

## A Microkinetic Model for the Vapor Phase Upgrading of Biomass-Derived Acetic Acid

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### Highlights

- A microkinetic model was developed for the upgrading of acetic acid over acidic zeolites.
- An automatic network generator constructs a mechanism from elementary reaction families.
- The major experimental products are acetone, isobutene, and aromatic compounds.
- The model revealed the relative contributions of the main pathways to key products.

### 1. Introduction

The non-renewable nature and adverse environmental impacts of petroleum, coal, and natural gas have motivated the development of renewable sources of energy, particularly biofuels, which can be produced from many different sources such as manure, crop waste, and biomass. The use of computational modeling has revolutionized our ability to investigate individual reaction pathways, predict product distributions, and optimize process conditions. While fast pyrolysis can produce bio-oil in high yields, it can contain significant amounts of oxygenated compounds (e.g. acids), rendering it highly corrosive and unsuitable as a feedstock for existing refinery infrastructure [1]. The poor quality of this bio-oil can be improved by removal of oxygenated products, typically through catalyzed conversion of the pyrolysis product vapors before condensation into specialty chemicals and fuels. In this work, we developed a microkinetic model for the acid-catalyzed upgrading, or catalytic fast pyrolysis, of a bio-oil model compound, acetic acid, a simple compound representing the carboxylic acids in the bio-oil and contributing to the low pH. The catalyst used was HZSM-5, a common zeolite serving as an acid catalyst.

### 2. Methods

The flowchart in Figure 1 outlines the process by which the microkinetic model, one in which all elementary steps are considered, was constructed and lists all the relevant variables and parameters that were calculated and estimated. Formulating all the elementary steps for a large system presents a significant challenge, and rate constants for these elementary steps cannot always be regressed from experimental data. To combat these issues, a reaction family approach was used, in which reactions of the same type were grouped together as a single elementary reaction. We then utilized automatic network generation to construct a reaction mechanism, considering all possible reactions given the reaction families that were defined.

Rate coefficients,  $k$ , were calculated via the Arrhenius equation. The pre-exponential factor,  $A$ , was estimated from transition-state theory (TST), while the activation energy,  $E_a$ , was related to thermodynamic properties through a structure-reactivity relationship, the Evans-

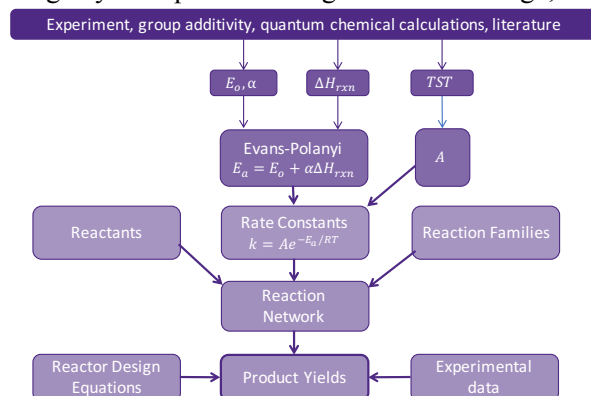


Figure 1. Flowchart for constructing a microkinetic model.

Polanyi equation, where  $E_o$  and  $\alpha$  are parameters in the model. The heat of reaction,  $\Delta H_{rxn}$ , on the zeolite surface included the gas phase heat of reaction, heats of adsorption for the neutral species, and stabilization energies for the ionic species. The gas phase heat of reaction was calculated from the heats of formation of all the reacting species, which were generated primarily from a group contribution method, whereby 71 group additivity values were regressed for oxygenates, oxonium ions, and oxygen-containing carbenium ions [2].

The reaction mechanism was coupled with reactor design equations for a plug-flow reactor. The resulting system of differential and algebraic equations was numerically solved to predict product yields and to explore the effect of various operating parameters (e.g. temperature, acidity) on the product distribution. In addition, the microkinetic model can be used to predict optimal operating conditions, such as catalyst loading and acidity, and give insight into coke formation mechanisms.

### 3. Results and discussion

The acid-catalyzed chemistry imparted by the zeolite includes common reactions of carbenium ( $C^+$ ) and oxonium ( $O^+$ ) ions such as protonation, deprotonation, hydration, dehydration, hydride transfer, oligomerization, and beta scission. However, another potential reaction family, aldol condensation, is specific to ketones and carboxylic acids, such as acetone and acetic acid. While literature reports contend that aldol condensation occurs through the enol form of acetone (or related compounds) [3-4], the equilibrium constant governing keto-enol tautomerization revealed that the ratio of the enol form to the keto form at 450°C is on the order of  $10^{-8}$ . Additionally, model results showed that this tautomerization step is quasi-equilibrated, and the resulting low concentration of the enol resulted in rates of aldol condensation that were too low to create any significant yield of products. Alternatively, a recent density functional theory (DFT) study by Herrmann and Iglesia [5] explored aldol condensation as the reaction of protonated acetone with gaseous (keto) acetone. This new perspective for the key reactants governing aldol condensation in zeolites provides a serviceable mechanism for the transformation of acetic acid to acetone and of acetone to isobutene, two key steps in the catalytic upgrading of acetic acid. With all the elementary reactions in hand, an automatic network generator constructed a preliminary reaction mechanism consisting of ~300 species and ~900 unique reactions that was then coupled with reactor design equations and solved to predict the major reaction pathways and explore the effect of process conditions on the product distribution.

### 4. Conclusions

The microkinetic model revealed mechanistic details underlying conversion of acetic acid on HZSM-5 that significantly expanded our understanding of this complex system beyond what is currently known from experimental studies. While it has been posited that aldol condensation proceeds through the enol form, quantitative analysis using our model showed that this is not feasible. Further, we were able to suggest an alternative mechanism through which acetic acid is upgraded to valuable fuels and chemicals that was kinetically significant. The microkinetic model is sufficiently general that it can be extended to the conversion of other oxygenated compounds on zeolites of various topologies and acid strengths.

### References

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### Keywords

catalytic upgrading; zeolite; microkinetic model; acetic acid