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Polysaccharide and lignin modification using reactive extrusion (REX)

Romain Milotskyi, Christophe C. Bliard

► **To cite this version:**

Romain Milotskyi, Christophe C. Bliard. Polysaccharide and lignin modification using reactive extrusion (REX). 14ème Journée scientifique du GFP Section Grand-Est, Jun 2016, Nancy, France. , 2016. hal-02297394

HAL Id: hal-02297394

<https://hal.science/hal-02297394>

Submitted on 2 Oct 2019

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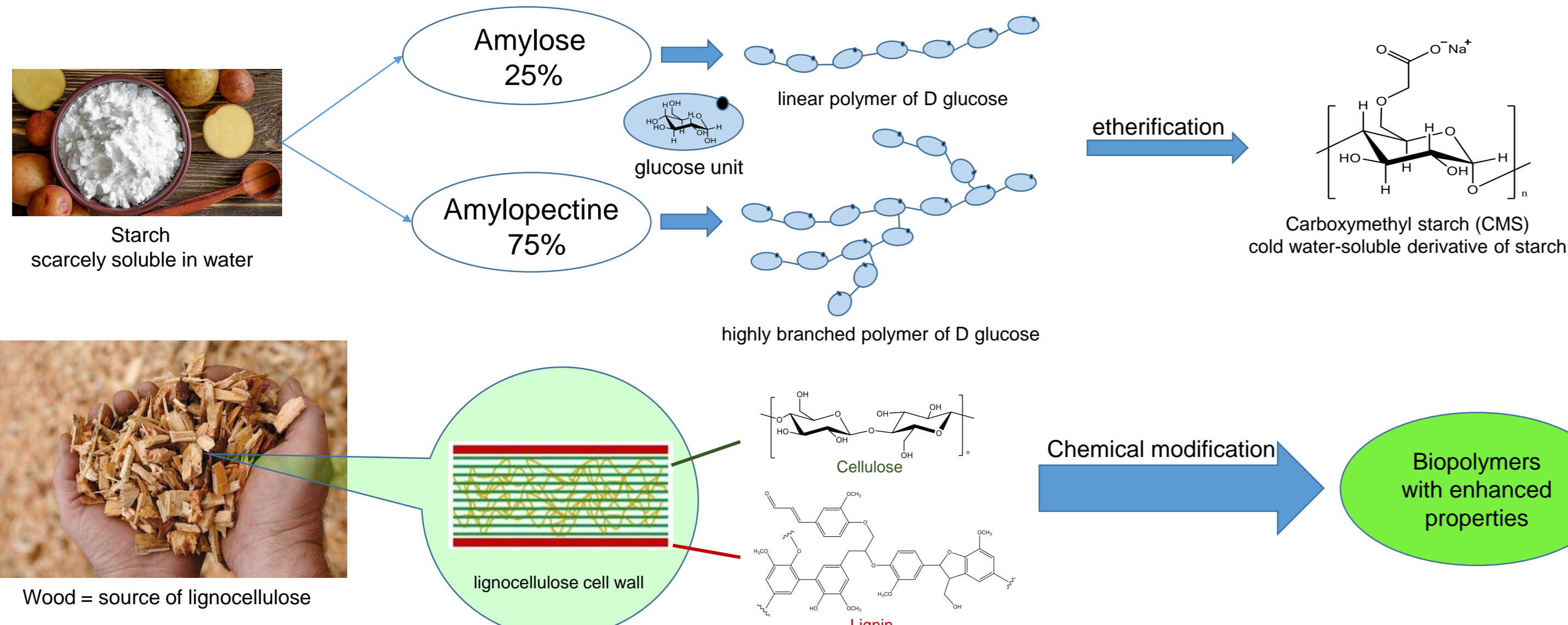


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Natural polymers possess physicochemical properties in their native state, which limit their use in many industrial sectors. Even limited chemical modifications radically change the properties of these macromolecular entities. Chemical modifications commonly performed at industrial-level production in solution or in batches [1] are often laborious and difficult to monitor. In addition, these processes suffer from energy cost and environmental issues caused by unreacted components and co-products. Reactive extrusion offers a simple process, using no solvents, shorter reaction time and improved efficacy [2-4].

