

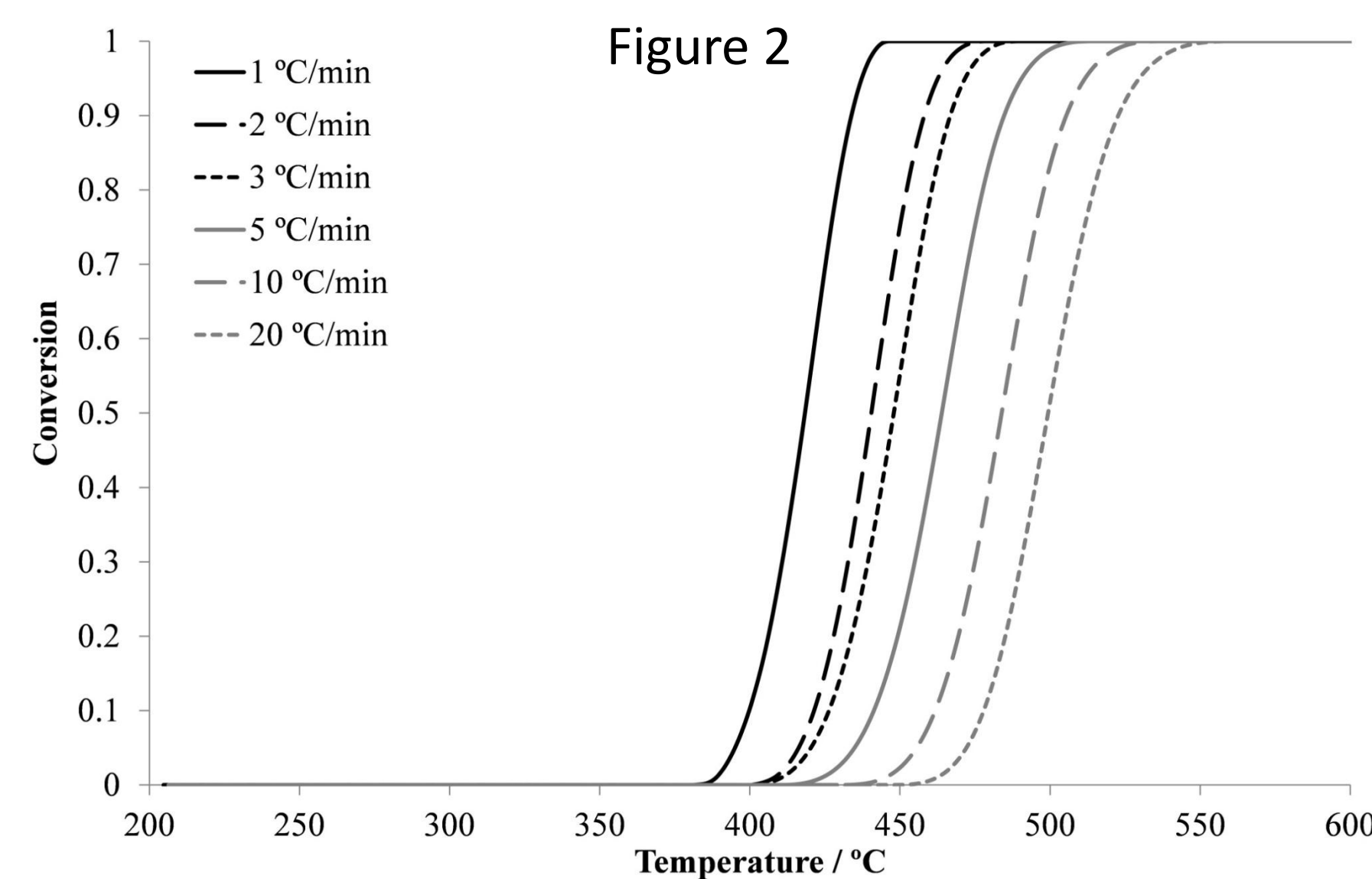
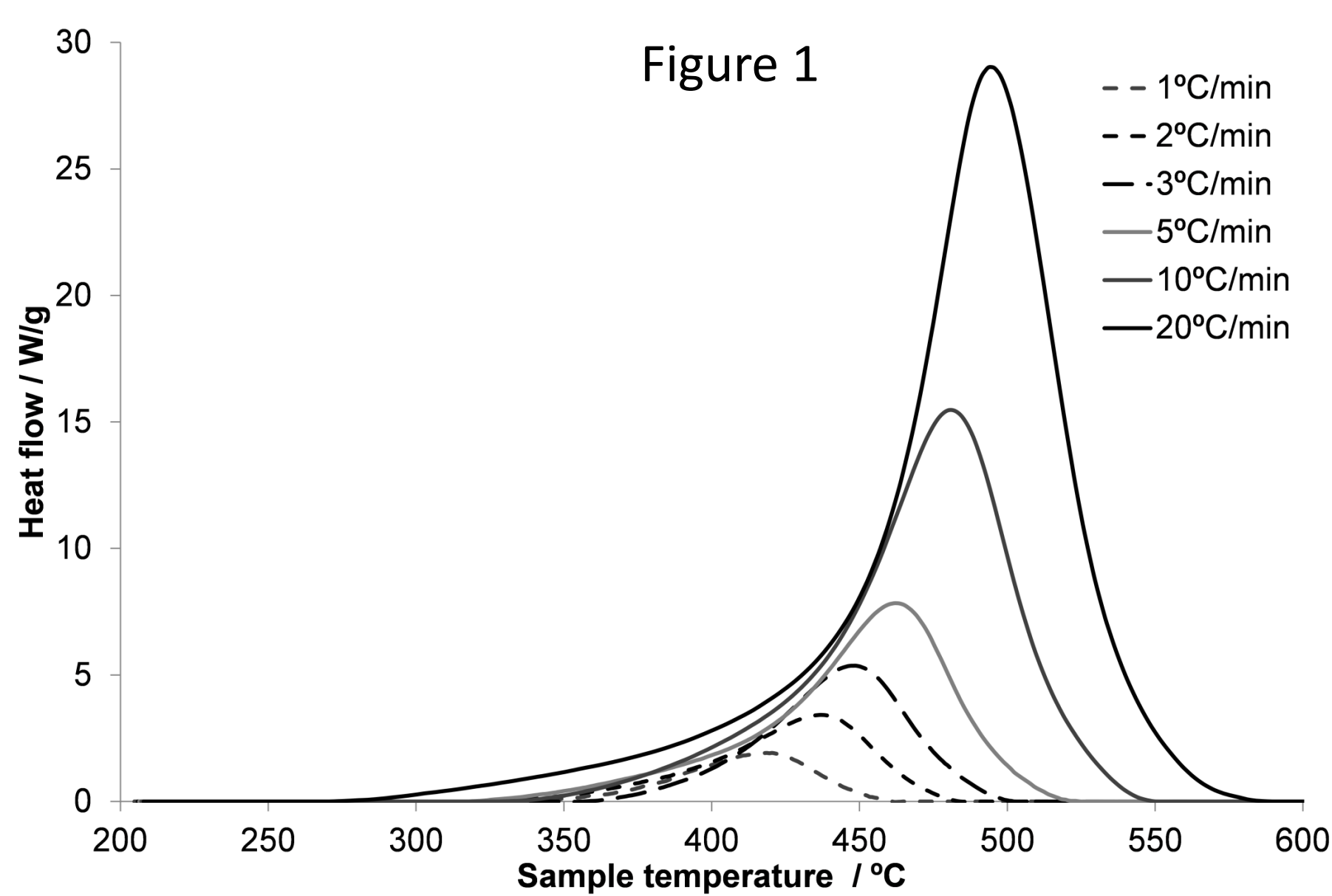
Sempere, J., Nomen, R., Serra, E. and Sempere, B.  
IQS School of Engineering. Universitat Ramon Llull. Via Augusta, 390. 08017 Barcelona (Spain).  
[julia.sempere@iqs.url.edu](mailto:julia.sempere@iqs.url.edu)

