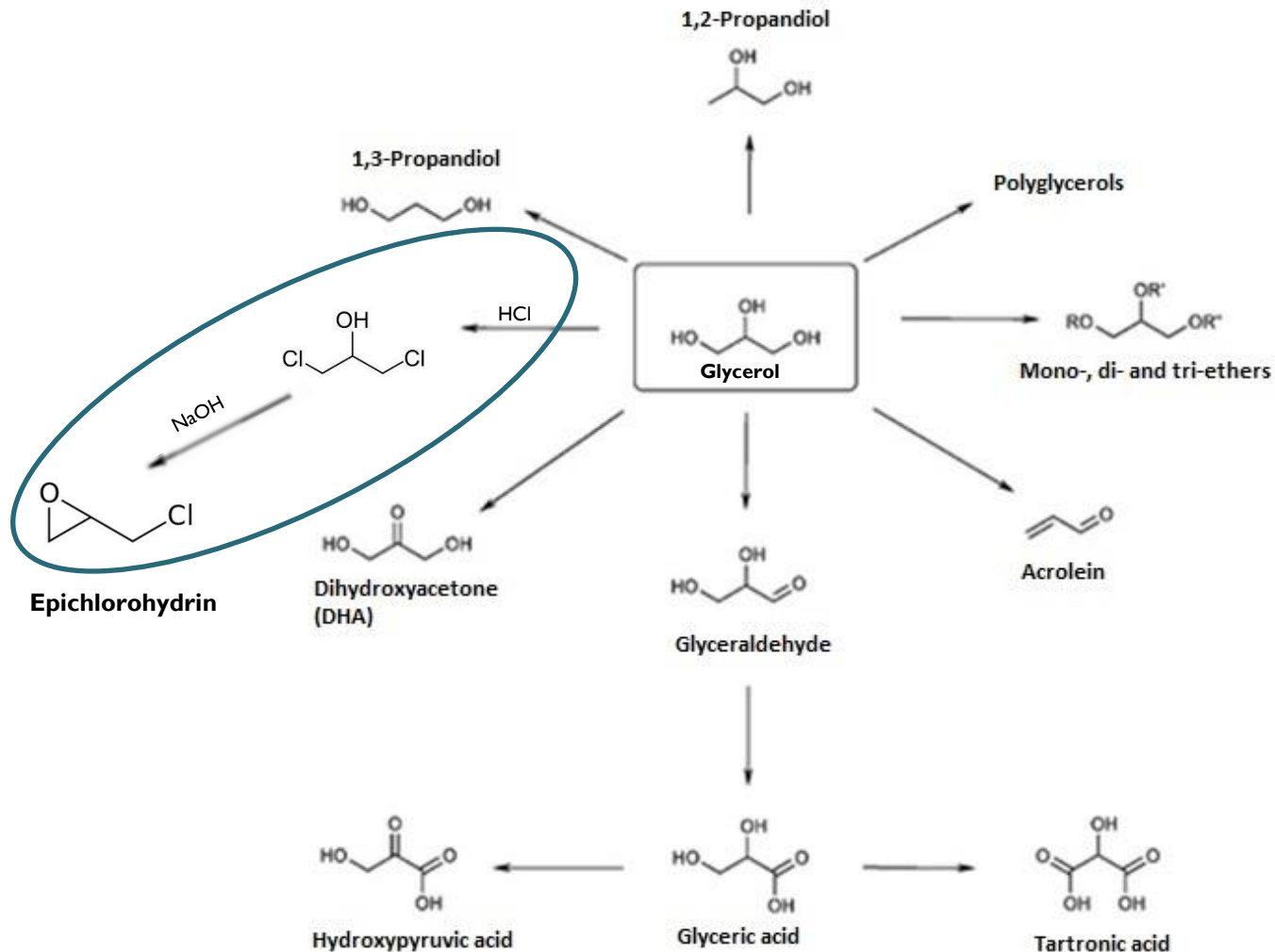
Saaremaa Summer School, August 2014

# Glycerol: From by-product to waste

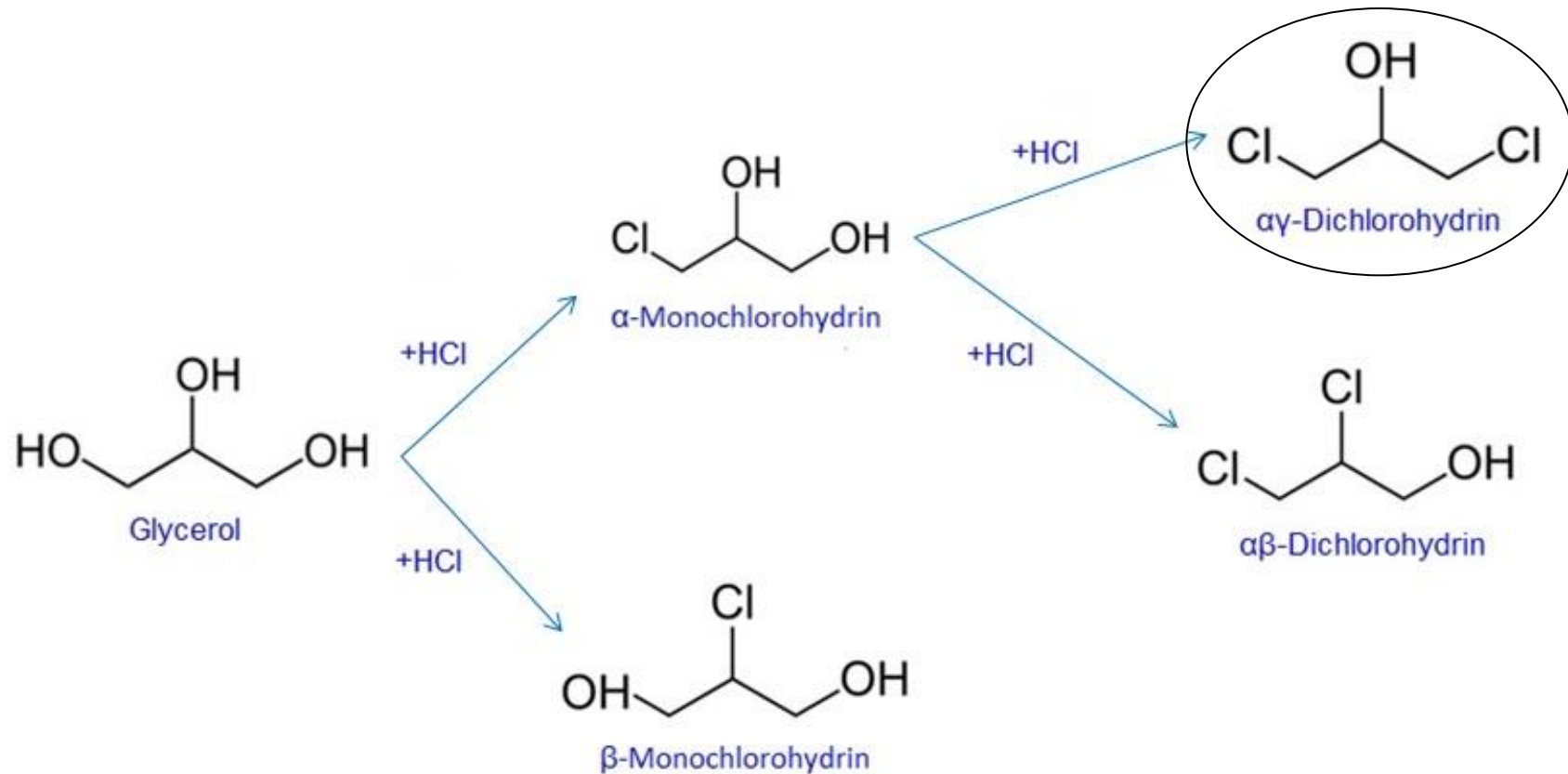


- ≈10 tones of glycerol /100 tones of biodiesel produced

