FINAL REPORT

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Modeling of Reactor Design and Optimization for Scale-Up of the Catalyxx Process for Ethanol Conversion to Higher Alcohol Biofuels

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Summary

This report summarizes the results of a collaborative efforts between Oak Ridge National Laboratory (ORNL) and Catalyxx Inc. to investigate scale-up of Catalyxx's Ethanol upgrading to higher alcohols process. The study was funded by the U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) under CRADA (Cooperative Research and Development Agreement) No: NFE-20-08396. The project is part of the Direct Funding Opportunity (DFO) for Computational Science to Enable Bioenergy program which utilized computational toolsets developed by the Consortium for Computational Physics and Chemistry, a multi-laboratory consortium in BETO. The report here summarizes a packed-bed reactor modeling effort spanning the range from lab to industrial scale (from 4 gram to 5-ton catalyst beds), and examining reactor design, process optimization strategies, and suggested design and operating conditions for Catalyxx's ethanol upgrading plants. The results in this report have been shared in monthly steering meetings and presentations are available in the shared data house owned by Catalyxx. The modeling effort helped to define optimum operation conditions for maximum alcohol selectivity and yield: i.e., temperature control scenarios ranging from adiabatic to isothermal, feed rate, pressure, and inlet H_2/Ethanol ratio. The modeling results were verified at lab-(4 gram) and pre-pilot (4 kg) scales and has been used to evaluate a 5-ton packed-bed reactor and identify operating conditions to maximize the butanol yield.

Special focus was given to understanding mass-transfer effects in the pre-pilot and pilot-scale reactors, over the domain of flow rate, pressure, feed composition, pellet size, shape, porosity, bed voidage, and reactor dimensions (i.e., length/diameter). Modeling was also used to evaluate innovative reactor design concepts such as water removal to improve alcohol selectivity and yield, and a reactor with an additional side inlet to facilitate quenching. These concepts were thoroughly explored, and potential benefits were disclosed.

The results in this report are summarized and described qualitatively to protect the IP rights of Catalyxx. The details have been shared with the Catalyxx team in the regular steering meetings. At the end of the project, Catalyxx Inc. announced a successful demonstration of pilot scale operation in Seville, Spain [1].

1. Scope of the work

Catalyxx Inc. aims to commercialize thermocatalytic processes for converting ethanol into n-butanol, octanol, and other biofuels and bioproducts, including intermediates for synthetic aviation fuel (SAF). The process is based on the Guerbet reaction in which alcohols undergo dehydrogenation to form aldehydes, which then combine with alcohols to form aldehydes via aldol condensation, followed by hydrogenation to form higher C alcohols. The Guerbet mechanism yields a fairly broad range of linear and branched α-alcohols having even carbon numbers. ORNL's modeling work supported scale-up operations and explored reactor configurations and operational strategies to optimize the conversion of ethanol to higher alcohols. Model development was supported by the experimental data at lab and pre-pilot scale provided by Catalyxx.

The project objectives were as follows:

- Determine reactor geometries and control parameters to achieve maximum conversion of ethanol
- Optimize the ethanol to butanol reaction step
- Enable successful scale up from a 4 kg catalytic reactor to a 200 kg reactor

The primary benefit of the project to BETO and the US bioenergy industry is the mitigation of risks associated with the scale-up of critical processes in thermocatalytic conversion of ethanol to biofuels and bioproducts, which is a promising route to help decarbonize the petrochemical industry. Specific technical outcomes of the project toward these derisking goals include:

- Definition of the reaction rate kinetics for the conversion of hexanol to octanol needed to complete the existing Catalyxx kinetics data set,
- Understanding the inhibition effects of water and investigation of potential operating and reactor design practices that can minimize the negative impacts of H_2O,
- Optimization of operational parameters to maximize reactor productivity and efficiency with minimal catalyst degradation.