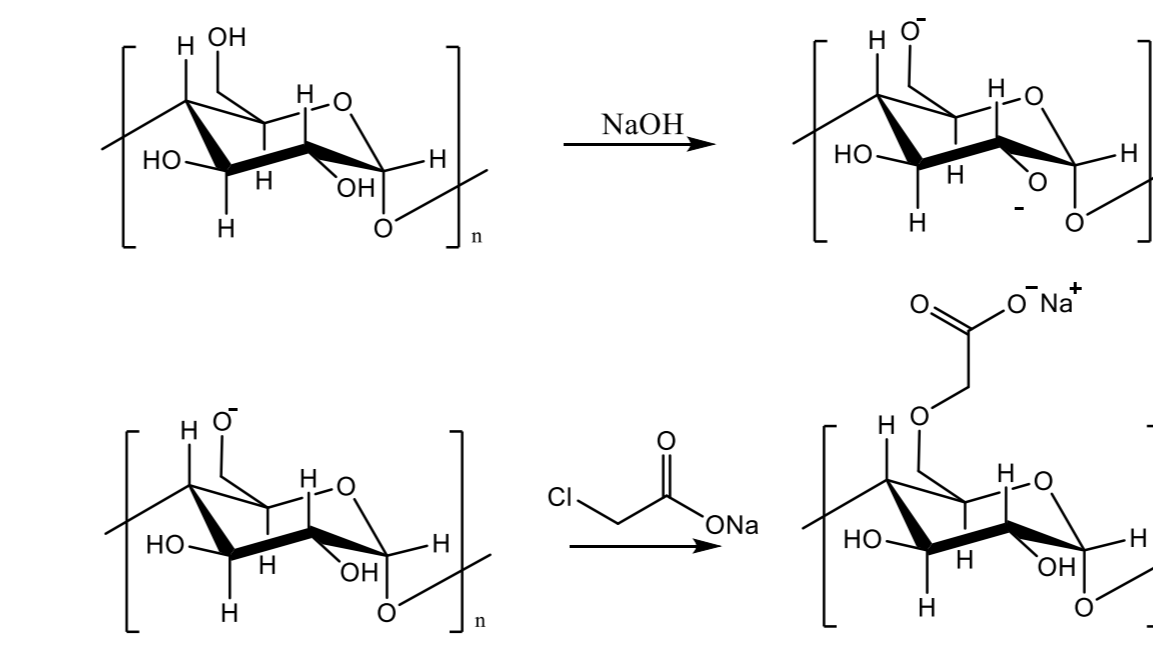
In the present work we describe a method of chemical modification using reactive extrusion process (REX). In this project three families of biopolymers: starch, cellulose and lignin are studied. In the following example carboxymethyl starches (CMS) with various degrees of substitution (DS) were synthesized in one step and with high levels of reaction efficiency (RE). The results on the distribution of the carboxymethyl functions on the three different positions of the glucose monomer as well as the kinetics of the reaction are analyzed and discussed.