# Glycerol Potential



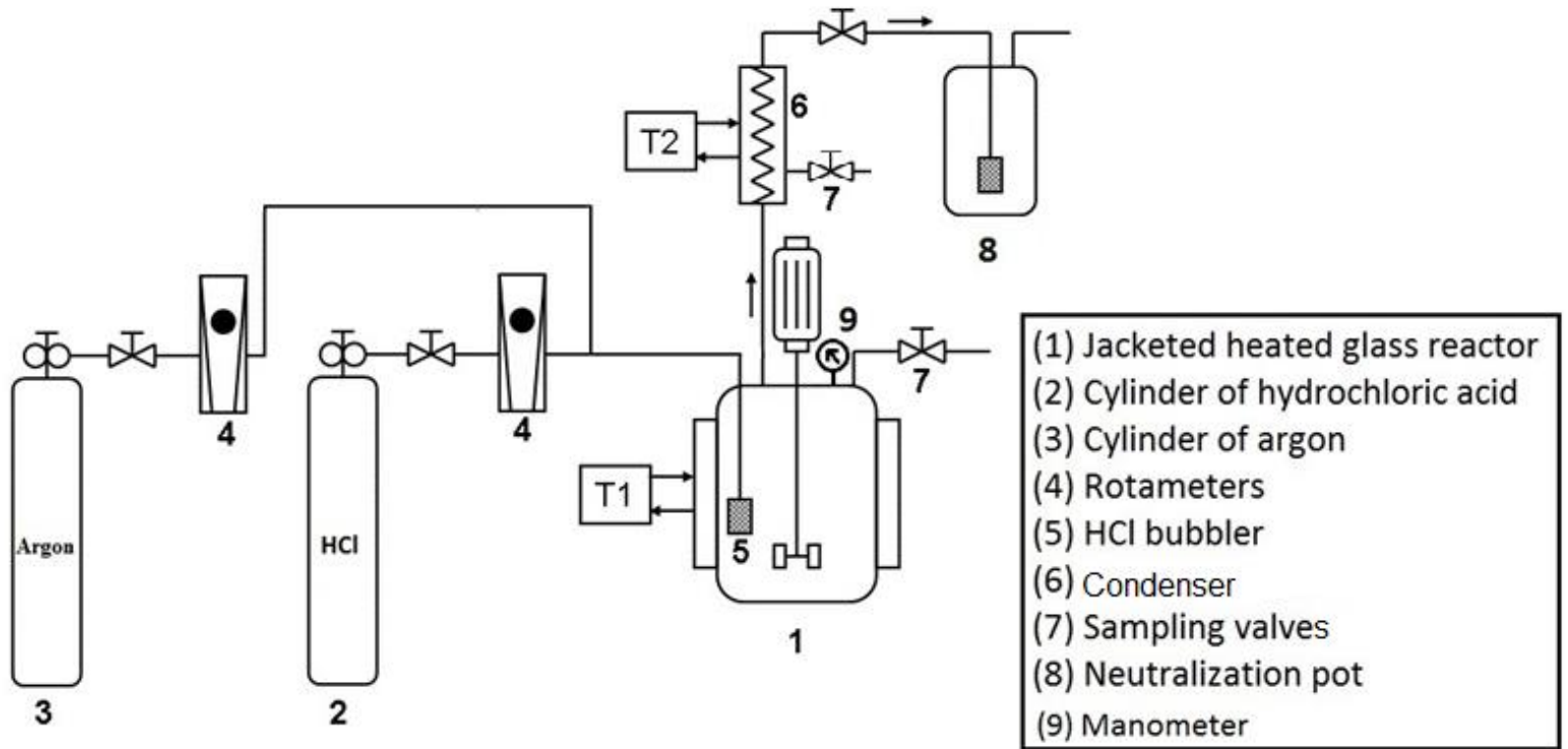
# Glycerol Chlorination: Overview



# Motivation

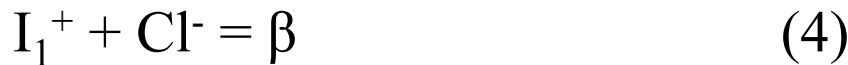
- Mechanism and kinetics revealed using semi-batch reactor mode. (*Accepted Manuscript, Chemical Engineering Science*)
- Next step: reaction intensification. Evaluate the performance of a coupled reaction-separation system, namely, reactive distillation

