

Automated calibration of thermochemical models using MoDS-kinetics™ workflow applied to biomass gasification

N. Bianco, D. Nurkowski, G. P. E. Brownbridge, A. N. Bhave

Computational Modelling Cambridge Ltd. (CMCL Innovations), Cambridge – UK

INTRODUCTION

Results are presented from the calibration of thermochemical models using a novel strategy that automates the estimation and optimisation of model parameters and reaction rates for any given process. Two of CMCL's proprietary software, namely *kinetics™* and MoDS (Model Development Suite), have been integrated via a workflow that allows to build and simulate any chemical kinetic mechanism in a number of reactor configurations, assess the global sensitivity of target outputs from the process reaction rates and other model parameters (*kinetics™*), and calibrate the model against experimental data by using robust optimization routines (MoDS).

MoDS-kinetics™ WORKFLOW

kinetics™ finds application in the automotive/non-road, energy, and chemical processing industries. It is used to build, maintain, and apply chemical kinetics reaction models to engineering problems using a simplified approach through its easy to use interface. *kinetics™* uses various reactor configurations to evaluate process performance and species evolution [1]. The analysis of chemical kinetics can become challenging as the number of interacting chemical species increases. A sensitivity analysis is then required and it was performed using *kinetics™* on most parameters within the process studied here, including reaction rates, initial temperature and pressure, flow rates, reactor dimensions, etc.

MoDS uses a suite of numerical and statistical analysis techniques to gain insight from any model, simulator or CAE (Computer Aided Engineering) toolkit. Results from these analysis are used by MoDS to identify trends and provide predictions by treating the model or toolkit as a black box [2]. The software was used here to calibrate against existing experimental data a model created in *kinetics™* to describe biomass gasifiers.

The *kinetics™*-MoDS workflow is used to perform model calibration and optimal parameter estimation. It provides a seamless handover between the *kinetics™* model setup. Any model parameter available to *kinetics™* can be estimated using MoDS via the workflow. MoDS provides recommended calibration settings and can validate settings that the user customises. Experimental data can be read directly from comma delimited variable files. MoDS automatically interpolates profile data to compare model and experiments at different times or reactor lengths [3]. The optimization algorithm choice and configuration can be

tailored to fit the specific model and problem. A schematic of the workflow implementation, which also include the data visualization toolkit CMCL Explorer, is presented in Figure 1.

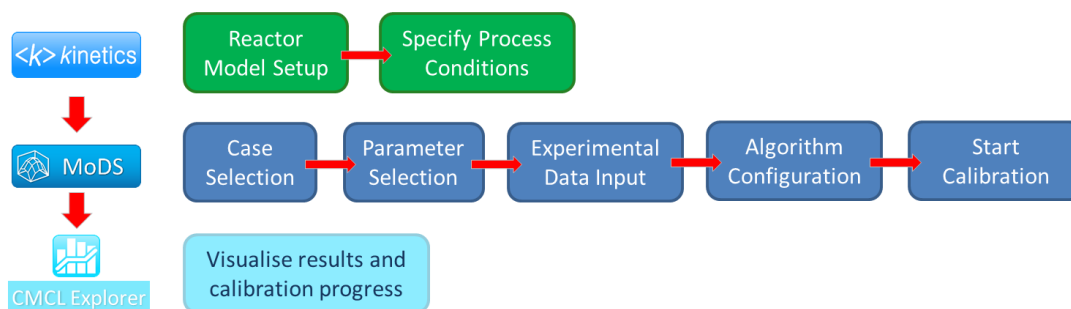


Figure 1. Parameter estimation workflow.