## Introduction

Working with nanoscale structured materials constitutes one of the major subjects for investigation. In addition and there is a big lack of knowledge when talking about safety. The behavior of these type of materials is still unknown in many times and it is suspected that the classical models do not provide satisfactory results.

In the present work the use of the Non-Parametric Kinetics (NPK)<sup>1</sup> method is applied for the oxidation of titanium nitride and titanium carbide (supplied by Flubetech S.A.) to assess its validity for nanoscaled samples. This method was developed for simulation purposes but also allows the determination of kinetic parameters without having to assume any functionality for the function of temperature (activation energy) or the function of concentration (reaction mechanism).

## Experimental

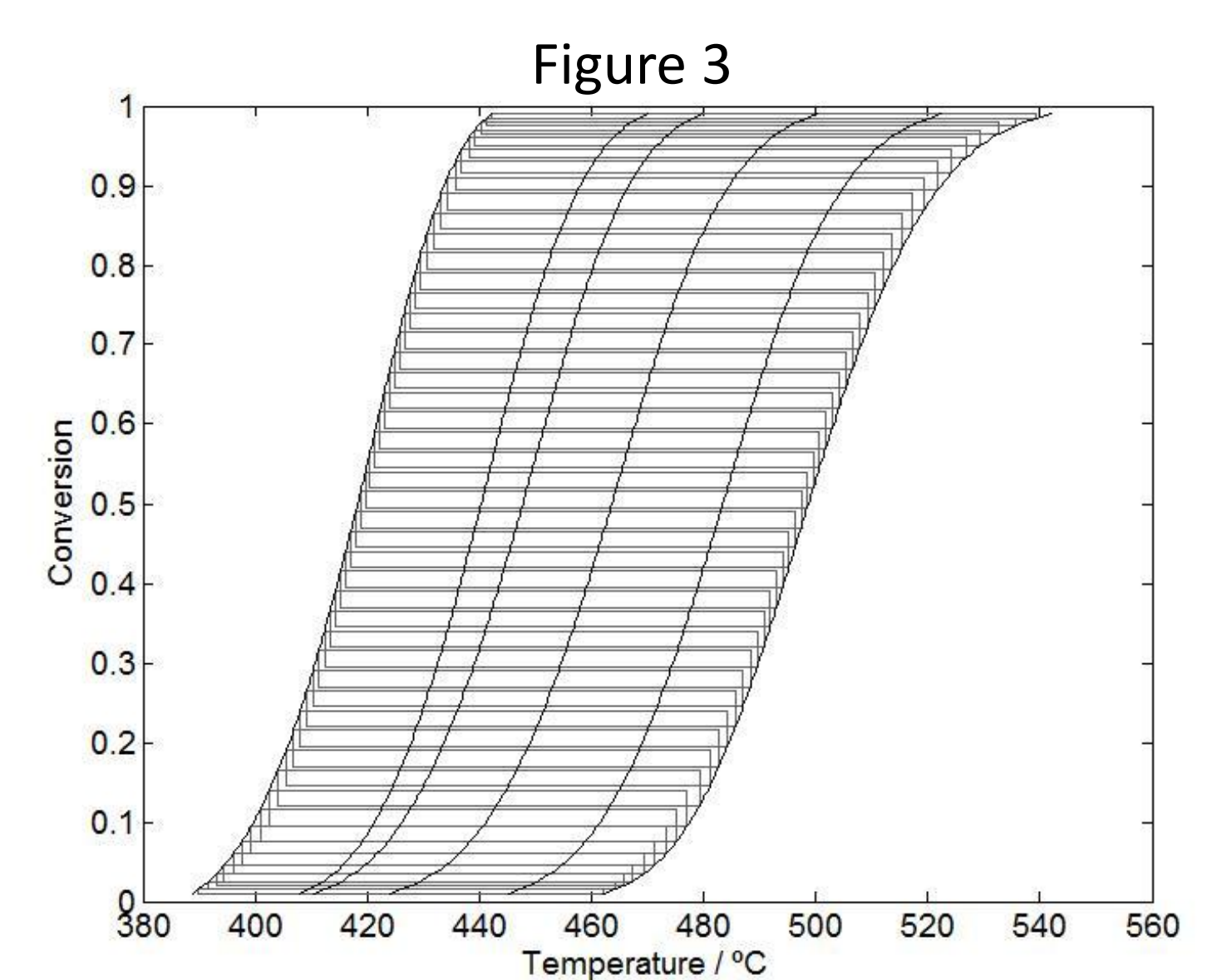


DSC curves obtained at different heating rates (Figure 1 shows the results for TiN samples) are used to determine the conversion of the desired phenomenon. It is critical to ensure no intersections between the integral curves (Figure 2).

## Non-Parametric Kinetics (NPK)

Figure 3 shows the submatrices constructed by the NPK algorithm for processing data. The results are represented by two vectors:

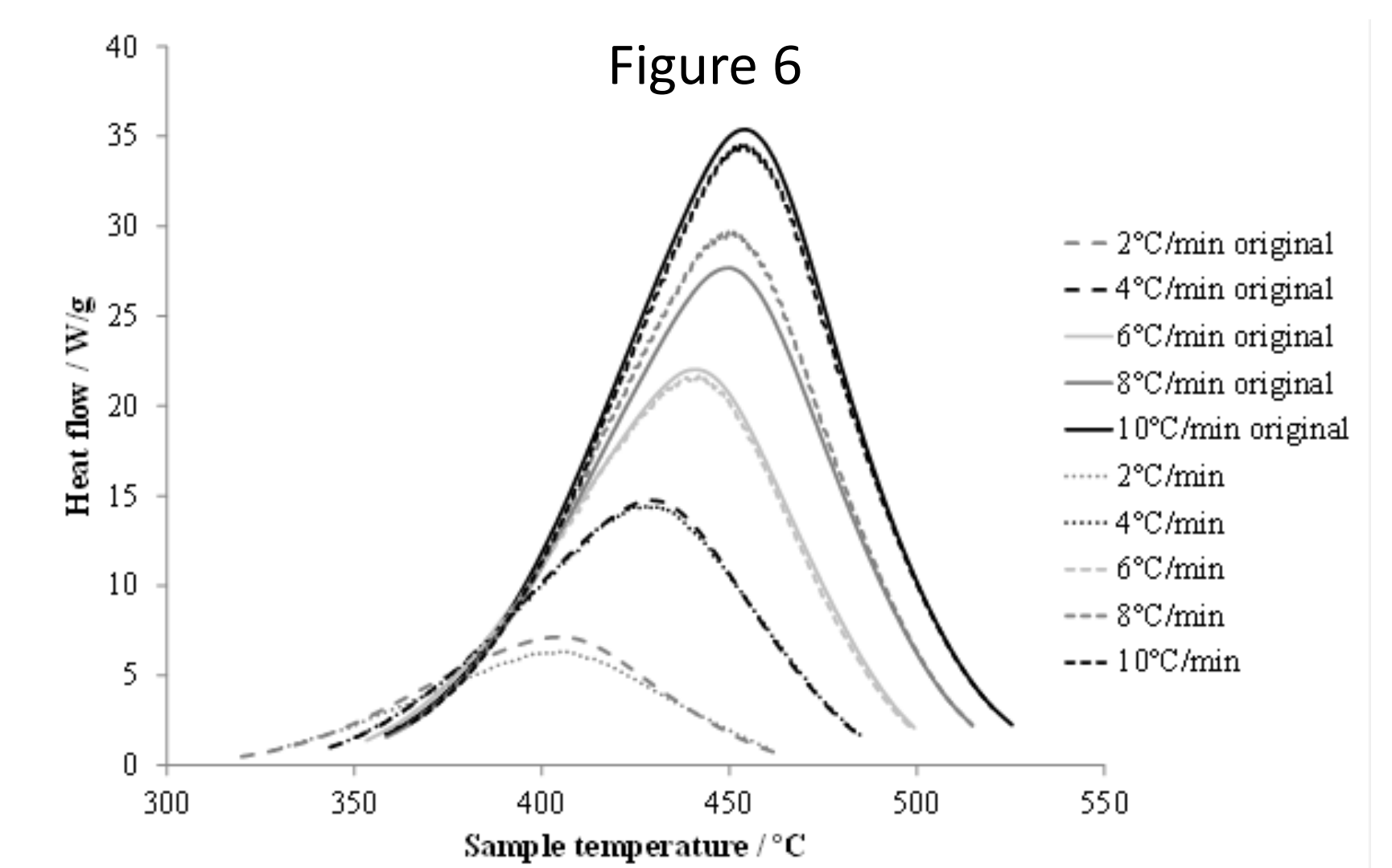
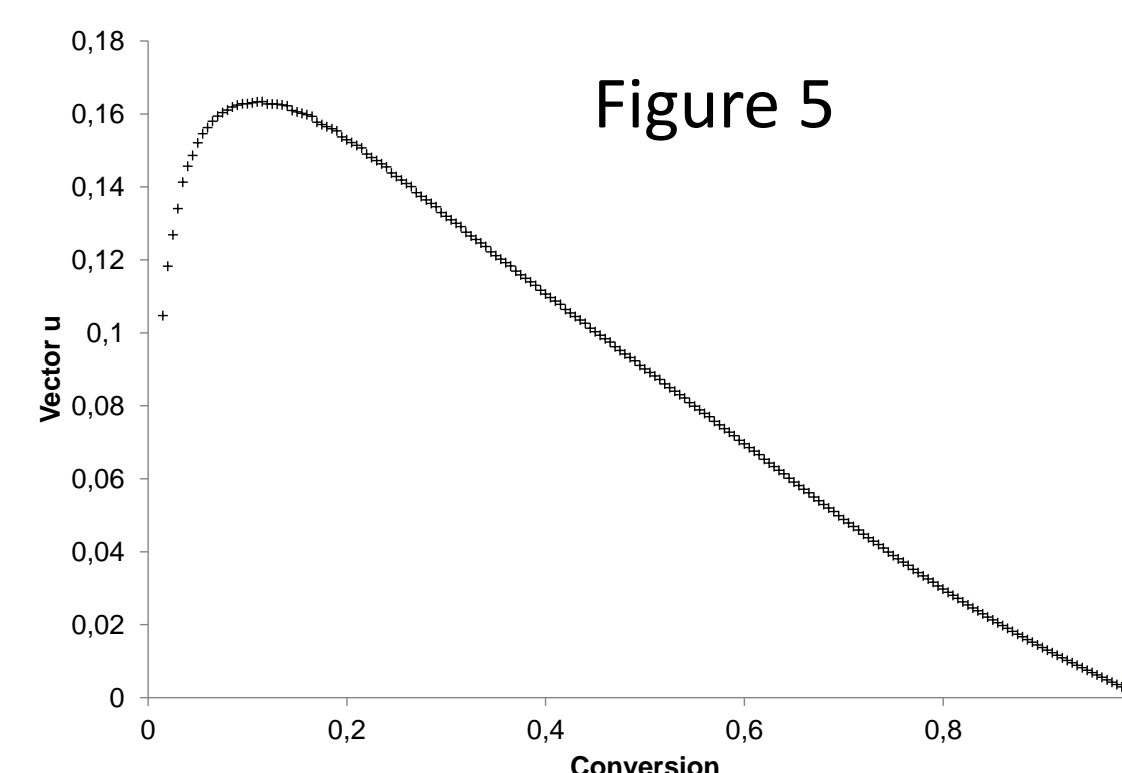
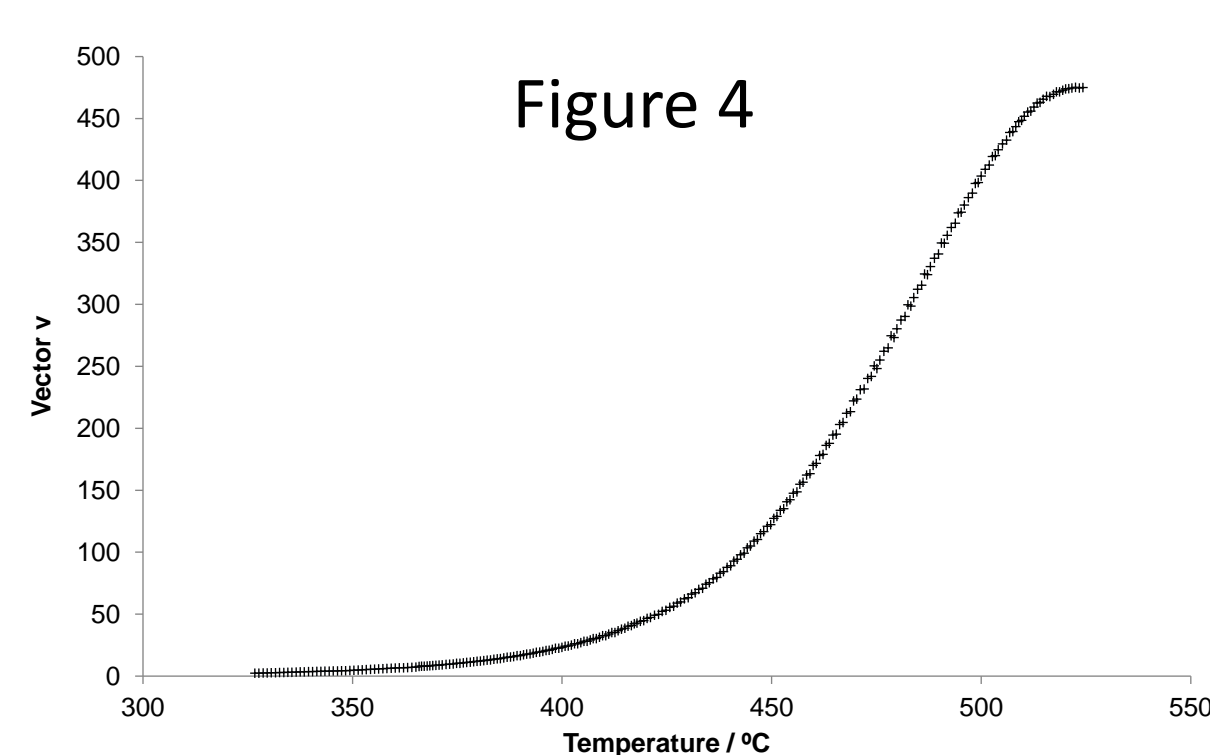
- **Vector u:** used to try and fit a kinetic model (function of concentration).
- **Vector v:** representing the function of temperature. It could be used to calculate the activation energy through the linearization of the Arrhenius equation.