# Reaction Apparatus

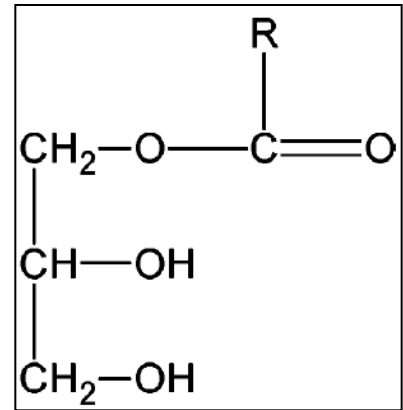
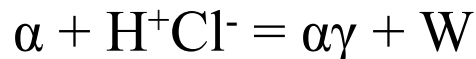
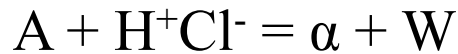


Analytical methods: Gas Chromatography and Acid-Base Titration

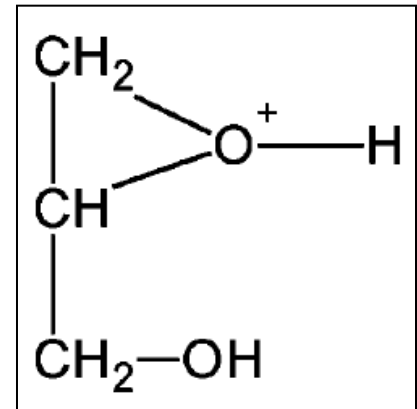
# Reaction Mechanism



Overall reactions:

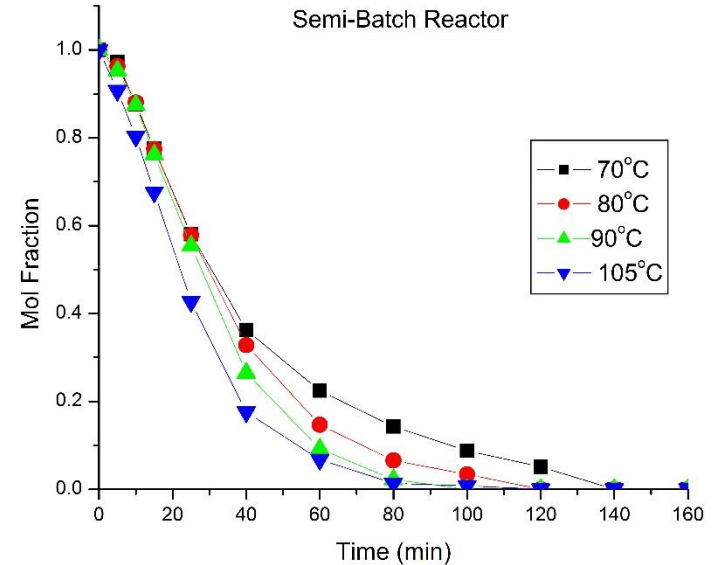
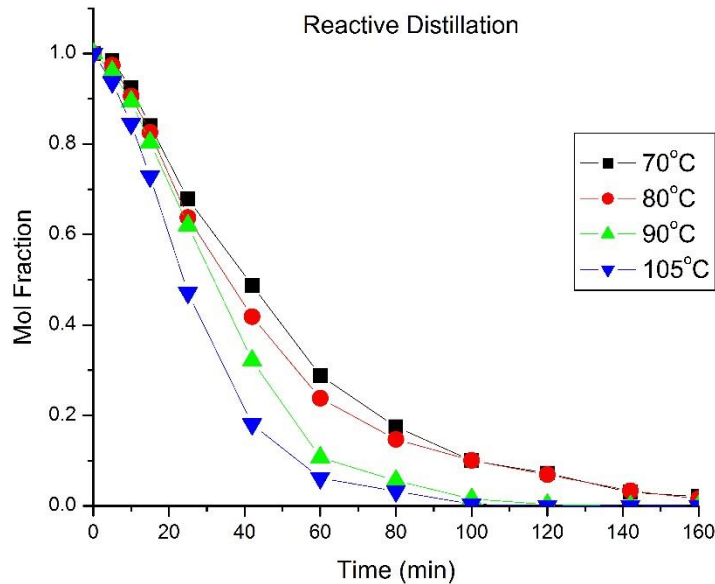


