Modeling inulin depolymerization through a Monte Carlo based approach

Riccardo Tesser[1*], Henrik Grénman[2], Tapio Salmi[2], Vincenzo Russo[1,2]

1 Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy;
2 Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku-Åbo Finland
**Corresponding author: riccardo.tesser@unina.it*

Highlights

- The reaction of inulin depolymerization was modeled by using a Monte Carlo based stochastic approach.
- The reaction mechanism of inulin chains fragmentation was encoded in the statistical approach.
- Numerical simulation and parametric study were developed, and a successful description of literature data was achieved.
- Detailed information about molecular weight distribution of the fragmentation products is obtained.

1. Introduction

The topic of polymer degradation and fragmentation is still a challenge from the viewpoints of chemical kinetics and reaction engineering, mainly when the interest is focused on the product distribution as the reaction proceeds and when a complex structure of the polymer is considered. In these cases, the classical deterministic approach presents strong limitations in the detailed description of complex reaction schemes and mainly in predicting product distributions. The depolymerization kinetics, both related to natural and synthetic polymers, can be tackled in a more rigorous way by using statistical approach such as the Kinetic Monte Carlo method [1,2].
In the present work, we propose a stochastic method that describes polymer fragmentation by assuming that a completely random process is operative during the reaction and that polymer chains can be cut through two different reaction mechanisms: (i) end-biting in which a terminal monomer is removed by bond scission of a chain resulting in a monomer concentration increase and (ii) chain scission in an internal random position giving place to chain fragments with lower molecular weight. This concept was applied in the present work to inulin hydrolysis. The structure of inulin is well suited to testing the developed stochastic model as the polymeric linear chains of inulin are constituted by sequences of fructose with a terminal glucose unit in both ends. The model including the double fragmentation route described above, can be used to accurately describe experimental data on inulin hydrolysis monitored by measuring the concentration of glucose and fructose concentrations as a function of time [3].
The model has two advantageous characteristics, which can be considered the main novelties of the model as summarized in the following points:
(i) the polymeric chains are described through characters encoding, allowing the flexible simulation of decomposition reactions;
(ii) a specific molecular weight distribution can be used as the starting point in the stochastic simulations instead of a monodisperse polymer solution. This aspect allows a more realistic simulation, as it is more representative of the real polymeric structures.

2. Methods

Monte Carlo algorithm, initially proposed by Gillespie [1,2], has been employed for the description of inulin fragmentation to simpler sugars units. The considered fragmentation mechanism is represented by the two following possibilities:

1) An Internal scission in a random position of the inulin chain:

$$G(F)_n G \xrightarrow{H^+} G(F)_k + G(F)_j \qquad j + k = n$$

2) End-biting of a terminal sugar:

$$G(F)_nG \xrightarrow{H^+} G(F)_n + G$$
$$G(F)_k \xrightarrow{H^+} G(F)_{k-1} + F$$
$$G(F)_k \xrightarrow{H^+} (F)_k + G$$

3. Results and discussion

Monte Carlo method has been applied to inulin depolymerization according to the kinetics mechanism described schematically in the previous paragraph. In the following Figure 1, the agreement between the model and the data from [3[is reported. the model was tested on literature data and RC experiments were conducted pulsing levulinic acid (6mol/L in ethanol) at *T*=303 K to a stream of ethanol, varying the volumetric flow rate. The UV spectra collected are reported in Figure 1A. As

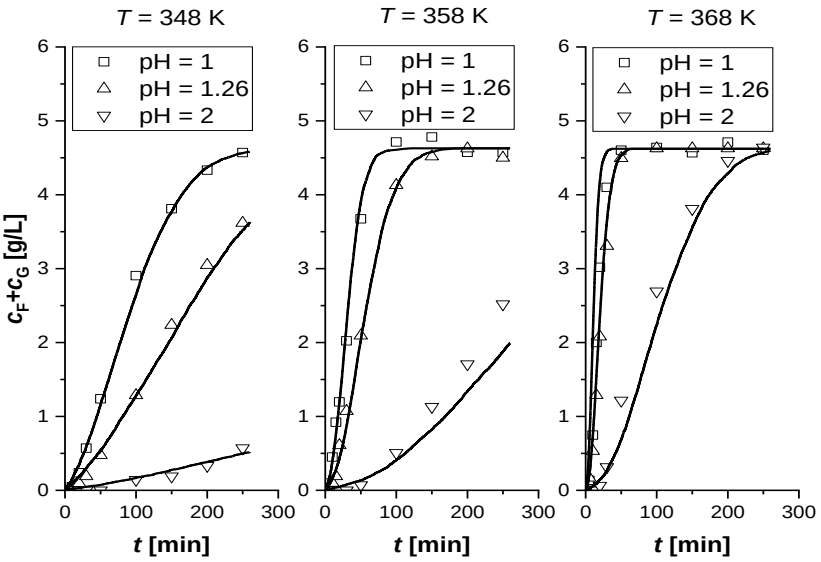

Figure 1. Evolution of the sum of fructose and glucose concentration vs the experimental time, for experiments conducted at different temperatures and catalyst loading (pH). Experimental data from [3].

4. Conclusions

A novel Monte Carlo approach was applied on the acidic hydrolysis of a naturally appearing polysaccharide inulin to fructose and glucose in the presence of a heterogeneous catalyst. The model consists in the case of inulin, of two parallel reactions, which differ in the type of reaction mechanism: (i) end-biting and (ii) intra molecular random cleavage. The model has a high flexibility in describing a wide variety of cases when a systematic sensitivity analysis was performed. It was demonstrated that the shape of the curves is directly related to the type of cleavage involved. Experimental data published in literature were correctly interpreted by the model, described in this work which enabled obtaining realistic and statistically significant values of kinetic parameters.

References

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Monte Carlo Simulation, Polysaccharides, Inulin Hydrolysis, Depolymerization.