



národní
úložiště
šedé
literatury

Use of Microwave Heating in the Synthesis of Novel Polysaccharide Derivatives.

Taubner, T.
2015

Dostupný z <http://www.nusl.cz/ntk/nusl-263569>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

Tento dokument byl stažen z Národního úložiště šedé literatury (NUŠL).

Datum stažení: 10.04.2024

Další dokumenty můžete najít prostřednictvím vyhledávacího rozhraní nusl.cz.

USE OF MICROWAVE HEATING IN THE SYNTHESIS OF NOVEL POLYSACCHARIDE DERIVATIVES

TOMÁŠ TAUBNER^{a,c,*}, ANDRIY SYNYTSYA^a, JIŘÍ SOBEK^b, VERONIKA KORTÁNKOVÁ^a, and JANA ČOPIKOVÁ^a

^a Department of Carbohydrates and Cereals, UCT Prague, Technická 5, 166 28 Prague 6 Dejvice, ^b Institute of Chemical Process Fundamental, Czech Academy of Sciences, Rozvojová 135, 165 02 Prague 6 Suchbát, ^c Institute of Animal Science, Přátelství 815, 104 00 Prague 22 Uhřetěves, Czech Republic
TaubnerT@vscht.cz

Microwave-assisted modification of polysaccharides is a relatively new method. Microwave heating is used for improving of extraction, hydrolytic and synthetic procedures. Modification of polysaccharides with the microwave irradiation is effective, fast and economic. The aim of this study was to apply the microwave irradiation in synthesis of carboxymethylcellulose (CMC) derivatives. This polysaccharide and its methyl ester reacted with *n*-butylamine yielding *N*-butylamide. The reactions were subsequently monitored by FTIR and organic elemental analysis of the products. Degree of substitution (DS) and reaction yields were calculated based on nitrogen and carbon contents. The optimal reaction conditions were found to prepare product with the highest DS. Amino-de-alkoxylation of CMC methyl ester was significantly more effective than direct microwave assisted amidation of CMC, and microwave assisted significantly improved amino-de-alkoxylation.

Introduction

CMC (acidic or sodium salt) is a cellulose derivative with carboxymethyl (CM) groups $-\text{CH}_2\text{-COOH}$ bound by ether bonds to some of the hydroxyls in Glcp units that make up the cellulose backbone. CMC is widely used in food and pharmaceutical industries. It could be easily modified because of the presence of CM substituents. Introduction of alkyl groups onto CM moieties is possible by esterification with alcohols or amidation with alkylamines¹⁻³. Our goal was to find out how highly amidated CMC could be prepared. Microwave heating is known to be able to support extractions or chemical reactions. In this work microwave assisted reactions of CMC were compared and optimal reaction conditions were found to prepare highly substituted products.

Experimental

Materials and reagents

Acidic CMC was obtained by washing of commercial sodium salt of CMC (ROTH, Germany) with $0.4 \text{ mol} \cdot \text{l}^{-1}$ HCl in aqueous ethanol (80% v/v). *n*-Butylamine was purchased from Fluka (Germany). Organic solvents *N,N*-dimethylformamide (DMF), methanol, ethanol, acetone were purchased from Sigma Aldrich (Czech Republic).

Preparation of CMC derivatives

This work is focused on the amidation of CMC by two approaches (Fig. 1). First one included two steps: preparation of methyl ester of CMC and subsequent amino-de-alkoxylation of methyl ester with *n*-butylamine in DMF by specific reaction conditions and accurate procedure of purification. Another approach was focused on one-step direct amidation of acidic CMC with the same amine. The reactions were carried out using MicroSYNTH microwave reactor (MicroSYNTH, Milestone, USA). The aim of these procedures was to find optimal reaction conditions in microwave reactor for obtaining of highly substituted products. Power output was set on 150, 200 and 300 W. Microwave assisted reaction was conducted by temperature about 100 °C for 5, 7.5 and 10 min. Another approach included microwave assisted amino-de-alkoxylation of CMC methyl ester. Power output was set on 150, 150 (simultaneous cooling) and 200 W; reaction times were the same.

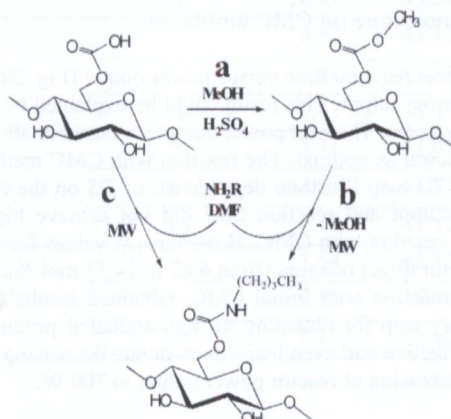


Fig. 1. Amidation of CMC: preparation of methyl ester (a), amino-de-alkoxylation (b) and direct amidation (c)