MODEL DESCRIPTION

Biomass gasification is an important technological process that transforms solid biomass fuel into combustible gases and chemical feedstocks (syngas). The process occurs via two interconnected steps: biomass devolatilisation and the gas phase reactions of the released gaseous species. Therefore, in order to control the whole process, these two steps need to be properly understood. In this abstract, a biomass gasification kinetic model from the literature is used to reproduce various experimental data. The biomass gasification kinetic model used in this report was taken from Ranzi et al. [4]. This model firstly characterises the biomass as a mixture of three key components: cellulose, hemicellulose and lignin. These components can be mixed in different proportions depending on the type of the biomass (e.g. softwood, hardwood, etc.). Secondly, the model provides a lumped kinetic scheme describing the devolatilisation of these components, with decomposition of the solid into permanent gases, condensable vapours (tars) and solid residue (char). Finally, the kinetic scheme is completed by adding secondary reactions of the released gas and tar species. Batch reactors were used to simulate the biomass gasifiers.

RESULTS AND DISCUSSION

Thermogravimetric (TGV) data were taken from the heated wire mesh reactor studies of Milosavljevic and Suuberg [5], who studied cellulose pyrolysis at three different heating rates (5 K/min, 100 K/min and 1000 K/min). Simulations were conducted in the *kinetics*TM software using a batch reactor model with an imposed temperature profile. It was assumed that at the beginning of the process only cellulose is present ($Y_{\text{cell}} = 1.0$) and that the remaining mass in the gasifier consists of only cellulose and char. Depending on the heating rate, each batch simulation was run for a different residence time until a temperature of 550 °C was reached. Figure 2 (a) depicts obtained simulation results. It can be seen that a very good agreement with the experimental data of has been obtained. Small differences in the remaining mass at the end of the process may be explained by the presence of some solid/liquid pyrolysis by-products that are unaccounted for by the current kinetic model.

Levogluosan (LVG) and hydroxyacetaldehyde (HAA) are two major intermediates produced from cellulose pyrolysis. Piskorz et al. [6] measured yields of those species produced during pyrolysis of a microcrystalline cellulose (Avicel pH-102) at different temperatures and at an

average residence time in the reactor of 0.5 seconds. Simulations were conducted in the *kinetics*TM software using a constant temperature batch reactor model. The moisture content was set to $Y_{H_2O} = 2.9\%$ according to [6]. The simulation time was set to an average experimental residence time. Obtained simulation data are shown in Figure 2 (b). It can be seen that again a good agreement with experiments was achieved given the overall complexity of the pyrolysis process.