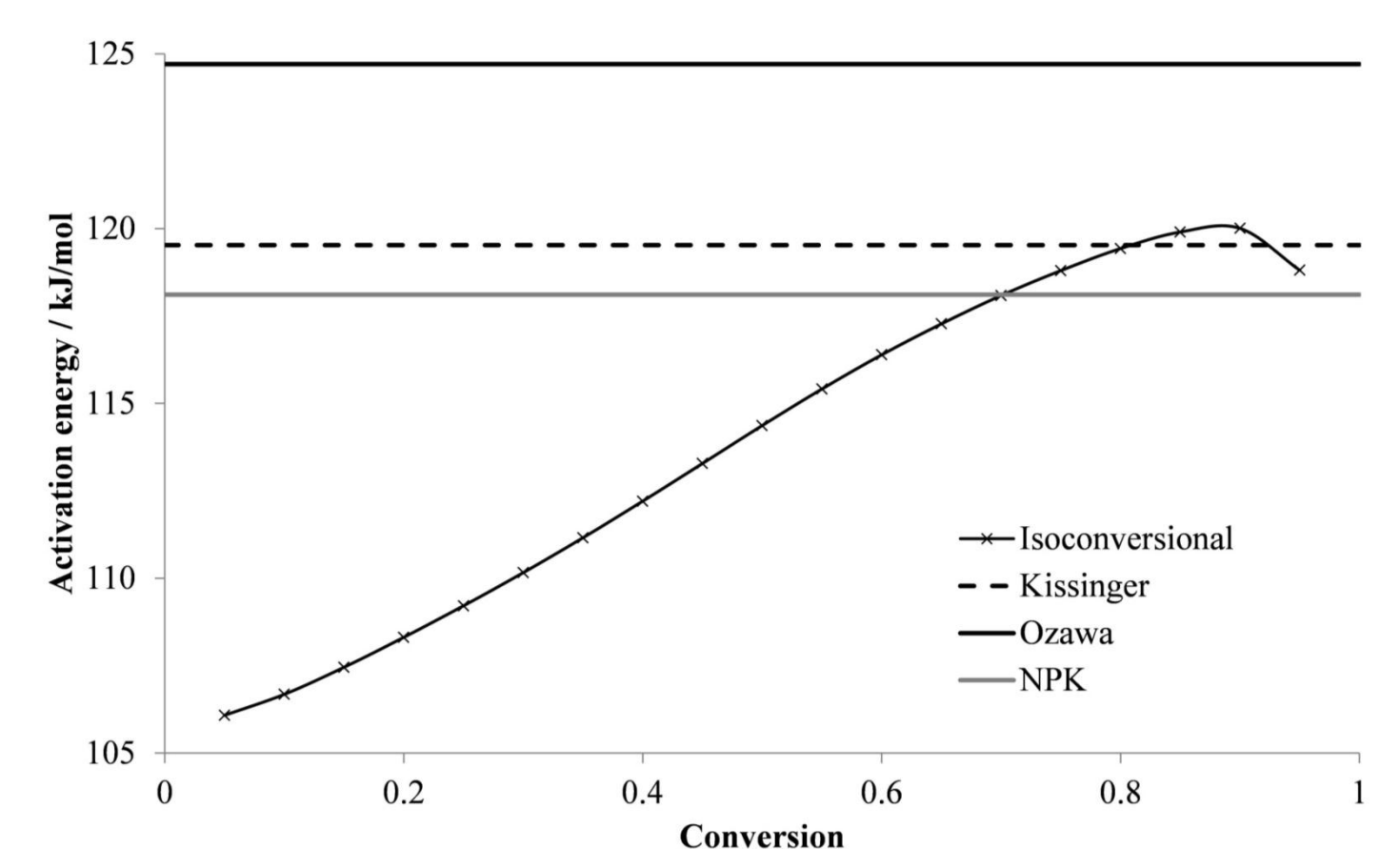