Ester ( $\text{E}_1$ ) Intermediate



Epoxide ( $\text{I}_1^+$ ) Intermediate

# Glycerol Conversion

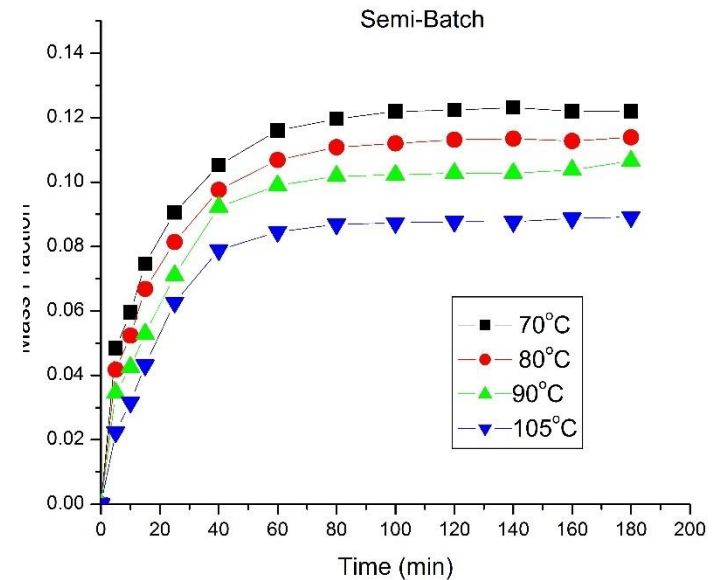
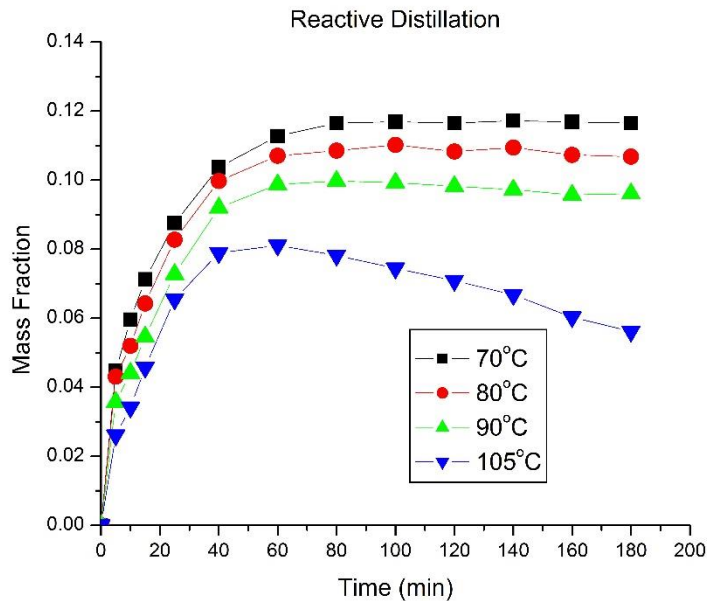


The temperature shows a slight bigger effect on the glycerol conversion in the reactive distillation system