Introduction

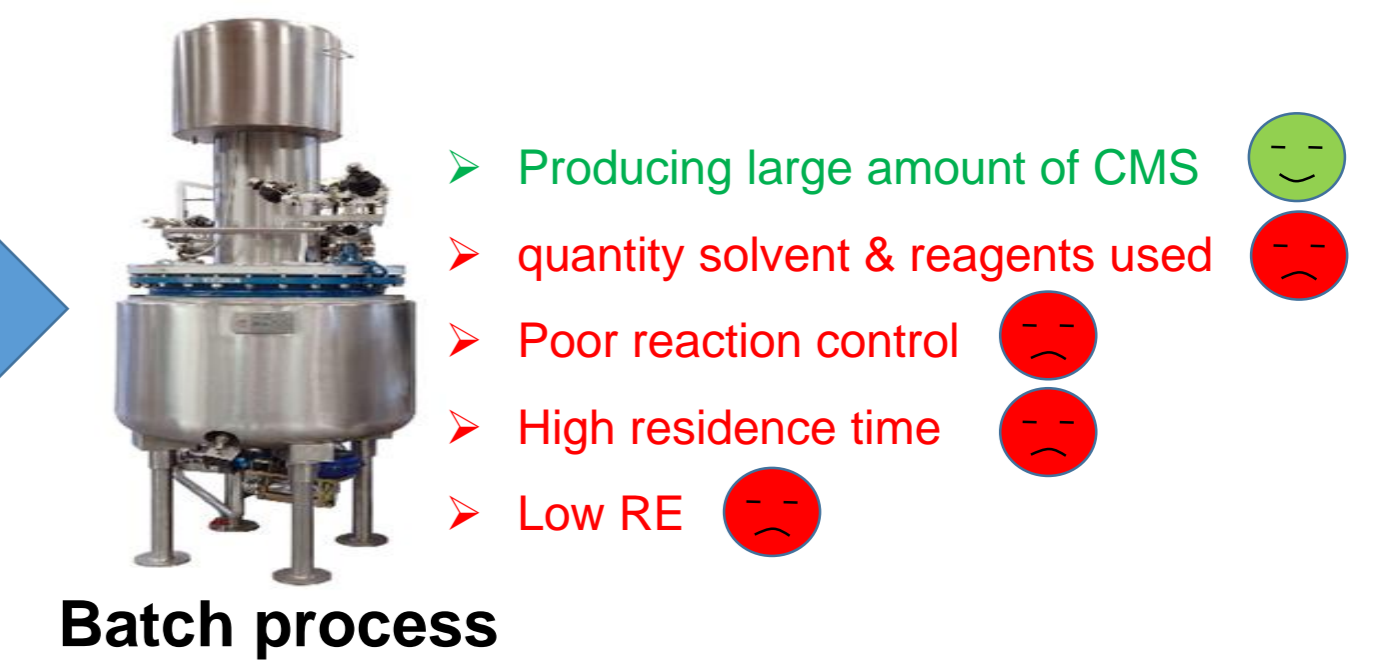


Industrial chemical modification

Industrial process of Starch carboxymethylation with sodium monochloroacetate (SMCA):