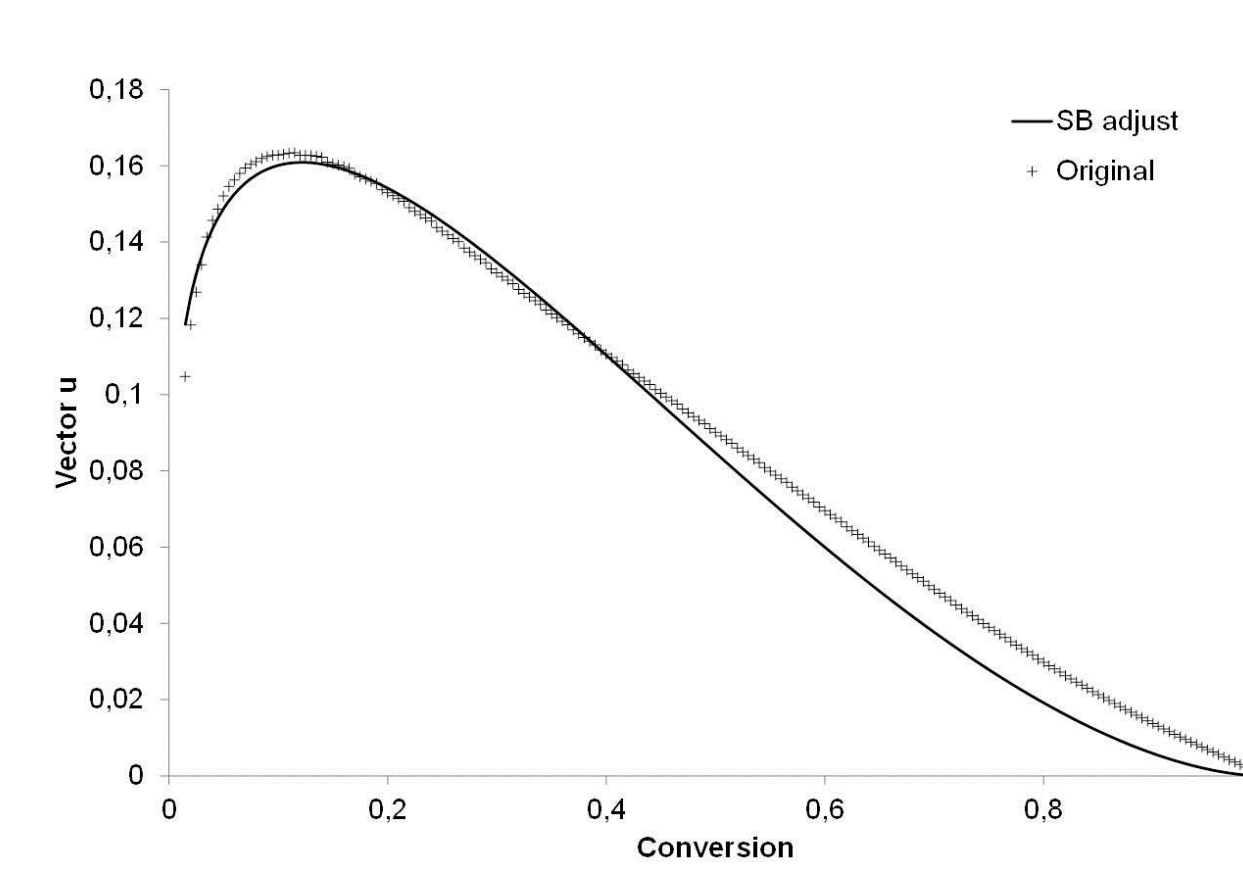
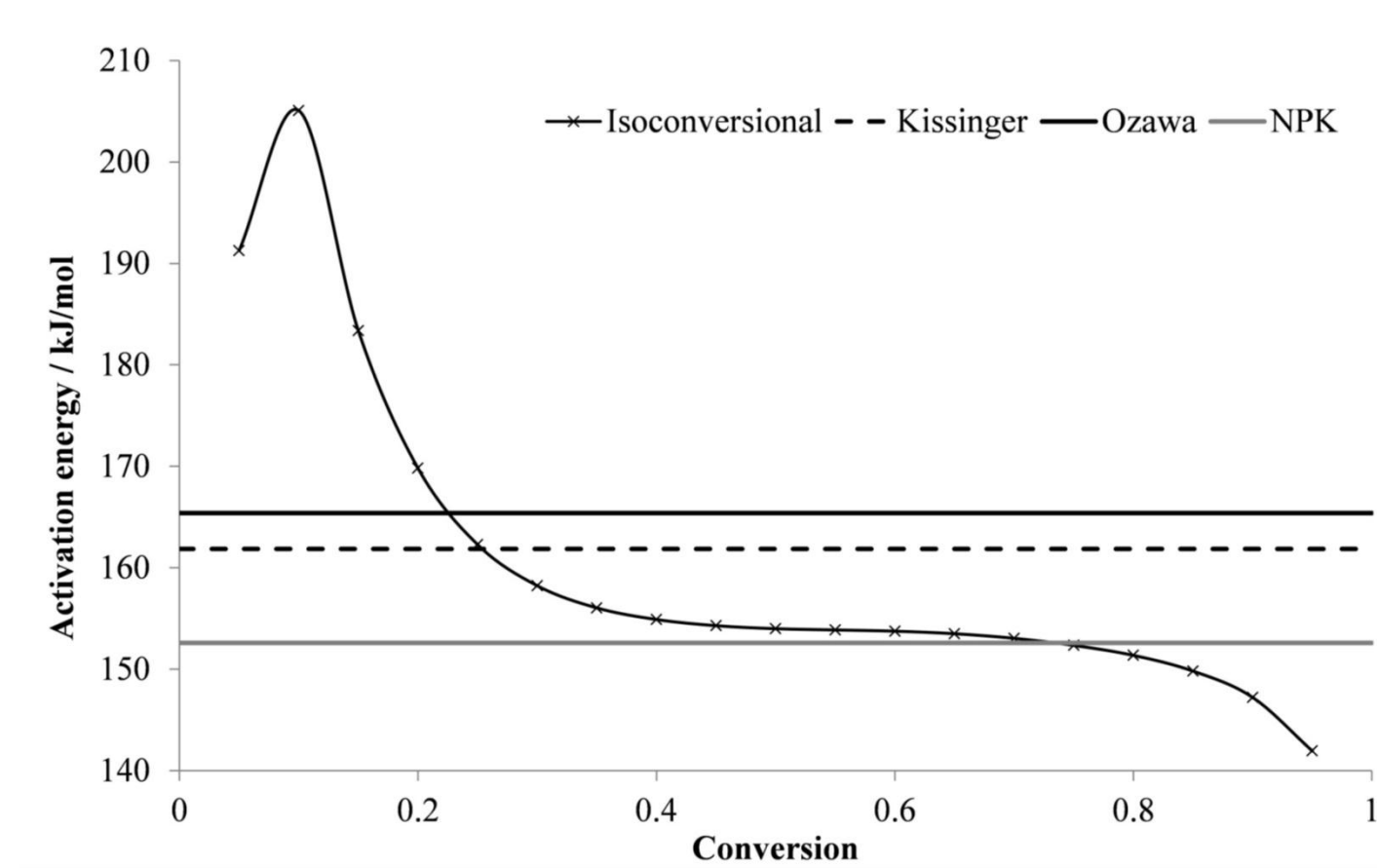