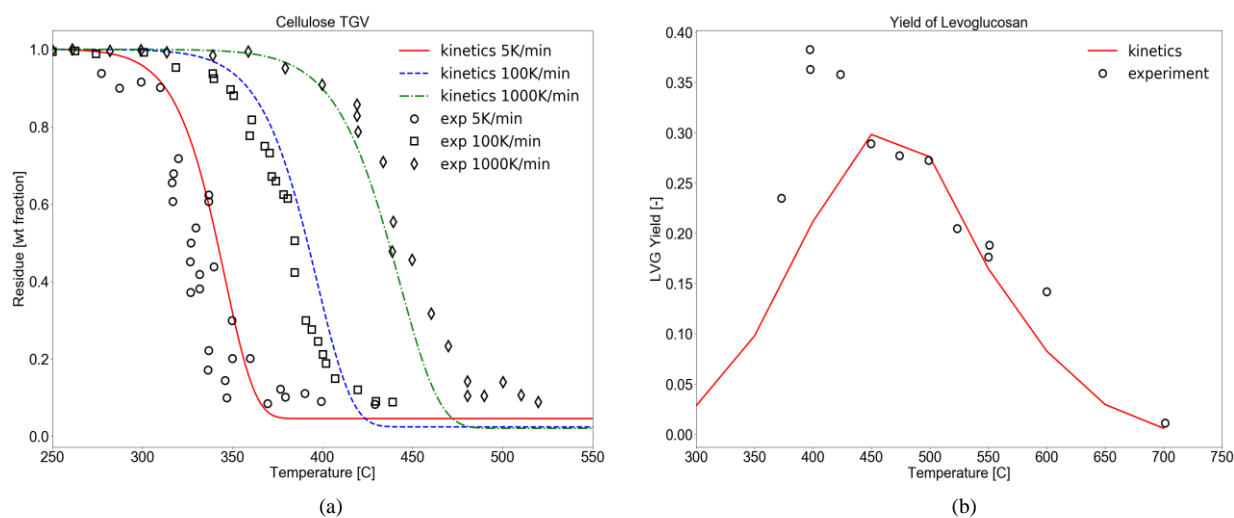


Figure 2. (a) Pyrolysis of cellulose [5]. (b) Variation of pyrolysis yield of levoglucosan with temperature [6]. Model predictions (lines) and experimental data (points).

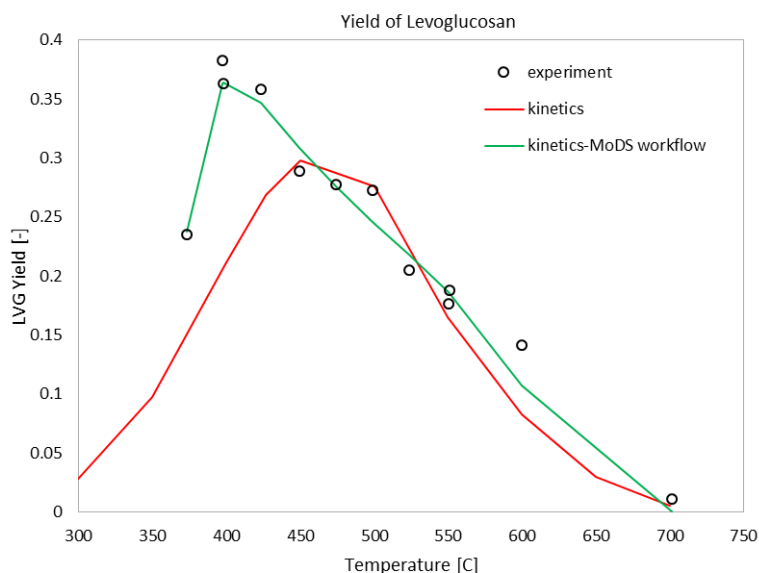


Figure 3. Variation of pyrolysis yield of levoglucosan with temperature. Model predictions with original kinetic mechanism (red line), model predictions with kinetics parameters calculated using the *kinetics*TM-MoDS workflow (green line) and experimental data (points) [6].

To improve these results, a combination of sensitivity analysis, flux analysis and mechanism reduction strategies were implemented in *kinetics*TM to identify the set of reactions to which the LVG yield was most sensitive to. Using DRGEP (Directed Relation Graph with Error

Propagation) as mechanism reduction strategy, we were able to reduce the original mechanism of Ranzi et al. [4] from a total of 20268 to 20 most sensitive reactions. Using the *kinetics*TM-MoDS workflow to adjust the reaction rates of these 20 reactions we were able to achieve a considerable improvement in the match with the experimental results, as can be seen in Figure 3. The same process can be implemented to the entire set of outputs of interest, with the calibration process automatically performed through the *kinetics*TM-MoDS workflow after we have identified the target outputs, and performed the sensitivity analysis and the mechanism reduction for each one, or a combination, of these outputs.

CONCLUSIONS AND FUTURE WORK

The *kinetics*TM-MoDS workflow proved to be a valuable method for model calibration. Focusing on the chemical kinetic mechanism, we were able to identify a sensitive set of reaction rates through *kinetics*TM, which were then successfully tailored to match available experimental data. To identify a robust set of kinetic parameters, valid for the whole spectrum of feedstocks, operating conditions and target outputs we will need to perform the process illustrated above for a larger number of cases, covering adequately all the above aspects and then estimate a weighted-average set of parameters to be used in the calibrated chemical mechanism. Test cases to validate the calibrated model will also have to be identified.

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