2. Catalyxx's ethanol upgrading process

Catalyxx's ethanol to higher alcohol conversion process takes place in a packed-bed catalytic reactor. Catalysts pellets are packed in a heated stainless-steel cylindrical tube and reactants are fed through the inlet at the top of the bed. The outlet composition of the reactor is analyzed at steady state. The dimensions of the reactor tube and the catalyst properties, and hence the bed properties, change depending on the scale of the experiments i.e., 4 gram to 4 kg bed scale.

A two-dimensional axisymmetric, non-isothermal packed-bed reactor model has been developed which treats reactor and bed dimensions parametrically. COMSOL Multiphysics 6.0 software was used for model development [2]. A powerful feature of the reactor model is that it solves the fundamental heat and mass transfer equations at both particle and reactor scales simultaneously. This powerful

feature differs from a more traditional homogeneous-bed approach in that it addresses potential mass and heat transfer limitations in all relevant size scales in the reactor.

The traditional packed-bed reactor model treats the catalyst as a single porous medium and solves the transport problem in a single reactor domain, assuming a continuum heat and mass transfer between the gas phase and the porous medium. The traditional single domain approach is quite successful when modeling lab-scale reactors where particles are relatively small (< 500 μm) and experiments are designed to keep the Thiele Modulus small, allowing intrapellet mass transfer limitations to be neglected. However, in beds larger than typical lab-scale reactors (<100 gram), it is not uncommon to find larger Thiele moduli, and depending on the operating conditions (T, p, and Weight Hourly Space Velocity (WHSV)), intrapellet mass transfer resistances can limit reactor performance and hence the overall production rates. Reactor packing strategies, changes in pellet properties (size, shape, and porosity) and reaction conditions (T,p, WHSV) can eliminate intrapellet mass transfer limitations.

3. Modeling Concept

The model uses 2D axisymmetric cylindrical geometry to represent the tubular reactor bed. For bulk heat and mass transport, the catalyst bed is modeled as a porous medium. To capture heat and mass transfer within the catalyst pellets, an extra dimension is added to create a pellet domain. The model solves the mass transport, heat transport and reaction equations simultaneously for the porous bed domain and the pellet domain. The velocity and pressure field across the porous reactor bed with a uniform voidage (ϵ_{bed}) are calculated for a single-phase, compressible laminar flow field in a porous media. The bulk species transport mechanism in the porous media is modeled using Fick's law in combination with the Ergun equation, whereas species transport within the pellets is modeled using the Knudsen equation.

Heat transfer in the packed-bed reactor is also modeled as a porous medium where both solid and fluid phase participate in the heat transfer. Conductive and convective heat transfer between the solid matrix and the fluid phase (i.e., the void volume filled with the reactive fluid) are modeled, and radiant heat transfer is neglected. Wall and inlet temperature boundary conditions are used to constrain the heat equations. The model allows various heat transport mechanisms to be included depending on the dominant mechanism.

When the pellet particles are relatively small and densely packed, and the pellet Biot number is low, the model assumes "local thermal equilibrium" (LTE) between the solid catalyst particles and the fluid phase. In this mechanism, there are no temperature gradients within the pellets, and hence the pellets are treated as isothermal pellets in thermal equilibrium with the bulk fluid temperature.

An alternate approach is to consider heat transfer within the pellet and across the boundary layer between pellet and fluid. This mechanism is named "local thermal nonequilibrium packed bed" (LTN-PB) and was first made available in COMSOL v6.0. At the current stage of development, LTN-PB only assumes pellet-fluid heat transfer and neglects pellet-pellet heat transfer, which can be considerable. In a different project, this model was researched at pilot scale (four 16 kg beds) using real heat-up data and found to give insufficient heat flow. This led to the development of a non-proprietary hybrid heat transfer model which is being prepared for publication. In the final month of the Catalyxx project, standard LTN-PB calculations were compared with LTE, for 100 gram and 5-ton beds. For the 100 g bed, minor effects on conversion and selectivity were noted, but these were associated with bed-level heat transfer and not intrapellet temperature gradients. The 5-ton bed was

much closer to fully adiabatic, so the differences were completely negligible.