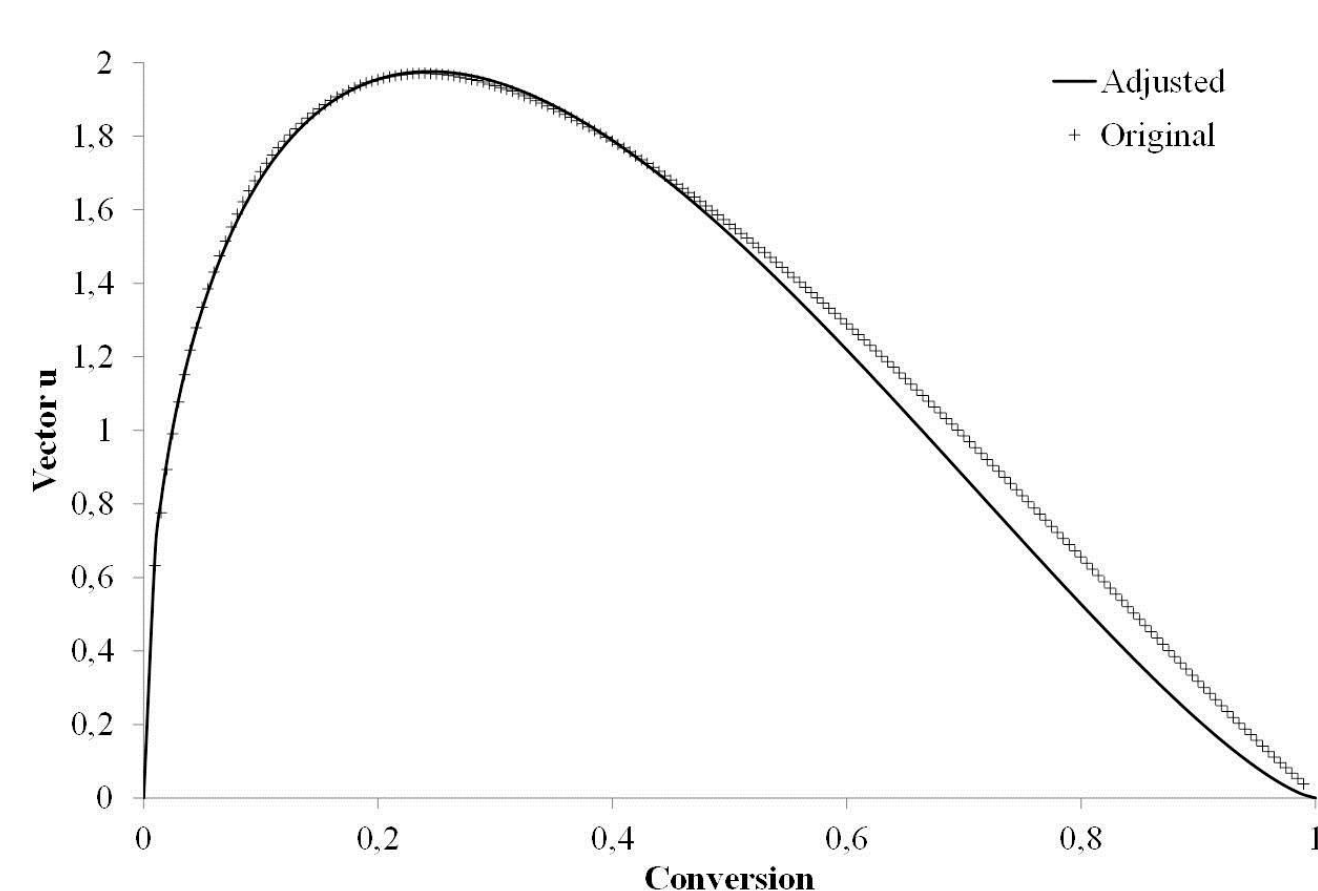
## Results