\*12% of catalyst used in both reaction modes

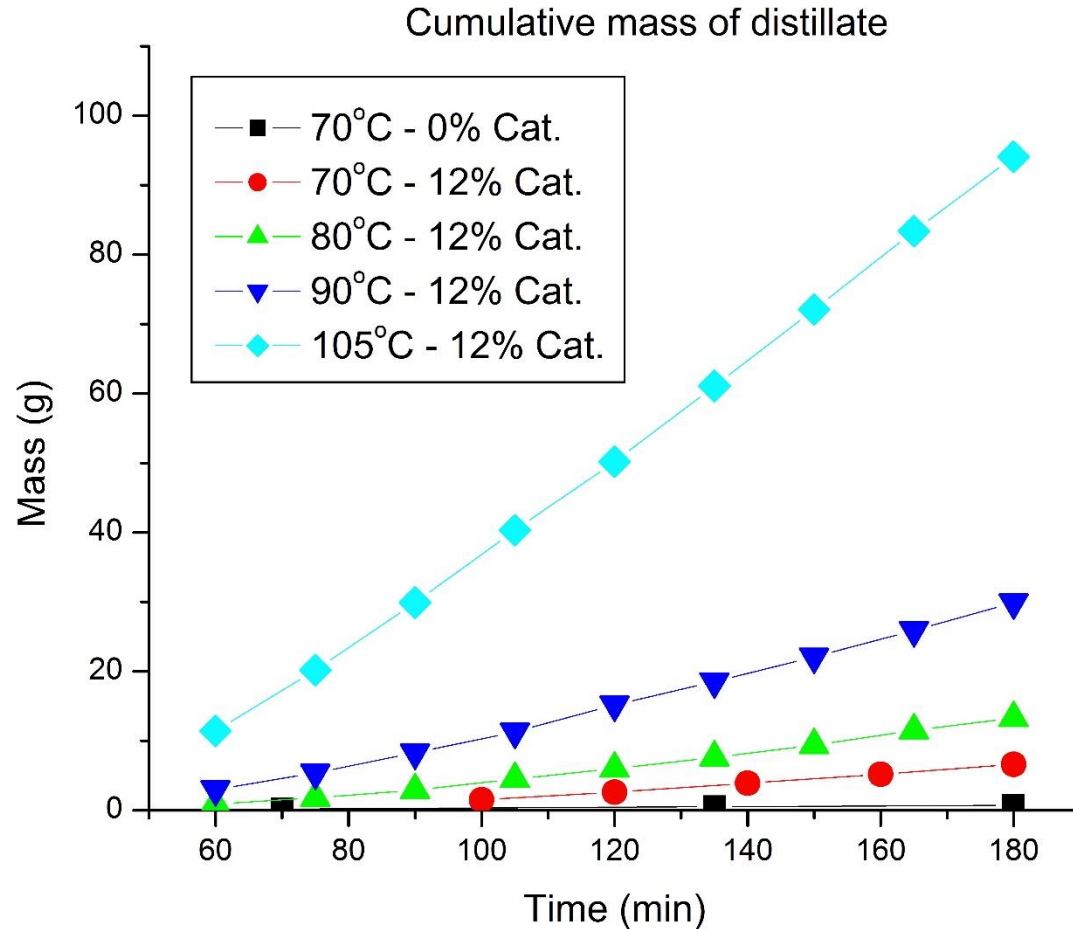


# HCl Liquid Uptake

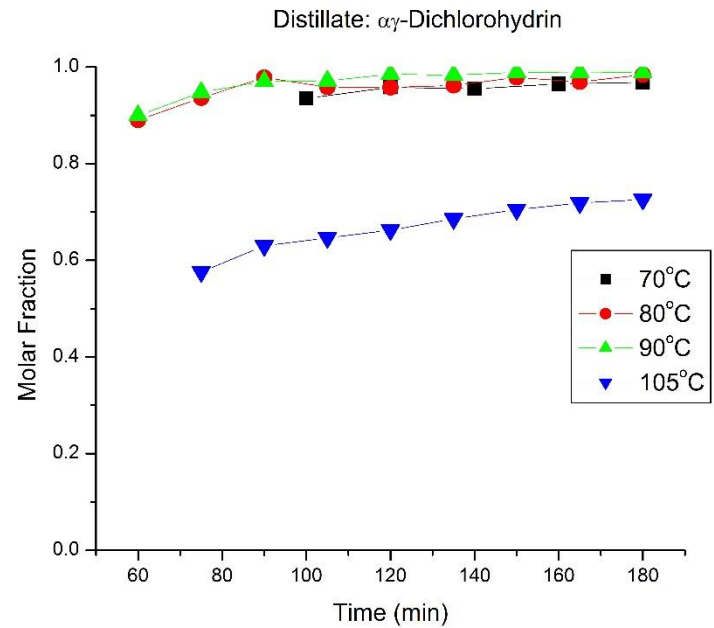
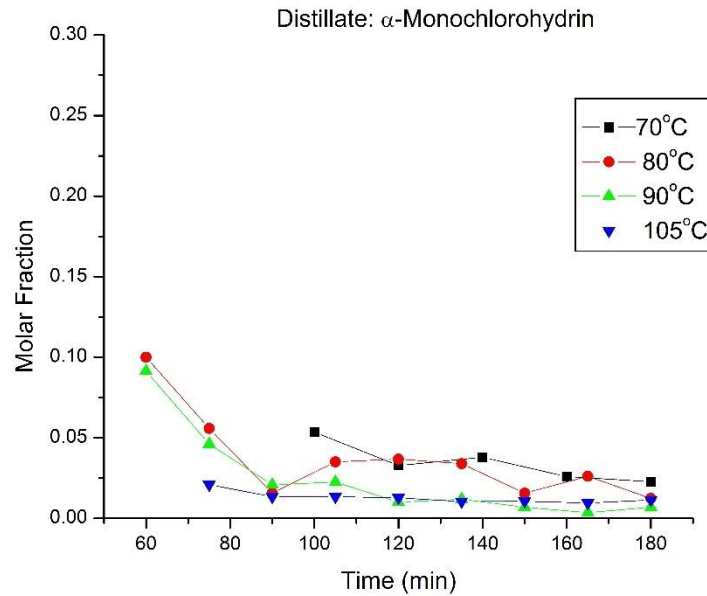