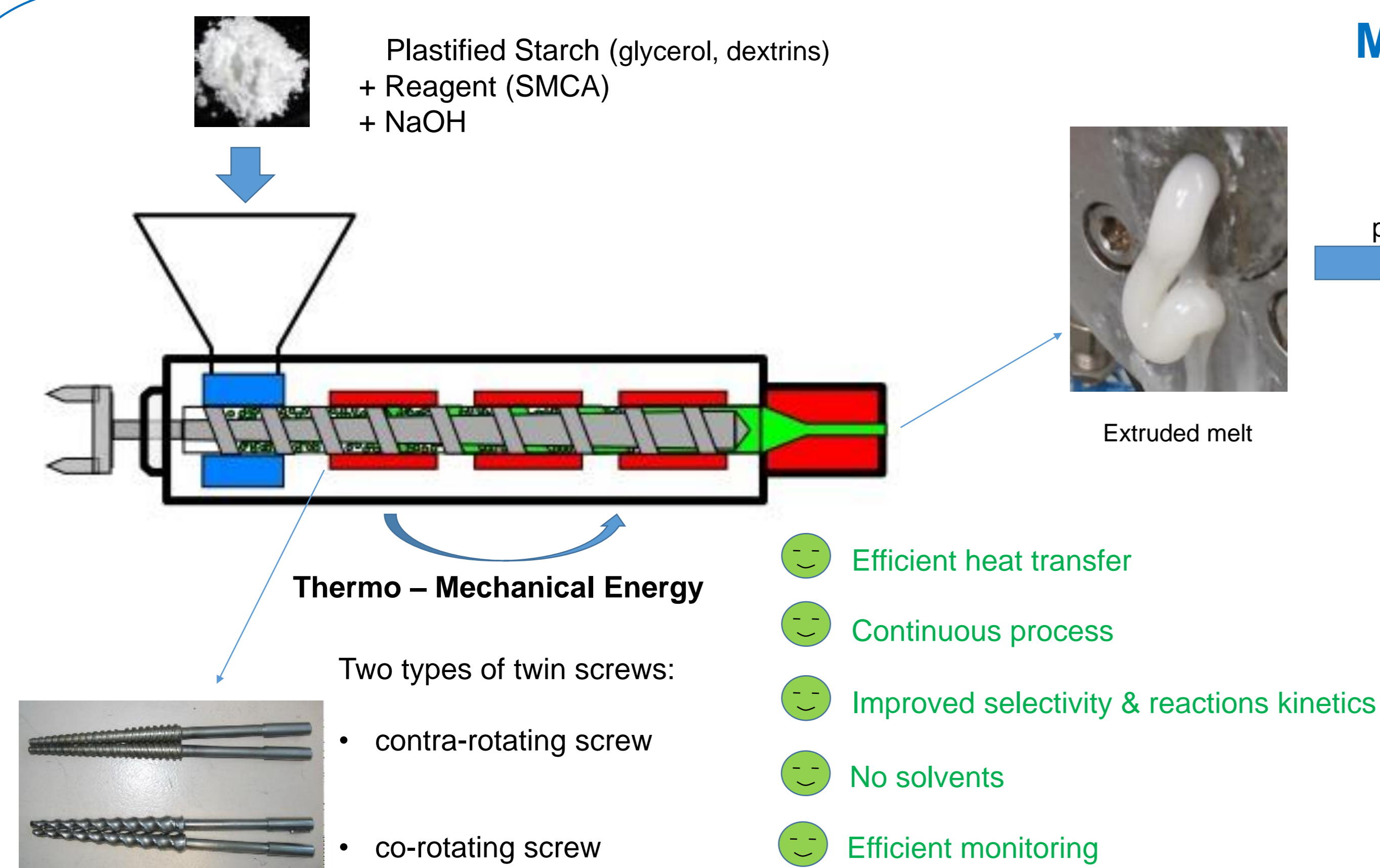
Industrial production



Batch process

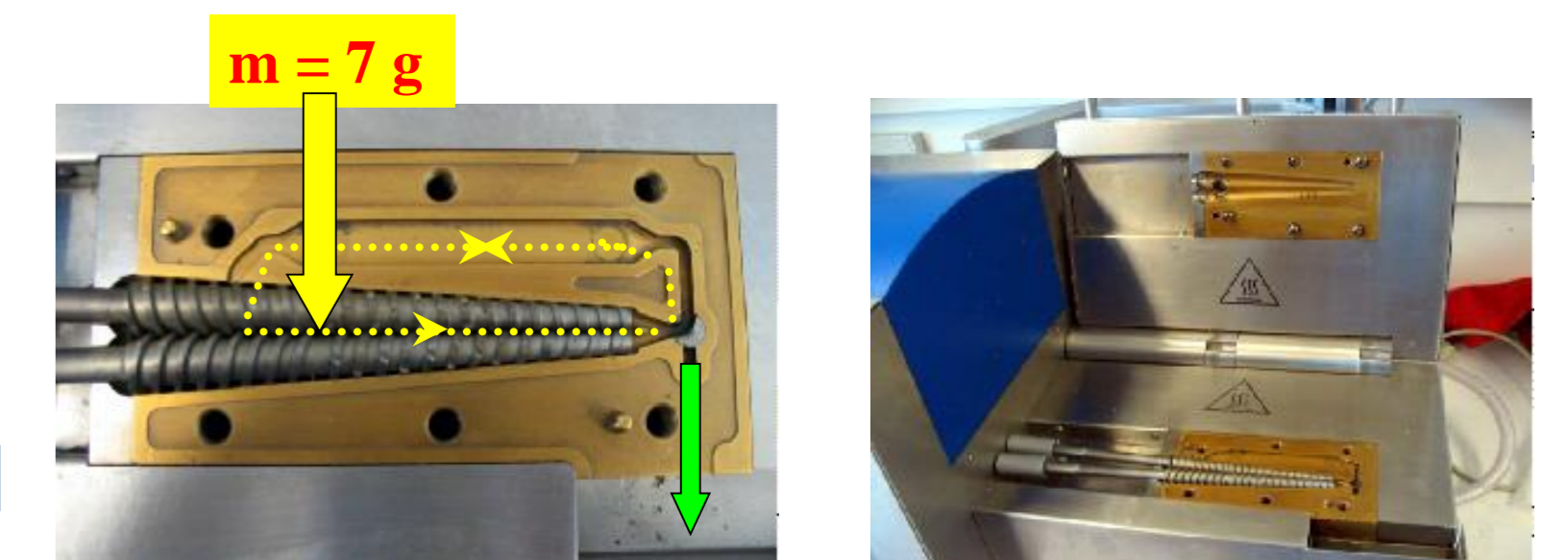
The substitution is shown only in the C6 position of the AGU for simplicity reasons here, but it can also occur at the C2 and C3 positions.