4. Project outcomes

The model has been used to design and optimize the ethanol upgrading reactor to enable scale-up. For a reliable, high fidelity modeling concept, the scale-up strategy here covered the lab-scale to commercial scale reactor size. The lab-scale and pre-pilot scale unit experimental results are used to validate the model. Figure 1 summarizes the stage and scale of the modeling work and outcomes.

Suggested optimization strategies were verified in both lab-scale and pre-pilot scale units. Thus, model results are expected to be reliable for de-risking commercial scale reactor designs and operating regimes. Specific outcomes of the modeling results are listed below.

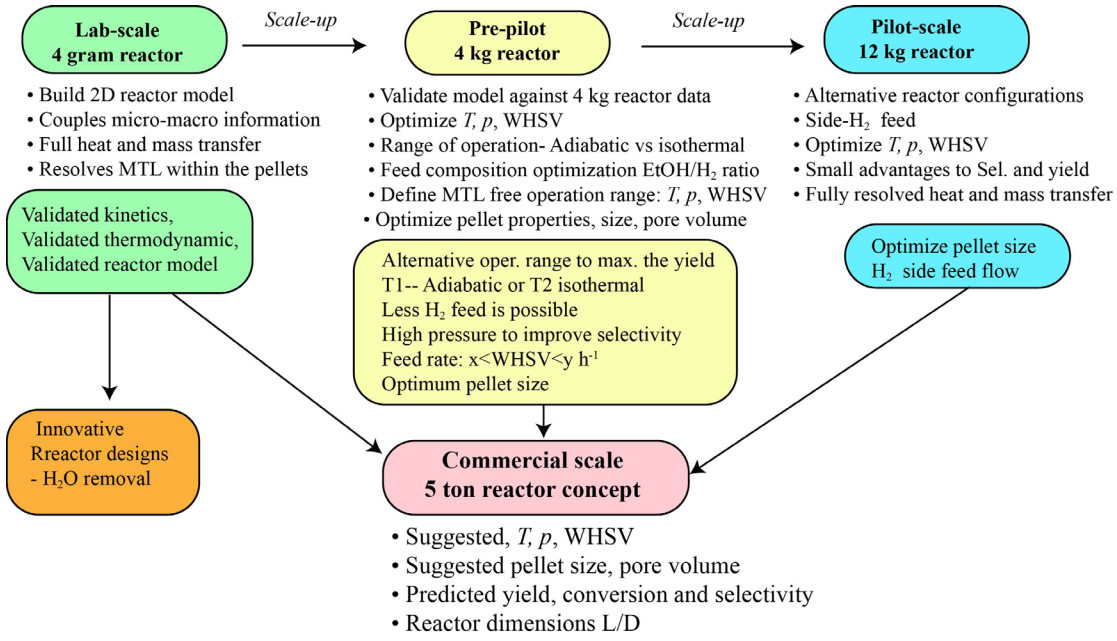

Figure 1: Scale-up methodology from lab-scale to commercial scale

- **Validated thermodynamic and transport database**

The first step of building a reliable non-isothermal, flow reactor model was to assemble a validated thermodynamic and transport database. COMSOL has a limited database of species' thermodynamic and transport parameters. The thermodynamic properties are needed to calculate enthalpy, entropy, Gibbs free energy and specific heat. Transport properties become critical when quantifying mass and heat transport. While there are available commercial licenses to import properties to COMSOL, it is a common practice in kinetic modeling to use "NASA polynomials" which are supported by the scientific community. COMSOL can import and use NASA polynomials in Chemkin format (14 coefficients, 7 for low temperature and 7 for high temperature). The most common library for the hydrocarbons and alcohols is maintained by Prof. Alexander Burcat and often referred as Burcat's database. (http://garfield.chem.elte.hu/Burcat/burcat.html).

While Chemkin NASA polynomial coefficients are widely used in the literature, there are known deviations between NIST and COMSOL's internal database for common species. The short list below shows a comparison between the NIST, COMSOL and Chemkin values for standard state enthalpies (J/mol) of several important species[4]. Differences are small, but it is important to realize that the magnitude of these enthalpies is such that small differences can lead to substantial differences in adiabatic product temperatures. Thus, temperature predictions are always subject to uncertainty due to the underlying thermodynamics, and these cascade into conversion and selectivity uncertainties as well.

