

# Progress in Automated Modeling of Biofuels: Updating Reaction Families and Rate Calculation Rules

Fariba Seyedzadeh Khanshan

Department of Chemical Engineering, Northeastern University, Boston, MA 02115

## Introduction

Biofuels contain many derivatives of lignin, hemicellulose, and cellulose. However, thermal conversion of biofuels is very sensitive to the fuel chemistry, and sometimes too complex to model by hand, especially for heavy heterocyclic molecules. It is preferable to teach fuel chemistry to computers, and generate detailed chemical models automatically. In this study, Reaction Mechanism Generator (RMG) [1], an open-source software, has been used to build detailed kinetic models for bio-oil gasification.

In order to generate complete detailed models, an extensive set of reaction classes, which would define how fuel species can react with each other, should be implemented in mechanism generators. In recent work, we have investigated that RMG is missing some ring opening reaction families for heterocyclic molecules in bio-oil gasification modeling. We have now updated RMG's kinetics database with reaction recipes for the new reaction families. Further, we've also specified rules to predict Arrhenius rate parameters for the new reaction classes.

The bio-oil gasification mechanism has been updated after adding these new reaction classes and associated kinetic parameter from rate rule calculations. There are some significant differences in simulation results between RMG- built models before and after updating the database, demonstrating the importance of these reaction families and their kinetic features when studying the thermal conversion of biofuels.

## Method

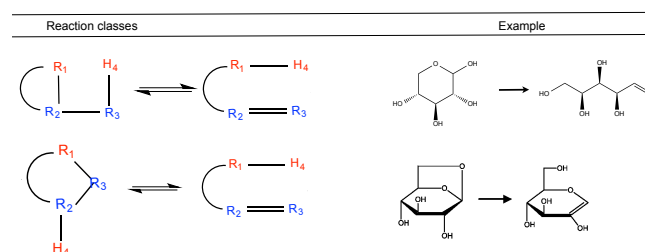
Two missed reaction classes for heterocyclic compounds are primary ring-opening isomerization reactions that can take place through direct C-C or C-O bond breaking and H-migration reactions at the same time, shown in Table 1.

However, the number of possible reactions in each reaction family is massive, and applying high-level electronic structure calculations for each would be prohibitively expensive. Instead, rate calculations were performed for a smaller set of reactants belonging to the particular reaction class, then the roles of the different functional groups were deliberated, and group-based rate rules were derived to estimate Arrhenius parameters for any reaction in the new reaction classes. All electronic structure calculations are performed in CBS-QB3 level of theory implemented in Gaussian 09 package [2].

## Results

RMG generated model for bio-oil gasification is compared with two sets of experiments [3], [4] covering different temperature ranges. Comparison shows that there is a difference in CO<sub>2</sub> and CO yields between the experiments and RMG-built model. Since, products from C-O bond breaking reactions are mostly H<sub>2</sub>O and CO<sub>2</sub> that are the main gaseous products of gasification, the bio-oil gasification mechanism has been updated after adding these new reaction classes and associated kinetic parameters.

Table 1: Two reaction classes for bio-oil gasification that are missing in RMG



There are some significant differences in simulation results between the RMG- built models before and after updating the database, Figure 1.

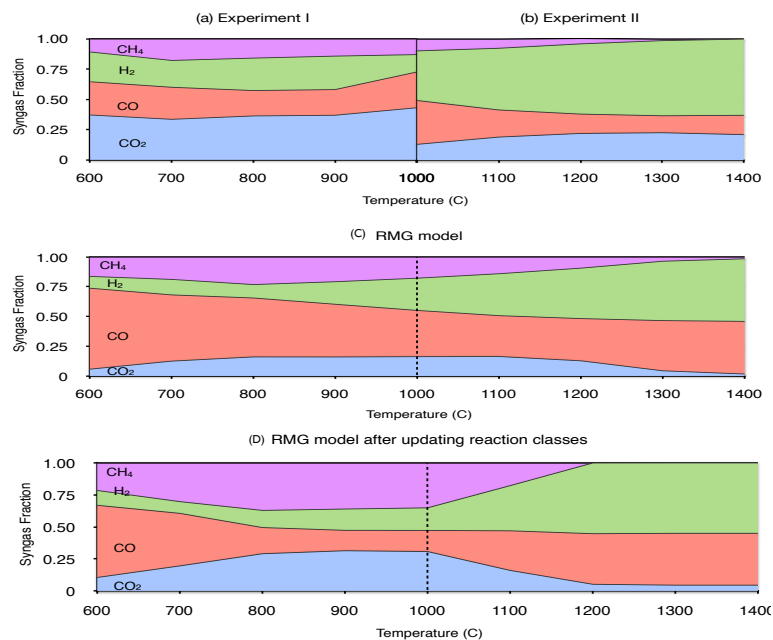


Figure 1: Comparison between two sets of experiments (a) and (b) for syngas production yield at different temperatures with RMG-generated mechanism before (C) and after (D) updating the database with new reaction families.

## Conclusions

Developing predictive detailed chemical models for heterocyclic compounds that are important intermediates in different biofuel processes is a challenging task. This work describes the reactions and rate constants, which are specific to these molecules. In particular, two specific reaction families as primary ring opening isomerization reactions, that have been found to be important initiation reactions in biofuels, are implemented in RMG. Furthermore, the key challenge after adding new reaction families is being able to accurately estimate rate coefficients for these reactions. Since, applying electronic structure calculations for each elementary reaction is expensive, rate rule calculations are used for these families. This study has shown that rate rules can be used for these new families and rate expression for similar reactions with similar functional groups can be replaced by generic rate expression.

## References:

- [1] W. H. Green, et. al. , “RMG – Reaction Mechanism Generator , Python version,” *rmg.mit.edu*. Massachusetts Institute of Technology.
- [2] M. J. Frisch, et. al. , “Gaussian09,” *gaussian.com*. Gaussian, Inc, Wallingford, CT.
- [3] M. Zhang, et. al. , “Experimental study on bio-oil pyrolysis/gasification,” *BioResources*, vol. 5, no. 1, pp. 135–146, 2010.
- [4] Y. Chhiti, “Non catalytic steam gasification of wood bio-oil,” Université de Toulouse, Toulouse, 2011.