Modification using REX



Residence time fixed by process

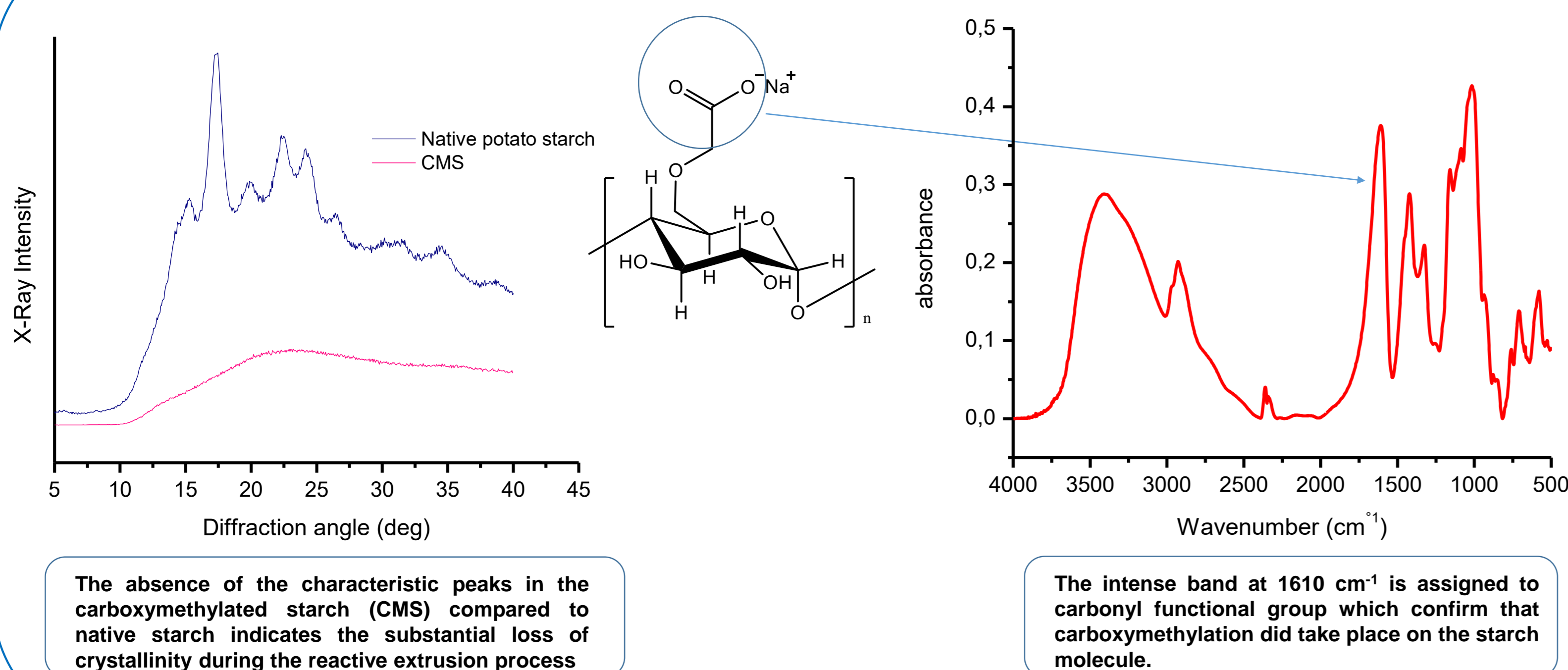
Recirculation mode Conical twin-screw micro compounder (Minilab Rheomex CTW5 Thermo Haake) :