### Reconstruction of experimental data:

- Figures 4 and 5 show vectors **u** and **v** obtained for the case of TiC.
- Figure 6 displays the reconstruction of experimental data (TiC) from vectors **u** and **v**.



## Data fitting



### Titanium nitride:

- An autocatalytic model reproduces the exothermy of the reaction.
- The activation energy calculated is more conservative than those from classical models<sup>(1)</sup>.

### Titanium carbide:

- No simple kinetic model fits data.
- Confirmation of diffusion controlled reactions<sup>2</sup>.
- The activation energy calculated is more conservative than those from classical models

## Conclusions

The Use of the NPK method provides interesting results. It shows itself as a powerful method to work with nanoscaled samples providing reliable results without having to assume, or know, the kinetic mechanism in advance. This results lead to the determination of the best kinetic mechanism for the present reaction and provide an activation energy that would provide more realistic results in risk assessment.

## References

- 1- Serra R, Nomen R, Sempere J. A new method for the kinetic study of thermoanalytical data: the non-parametric kinetics method. *Thermochim. Acta*, 1998;316:37-45.
- 2- Sempere, J., Nomen, R., Serra, E., Sempere, B. and Guglielmi, D. Thermal behaviour of oxidation of tin and tic nanoparticles. *J Therm Anal Calorim.* DOI 10.1007/s10973-010-1214-x.