

Intensification of C5 and C6 Sugars Dehydration in an Agitated Cell Reactor

Abdullahi Adamu¹, Kamelia Boodhoo¹, Fernando Russo Abegão*¹

¹School of Engineering, Faculty of Science, Agriculture and Engineering, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

*corresponding: fernando.russo-abegao@newcastle.ac.uk

Introduction

The conversion of hemicellulose sugars into valuable furans, such as 5-hydroxymethylfurfural (5-HMF) and furfural, through acid-catalysed dehydration faces limitations such as low conversion of sugars, selectivity and yield of the furans. These challenges arise from the high reactivity of furans in aqueous media, with subsequent decomposition to side products and/or formation of humic residues. To address these limitations, extractive-reaction using an organic solvent as an extractive phase has shown promising results. This technique prevents the degradation of furans in the aqueous medium by isolation of the furans whilst into the solvent phase whilst still in reactor, thereby improving selectivity and yield.

The use conventional reactors (*e.g.* continuously stirred tank reactors and tubular reactors) has drawbacks due to high concentrations of reactive products in the CSTR and inefficient mixing for slow reactions requiring long residence times in the tubular reactors and/or impractically long reactor lengths. Intensified flow reactors present an alternative solution by decoupling mixing from residence time. An example of such an innovation is the Agitated Cell Reactor (ACR), which utilises freely moving agitators to enhance mixing and mass transfer. The ACR, designed based on these principles, finds applications in various processes and proves effective in significantly improving product selectivity and yields. Importantly, it intensified the reaction and mass transfer and enables shorter reaction times, making large-scale production economically feasible.

The aim of this study is to intensify the conversion of hemicellulose sugars into valuable furans through the application of an ACR and investigating the impact of residence time and biphasic systems.

Materials and Methods

In this study, a series of single-phase (*i.e.* aqueous) and biphasic (*i.e.* aqueous/MIBK) experiments were conducted in the ACR to investigate the dehydration process of a sugar solution containing D-(+)-Glucose and D-(+)-Xylose. The sugar solution, with a concentration of 7.5 wt%, was prepared by combining these two sugars in a mass ratio of 1:1. The experiments were conducted at 5 Hz agitation, 3.5-4 bar, 125 °C and with three pumps for dispensing: (1) the sugar solution, (2) the extractive phase (MIBK, used only in the case of biphasic experiments) at the volume ratio of aqueous to organic phase of 1:1, and (3) the catalyst solution (0.2 M sulfuric acid). The impact of residence times of 30, 60 and 120 minutes, corresponding to flow rates of 3.3, 1.7 and 0.8 mL/min in the ACR, was evaluated.

The reaction samples were analysed using high-performance liquid chromatography with Shodex SP0810 and Restek ROC C18 columns for the aqueous and organic phases analysis, respectively, combined with a photodiode array and refractive index detectors.

Results and Discussion

In both the single-phase and biphasic systems, residence time plays a crucial role. Longer residence times generally lead to more extensive sugar conversion as depicted in Figure 1. For single phase experiments, there was a slight increase in selectivity for both 5-HMF and furfural as the residence time increased from 30 minutes to 60 minutes (Figure 2). However, at 120 minutes, there was a slight decrease in selectivity for both furans. This decrease in

selectivity could be attributed to the significant formation of solid humins residue at the longer residence time. It was found that longer reaction times have a dual effect: on one hand, they lead to higher sugar conversion, but on the other hand, they also result in higher degradation of these furans. Despite this, the yield of both 5-HMF and furfural increases with increase in the residence time due to the increase in conversion, with the yield of furfural significantly higher than 5-HMF.

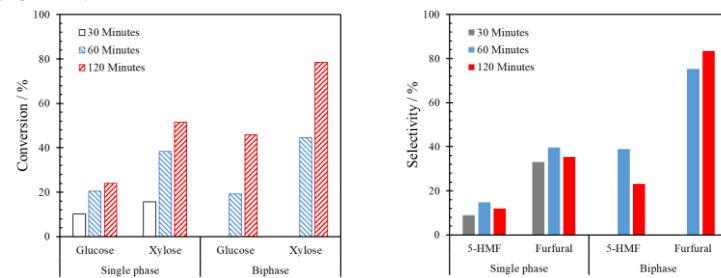


Figure 1. Glucose and xylose conversion at different residence time in single phase and biphasic systems.

Figure 2. 5-HMF and furfural selectivity at different residence time in single phase and biphasic systems.

The comparison of glucose and xylose conversion between the single phase and the biphasic system showed comparable values at 60 minutes, with glucose conversions of 20.5% and 19.1% and xylose conversions of 38.3% and 44.5% respectively. Nevertheless, a substantial increase was observed at 120 minutes, resulting in glucose and xylose conversion rates increasing to 45.9% and 78.5% in the aqueous/MIBK phase, compared to 24% and 51.5%, respectively, in the single phase alone.

In the biphasic system, the selectivity of 5-HMF at 60 minutes shows a remarkable increase by 1.64 times compared to the selectivity in the single phase alone. However, increasing the residence time to 120 minutes the percentage increase dropped to around 0.93 times in 5-HMF selectivity compared to the single phase alone. The total yield of 5-HMF and furfural at both 60 and 120 minutes is comparable, with 7.4% and 10.6% for 5-HMF, and while the selectivity for furfural almost doubled (33.5% and 65.5%). Furthermore, in the biphasic system, the yield of 5-HMF and furfural is more than doubled compared to that in the single phase alone at both 60 and 120 minutes. These findings indicate that the biphasic medium significantly enhanced furfural yield. When 5-HMF partition into the MIBK phase is lower than the partition of furfural¹. As a result, a significant portion of 5-HMF remains in the aqueous phase and subsequently leading to its conversion to humins, especially at longer residence time. On the other hand, furfural has a higher affinity for the MIBK phase due to its lower polarity compared to 5-HMF², leading to its rapid extraction into the MIBK phase and suppressing its degradation in the aqueous medium.

References

1. M. Sayed, N. Warlin, C. Hultberg, *et al.*, *Green Chemistry*, **2020**, *22*, 5402-5413.
2. J. Esteban, A. J. Vorholt and W. Leitner, *Green Chemistry*, **2020**, *22*, 2097-2128.

Acknowledgment

This project has received funding from the Bio-based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation program under grant agreement no. 887226. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio-based Industries Consortium.