- Co- and counter rotating conditions
- Bypass operation at the end of reaction time
- In flow viscosity measurement integrated in backflow channel in the range of $2 \cdot 10^4$ Pa*s
- Pneumatic feeding, option continuous or manual feed
- Temperature control
- Manual and computer control

Chemical kinetics study

Structural characterization



Distribution of carboxymethyl functions

The degree of substitution (DS) of CMS samples was studied by NMR. The samples of CMS were completely hydrolyzed to substituted monomeric glucose using H_2SO_4 .

Information about average distribution of the substituents is obtained from the hydrolyzed CMS 250 MHz NMR spectrum.

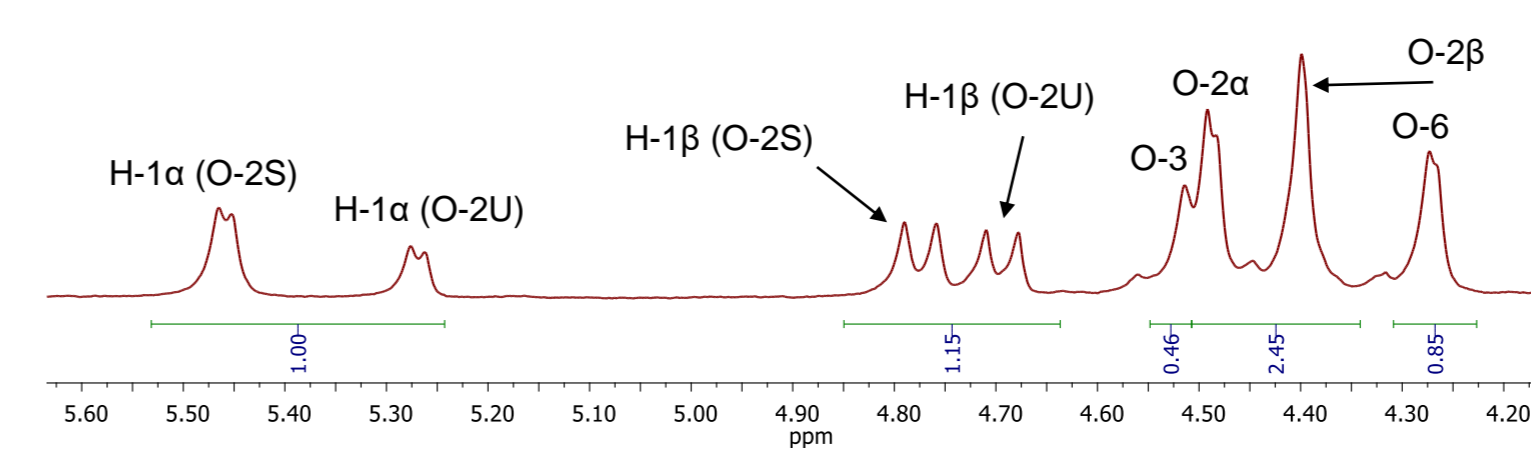
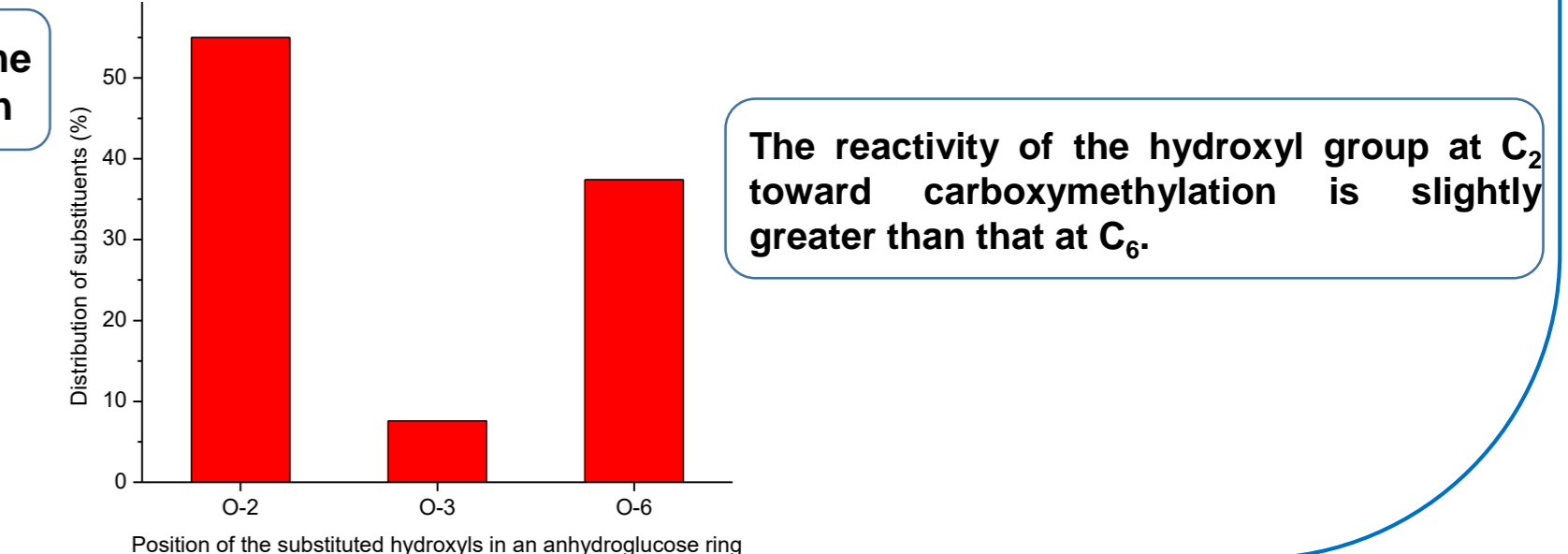