Analytical methods

FTIR spectra (4000–400 cm^{-1} , 64 scans, spectral resolution 2.0 cm^{-1}) of the initial polysaccharide and reaction products were recorded on FTIR spectrometer Nicolet 6700 (Thermo Scientific, USA) in KBr discs. The spectra were processed using Omnic 7.3 (Thermo Scientific, USA) and Origin 6.0 (Microcal Origin, USA) software. Organic elementary analysis (C, H, N) was made on Elementar vario EL III (Elementar, Germany). Degree of substitution (*DS*) was calculated according to the formulae:

$$DS = \frac{N \cdot 12 \cdot \left(6 + \frac{2 \cdot DCM}{100} \right)}{C \cdot 14 - N \cdot 4 \cdot 12} \times 100,$$

where *N* and *C* (% m/m) are nitrogen and carbon amounts, *DCM* is degree of carboxymethylation of initial CMC.

Results and discussion

Impact of microwave assistance on CMC amidation

FTIR spectra of CMC (sodium salt, acid and methyl ester) are shown in Fig. 2. Spectral changes confirmed subsequent modifications of carboxylic groups from COO^- to COOH and then to COOCH_3 . FTIR spectra (not shown) of CMC *N*-butylamides prepared by amino-de-alkoxylation of CMC methyl ester without microwave heating indicate no trace of band near 1740 cm^{-1} corresponding to COOH or COOCH_3 groups. New two bands were observed at 1680 cm^{-1} and 1510 cm^{-1} . These bands indicate newly formed amide groups. However, spectroscopic changes caused by direct amidation of CMC were significantly lower than in the case of two step reaction. By contrast, better results were observed for microwave assisted reaction with CMC methyl ester. The FTIR data well correlated with *DS* values based on the nitrogen and carbon contents.

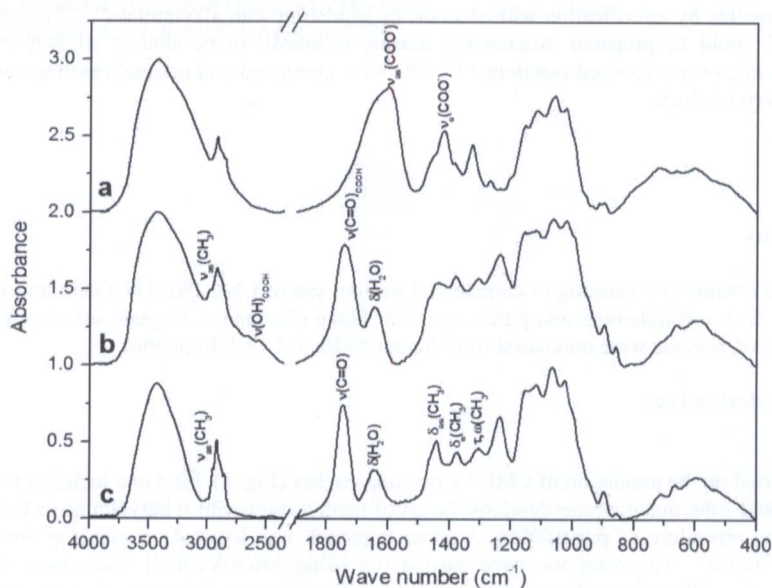


Fig. 2 FTIR spectra of CMC: sodium salt (a), acid (b) and methyl ester (c)

Influence of power output and reaction time on CMC amidation

From the 2D reaction map *DS* versus reaction time versus power output (Fig. 3 top) is evident that amidation decreases with longer reaction time and higher power output. This result could be explained by side effect of thermal degradation and cleavage of polysaccharide chain to oligomers. The best power output was used in all reactions of 150 W and a reaction time of 5 minutes. These conditions were chosen as optimal. The reaction with CMC methyl ester was more effective and led to significant substitution. Corresponding 2D map illustrate dependence of *DS* on the reaction time and power output (Fig. 3 bottom). Similarly, increasing power output and reaction time did not achieve higher amidation; the maximal *DS* was obtained at the same conditions like in reaction with CMC. However, *DS* values for methyl ester (from 43.61 to 84.03 mol %) were significantly higher than those for direct reaction (from 6.82 to 14.51 mol %). Therefore, the reaction of methyl ester of CMC was more effective than the reaction with initial CMC. Obtained results (Tab. I) support the claims that CMC esterification with methanol is necessary step for obtaining of high-amidated products. Tested simultaneous cooling with power output of 150 W was not very effective and even leads to moderate decreasing of *DS*. However, the cooling provided better results than results achieved by increasing of reactor power output to 200 W.

