

Adaptation of a Monte Carlo method to the hydrotreating of bio-oil model compounds

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Highlights

- Understanding the reactivity of bio-oil model compounds under hydrotreating conditions;
- Adjustment of the kinetic parameters of the model compounds reaction networks;
- Validation of the kinetic models of the model compounds.

1. Introduction

As a carbon matrix, lignocellulosic biomass can be used to produce transportation fuels. Through thermochemical processes, as pyrolysis, biomass is converted into a liquid, called bio-oil. Such an effluent has an extremely complex organic character with not only a high amount of carbon, but also a large quantity of oxygenated species. Since the presence of oxygen reduces the quality of bio-oils as a fuel source, the mixture must be converted into lighter and deoxygenated hydrocarbons by upgrading techniques, as hydrotreating. However, due to its high molecular and reactional complexity, the upgrading of bio-oil reveals to be difficult.

The present work describes a methodology for modeling the upgrading of bio-oils. The proposed method will be applied to construct kinetic models for the hydrotreating of bio-oil model compounds in order to illustrate its validity. This strategy will enable a further understanding of bio-oil reactivity, opening the doors for the modeling techniques for full-range bio-oils.

2. Method

As modeling strategy, a direct and discrete simulation of the reaction events was chosen. The approach is based on a kinetic Monte Carlo (kMC) method, termed Stochastic Simulation Algorithm (SSA) [1] [2], and describes the evolution of a molecular system, molecule by molecule. Unlike the classic procedures, this method can describe the evolution of a molecular mixture over time without a pre-defined reaction network.

The stochastic approach is based on the identification of all possible reaction events at a given moment in time and on the calculation of the reactivities for each event. Thanks to the work of Gillespie [1] [2] and recalculating apparent first order rate coefficients for the reactions, the reaction probability can be generated for each reaction event. By assembling all the probabilities of all molecules, the overall reactivity allows to determine, via Monte Carlo sampling, the time interval until the next reaction, while the normalized discrete probability density function allows to select a given reaction. The sampling process of both variables is then repeated until the final simulation time is reached.

The SSA requires as inputs a list of reactant molecules, the different types of reactions that can occur and the kinetic parameters associated to these transformations. Due to its stochastic nature, this method generates a different outcome for each simulation, which does not allow to construct the general evolution of the reaction system over time. Therefore, as with any stochastic approach, the method has to be based on several simulations, each of which calculates discrete time trajectories of molecular populations. Their average profile will converge to the same results as deterministic methods.

3. Results and discussion

For the hydrotreating of guaiacol, furfural and D-glucose, the reactions for hydrogenation, dehydrogenation, demethylation, demethoxylation, hydrodeoxygenation, transalkylation, decarbonylation, decarboxylation and hydration were implemented. For the various model molecules, the SSA method is able to predict the

expected trends, not only for the conversion of the reactants, but also for the generation of the various products and for the hydrogen consumption. Additionally, this approach also predicts the transformation of the several reaction products into smaller molecules.

Due to the high reactivity of guaiacol, the heating and cooling periods contribute significantly to the overall conversion. Hence, the reactor simulations need to account for these dynamic periods.

The model results were compared to the experimental data obtained by Ozagac [3] for the hydrotreating of guaiacol over a NiMo/Al₂O₃ catalyst in a batch reactor at 13 MPa and 300°C and for reaction times of 3h and of 5h. For the experiments, a blank run was performed and showed an initial conversion of 10% at 300°C after the heating up and cooling down the batch reactor.

Taking into account the thermal behavior of the reactor during heating, reaction and cooling, the kinetic parameters of the reactions were estimated based on the guaiacol conversion for the three batches. A good agreement is observed, as shown in Figure 1a. The comparison of the simulated and the experimental selectivities for methanol and dialcohols shows that the model predicts, within the error of the experimental data, the correct order of magnitude for both, as presented in Figure 1b and Figure 1c respectively.

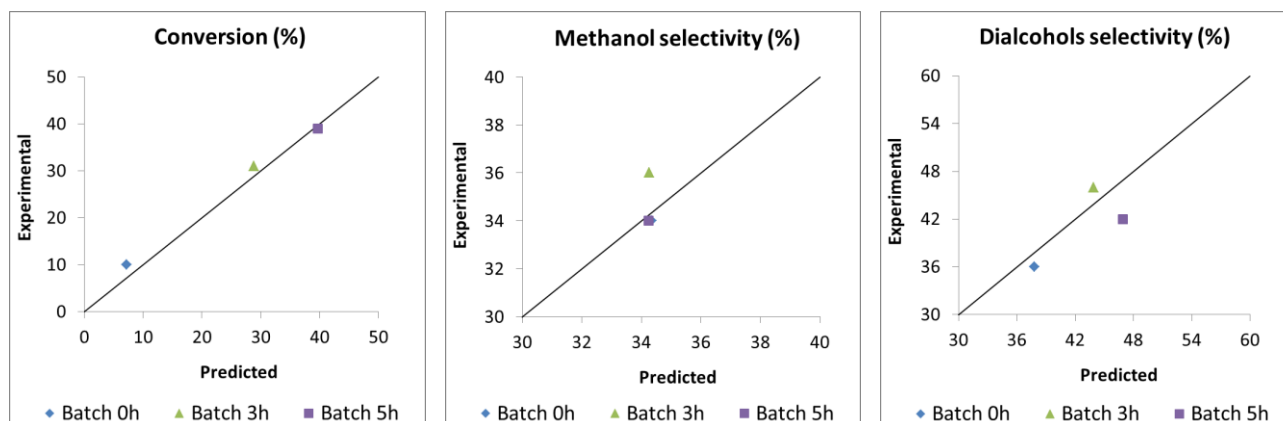


Figure 1. Stochastic simulation of guaiacol hydrotreating at 300°C using 10000 molecules and 50 simulations: (a) Conversion parity plot, (b) Methanol selectivity (%) parity plot, (c) Diols selectivity (%) parity plot.

4. Conclusions

The SSA methodology was applied to bio-oil model molecules and showed the correct trends when compared to available experimental data. Through this study, a kinetic model was generated that is able to simulate the reactions of guaiacol, furfural and D-glucose under hydrotreating conditions. It was shown that the SSA method is an excellent simulation tool for complex reaction networks without the need for a pre-defined reaction network. Furthermore, this method enables a better understanding of these systems, making it suitable to be applied to a full range bio-oil.

References

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Keywords

Bio-oil Model Compounds; Hydrotreating; Reactivity; Stochastic Simulation Algorithm.