Fig 1 : Carboxymethyl groups distribution (%) in different types of starch

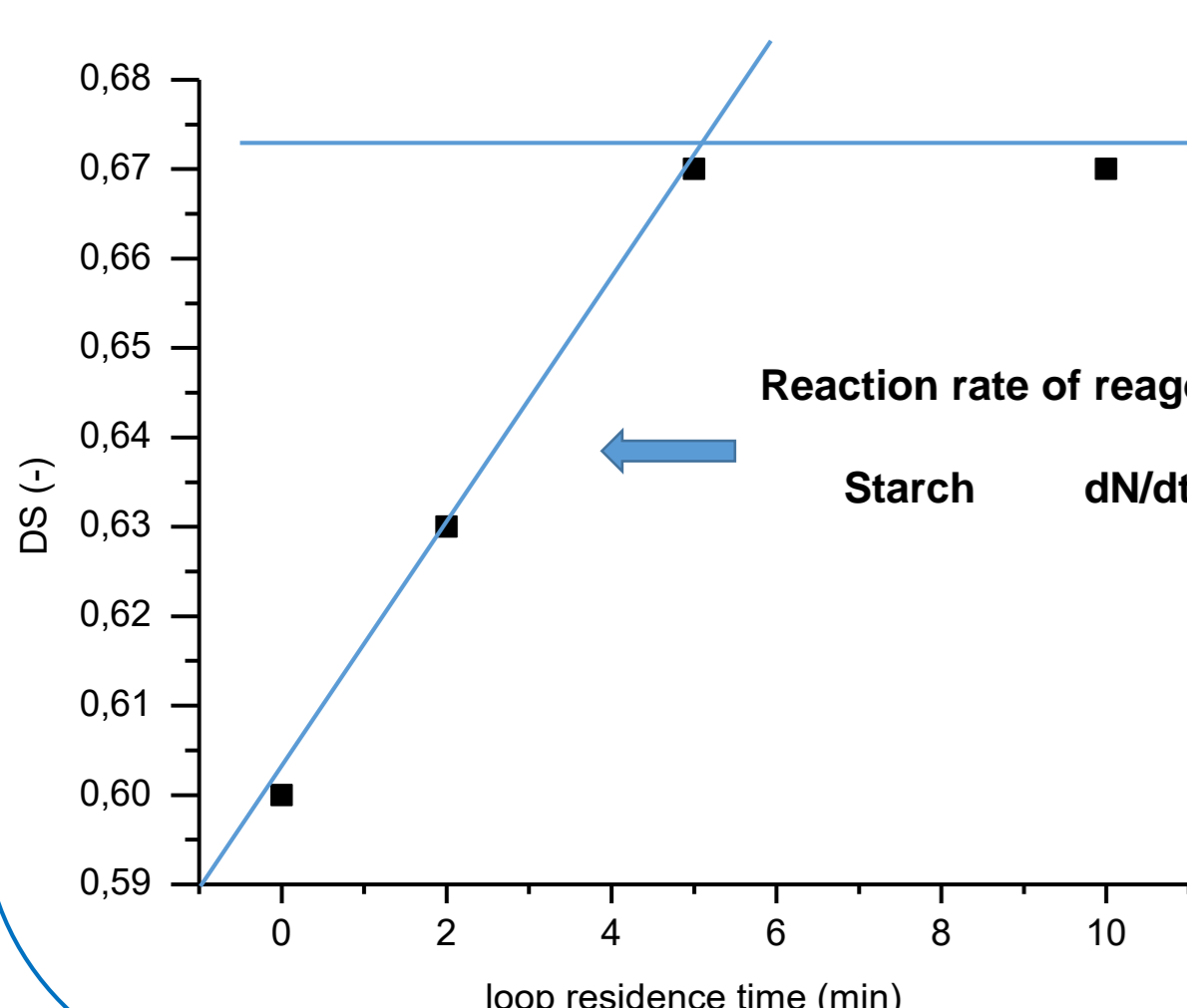
For ex. in (th.DS-1, 0.5 min reaction samples) show a higher 2-O-substitution. The distribution of carboxymethyl groups was in the order $0-2 > 0-6 > 0-3$, except in the case of corn starch where $0-3 > 0-6$.

Isolated fraction of amylose was modified with SMCA using the same reaction conditions in order to understand the carboxymethylation reaction



Kinetics study

The reaction kinetics was studied using loop (recirculation) mode of extruder by varying the residence time of the melt. Different residence times of the CMS samples were studied: continuous direct extrusion, 2 min, 5 min and 10 min.



It was found that the reaction was completed within 5 minutes with zero order reaction kinetics for the polysaccharide and Reaction Efficiency (RE) of 67%.

Zero order kinetics

Conclusions

- REX is a fast and efficient process for polymer chemical modification
- REX provides high reaction efficiency and selectivity
- Possibility of continuous on-line monitoring
- No apparent viscosity limits compared to other processes
- Kinetics of the reaction are optimal (zero order kinetics)
- Continuous process production
- Possibility to fit production with the demand

Perspectives

- Transfer the REX parameters to a bigger industrial scale

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⁴ Bhandari P.N., Jones D.D. and Hanna M.A. Carboxymethylation of cellulose using reactive extrusion, Carbohydrate Polymer 87, 2246-2254 (2012)