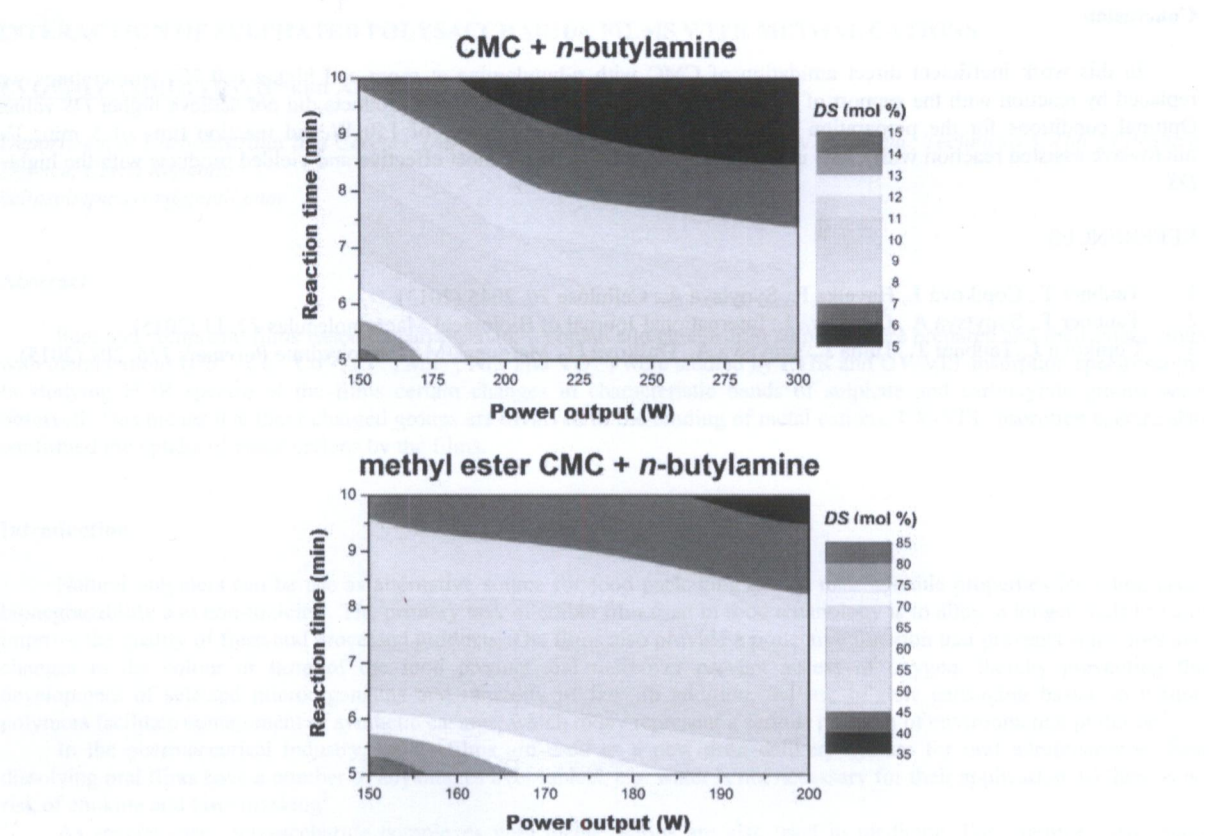


Fig. 3. 2D map of DS (mol. %) dependent on reaction time and power output of microwave reactor

Table I
Results from organic elemental analysis of microwave assisted reaction of CMC and methyl ester of CMC with *n*-butylamin by different reaction conditions

Polysaccharide	Power output [W]	Reaction time [min]	Content (% wt.)			DS [mol %]
			N	C	H	
CMC	150	5	0.99	46.65	6.20	14.51
		7.5	0.63	41.37	6.12	10.18
		10	0.41	39.50	5.92	6.82
	200	5	0.68	40.83	6.12	11.20
		7.5	0.48	41.37	6.12	7.66
		10	0.35	40.79	6.03	5.60
	300	5	0.66	41.22	6.00	10.74
		7.5	0.42	40.59	5.95	6.80
		10	0.31	40.24	5.87	5.02
Methyl ester CMC	150	5	3.93	43.12	7.26	84.03
		7.5	2.81	43.22	6.70	53.03
		10	2.42	43.47	6.56	43.61
	200	5	3.41	43.04	6.69	68.95
		7.5	2.62	43.52	6.77	48.08
		10	2.16	43.31	6.52	38.13
	150*	5	3.54	42.22	6.54	74.59
		7.5	2.46	39.48	6.14	50.22
		10	2.17	42.16	6.20	39.62

* simultaneous cooling

Conclusion

In this work inefficient direct amidation of CMC with *n*-butylamine at room and higher (60 °C) temperatures was replaced by reaction with the support of microwave heating. However, obtained products did not achieve higher *DS* values. Optimal conditions for the preparation of CMC *N*-butylamide were power of 150 W and reaction time of 5 min. The microwave assisted reaction with CMC methyl ester appeared to be the most effective and yielded products with the highest *DS*.

REFERENCES

1. Taubner T., Čopíková J., Havelka P., Synytsya A.: Cellulose 20, 2045 (2013).
2. Taubner T., Synytsya A., Čopíková J.: International Journal of Biological Macromolecules 72, 11 (2015).
3. Čopíková J., Taubner T., Tůma J., Synytsya A., Dušková D., Marounek M.: Carbohydrate Polymers 116, 207 (2015).