Significant change on the HCl liquid uptake behavior at 105°C may be explained by the water distillation from the system, diminishing the HCl solubility in the liquid phase.

# Distillate Analysis (I)



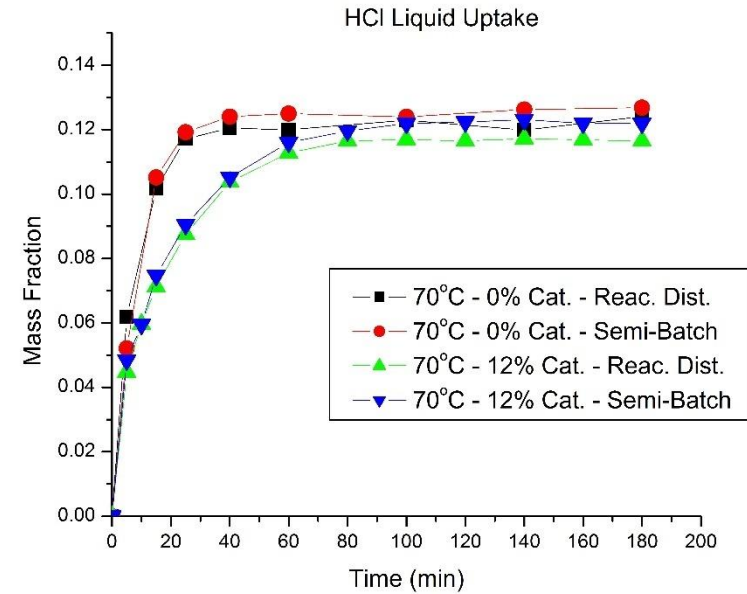
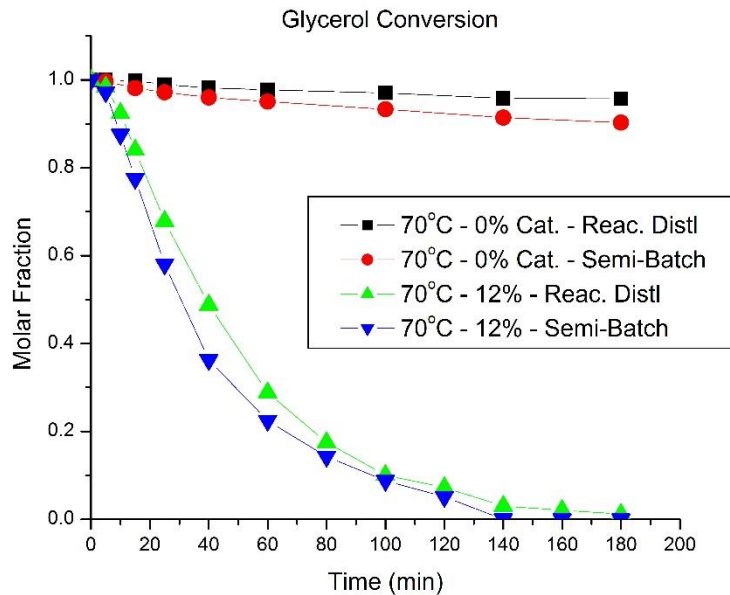
# Distillate Analysis (II)



