ISGC 2019 May 13rd - 17th

N°813 / PC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Anionic surfactants based on intermediates of carbohydrate conversion

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PURPOSE OF THE ABSTRACT

1. Introduction

Surfactants were first introduced 100 years ago and have become an important class of commodity chemicals. Their growing consumption leads to an increasing production and therefore an important goal is to reduce the CO2-footprint of surfactant-producing industry. To achieve greener processes, new bio-based surfactants and catalytic routes have to be developed. In the past, several studies on the synthesis of bio-based surfactants were published.[1]

In this work, we present the synthesis of novel anionic surfactants based on the platform chemicals 5?hydroxymethylfurfural (HMF) and furfural (FF), using stoichiometric and catalytic reactions. Starting from lignocellulose, a variety of possible substrates is accessible (Figure 1). Based on these, six different surfactants (1-6) with varying chain lengths were prepared (Figure 2). To assess their performance, industrially relevant properties such as critical micelle concentration (CMC) and interfacial tension were investigated.[2]

2. Results

Starting from hemicellulose, FF was converted into alkylated surfactants-precursors in a Grignard reaction with full conversion and yields above 96%. Complete hydrogenation of the alkylated product and subsequent sulfatation yielded surfactant 1 in quantitative yields. Applying furfuryl alcohol (FFA) in a Williamson etherification and subsequent sulfonation resulted in surfactant 2; however, cleavage of the surfactant and formation of dodecyl sulfate hindered isolation of the pure surfactant. Etherification of cyclopentanediol (CPD) was performed stoichiometrically via Williamson etherification or acid-catalyzed via homogeneous and heterogeneous acids. Subsequent sulfatation yielded surfactant 3. Utilizing cellulose, HMF was partially hydrogenated to 2,5-bis(hydroxymethyl)furan (BHMF) or completely to 2,5-bis(hydroxymethyl)-tetrahydrofuran (BHMTHF). Both compounds were alkylated via Williamson etherification or acid-catalyzed etherification. Sulfatation yielded surfactants 4 and 5, however, 4 was not stable and decomposed. Surfactant 6 was synthesized by alkylation of BHMTHF with an olefin over a zeolite. Here, yields of 32% and selectivities of 47% for the ether were achieved. Surface tension isotherms and interfacial tension towards isopropyl myristate were measured for the isolated surfactants, CMC was determined from the surface tension isotherms. All surfactants showed measurable values in a range of industrial used surfactants. Surfactant 6 was identified as most promising with a CMC-value for R=$C_{14}H_{29}$ of 0.02 g/L and thus performs competitively to an industrial used surfactant (CMC of 0.05 g/L).

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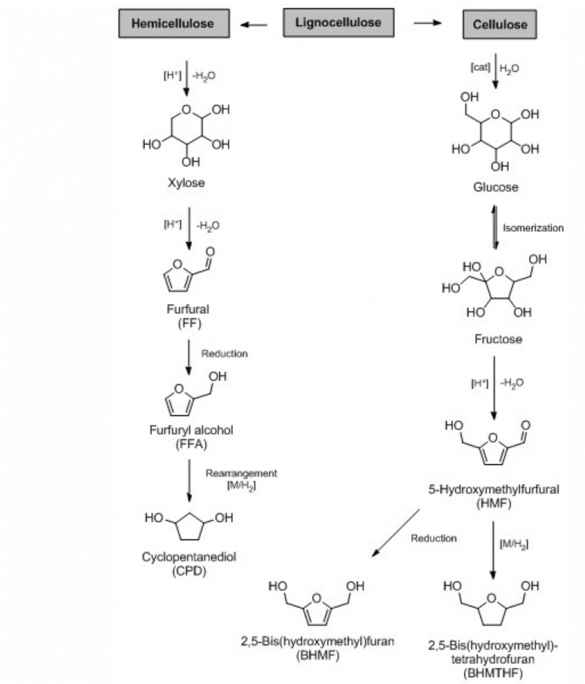
3. Conclusion

Surfactants 1-6 were synthesized based on HMF and FF derivatives. For their preparation, stoichiometric and catalytic etherification as well as sulfatation reactions were used. All surfactants showed measurable surface tension and interfacial tension values. Surfactants based on BHMTHF were identified as the most promising candidates for possible industrial applications. Variants with chain lengths of C14 exhibited the best results in terms of physico-chemical properties. These chain lengths are in well agreement with naturally occurring length of carbon chains e.g. in natural oils enabling a throughout preparation of biomass-based surfactants.

4. Acknowledgement

This research was funded by Henkel AG & Co. KGaA, Düsseldorf, Germany, as part of the Henkel Innovation Campus for Advanced Sustainable Technologies (HICAST) project.

FIGURES



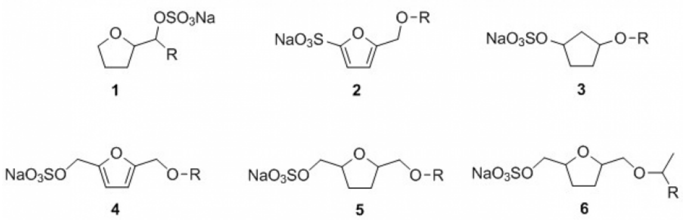


FIGURE 1

Feedstock and synthesis routes towards bio-based surfactant intermediates.

FF-based surfactants are derived from hemicellulose, HMF-based surfactants from cellulose.

FIGURE 2

Novel synthesized surfactants.

Structures 1-3 based on FF, 4-6 based on HMF

KEYWORDS

Surfactants | Biomass | Carbohydrates | Heterogeneous catalysis

BIBLIOGRAPHY