Distillate analysis show a high selectivity to  $\alpha\gamma$ -Dichlorohydrin compared to  $\alpha$ -Monochlorohydrin

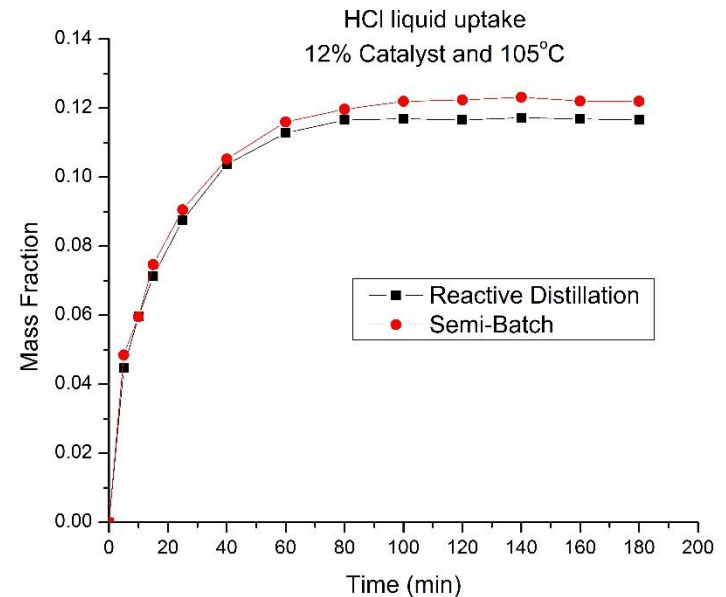
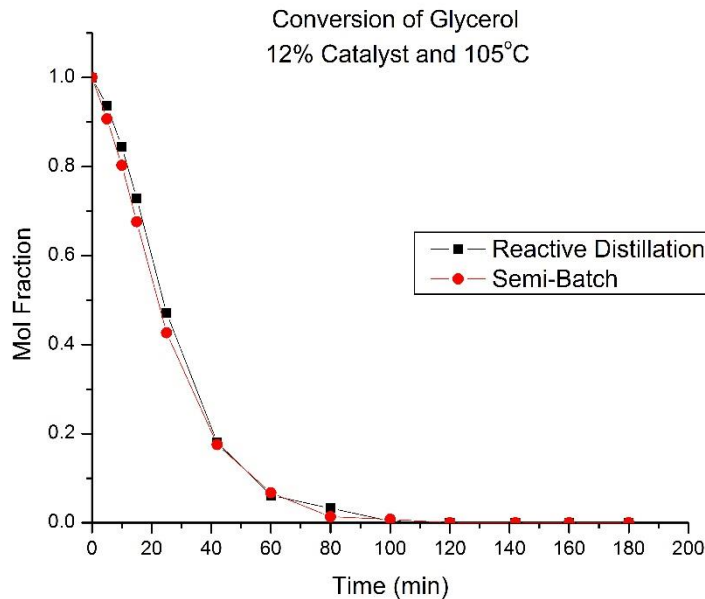
\*12% of catalyst used in both reaction modes

# Semi-Batch vs. Reactive Distillation (I)



The reactive distillation mode seem to decrease the reaction rate at 70°C.

# Semi-Batch vs. Reactive Distillation (II)



The reactive distillation mode seem to have little influence on the glycerol conversion and HCl liquid uptake compared to the semi-batch mode.

# Future

- More experiments are needed in order to fully cover the experimental matrix and ultimately draw the final conclusions. Although, it may be already observed that the reactive distillation system is not effective on increasing the reaction rates, it might serve as a good way to separate the desired product ( $\alpha\gamma$ -Dichlorohydrin).
- More details about the gas-liquid mass transfer of water and catalyst (acetic acid, B.P. 117°C) may be the key for explaining the observed behaviors.

# Acknowledgments



Thanks for your attention!