- **Validated kinetic model**

Catalyxx's ethanol upgrading process uses a multi-step packed-bed reactor application to convert ethanol to higher alcohols i.e.,octanol. The specific focus of the modeling work here is the first step where ethanol is converted to n-butanol and n-hexanol through a Guerbet chemistry. The process uses a continuous packed-bed reactor at elevated pressure (20-50 bar) and temperature (200-400°C) using a H_2-rich feed.

The reaction chemistry includes 22 reactions and 26 species (including N_2). The reaction network, rate expressions, and initial rate constants were provided by Catalyxx[3]. The reaction rate expressions were evaluated using the lab-scale (4 gram) reactor data provided by Catalyxx. Based on this evaluation, Catalyxx' rate expressions were partially rewritten, and rate constants were re-adjusted. The new chemistry set predicts the experimental data at the temperature range of $220 \leq T \leq 320$ °C for different feed composition and flow ranges. The new validated kinetic model is available as a deliverable in a word format.

- **Validated lab-scale reactor data**

The initial kinetic model provided by Catalyxx was designed for low temperature operation. Since Catalyxx decided to work mostly on the high temperature range the model's range was not sufficient. ORNL designed a set of experiments to improve the kinetic model to cover both high and low temperature range of operation, and in response, Catalyxx provided 3 new experimental datasets. With this new data, the kinetic model was updated to fit the operating range of low to high temperature bar low to high residence time, with a wide conversion range in a lab-scale 4 gram reactor. The model predictions on the operating conditions, e.g., temperature, pressure, H_2/EtOH ratio, flow rate is justified by the lab-scale experiments. The results support the model predictions on conversion, selectivity, and yield both qualitative and quantitatively.

The model was broadened to improve the conversion-temperature dependency. The kinetic model also fined-tuned to capture minor species of CO, CH_4, octanol, decanol, dodecanol, propanol, and ethyl acetate. Based on the new kinetic model, a process optimization methodology has been presented to be validated with lab scale experiments. Operating conditions have been presented to maximize conversion, selectivity, butanol and hexanol production rate. Additional reactor data was also provided for 4 kg scale, non-isothermal operation for validation. The model successfully predicted the temperature and concentration profile of the species at given conditions.

- **Process optimization for lab scale, pilot scale and commercial scale reactor**

The 2D non-isothermal reactor model enabled validating/fine tuning the reaction kinetics to be used from lab-scale (4 gram) to commercial scale (5-ton). The model analyzed the effects of operating regime for maximizing the butanol and hexanol yield, formation rate and the optimum operating pressure and

temperature regime for a scale-up methodology. Isothermal, non-isothermal and intermediate heat transfer operating regimes have been considered for optimizing the alcohol yield.

A specific temperature control strategy is provided to optimize the alcohol yield. A specific range of flow rate, pressure regime, inlet H_2/Ethanol feed composition has been determined for 4kg scale reactor. These model predictions were justified by Catalyxx's 4 kg scale reactor data.

The model analyzed the internal mass transfer limitations for various pellet size and porosity. The ideal pellet size and porosity have been given to Catalyxx to avoid internal mass transfer limitations when operating at the pilot and commercial scale. Internal mass transport analysis was conducted in lab-scale (4 gram) and pilot (4 kg) scale reactor concepts. Results indicate that with given catalyst properties, i.e., micron range, the reactor operates free of mass transfer limitations. When the scale is increased to 4 kg with mm scale pellets, results indicate the strong intra-pellet mass transfer limitations. Possible strategies to avoid the internal mass transfer limitations were investigated including changes in the pellet pore volume, pellet size, and weigh hourly space velocity (i.e., flow rate).

The results suggest that the pellet size (cylindrical) has a more significant impact on the internal mass transfer limitations. Smaller pellet size (smaller than the currently used by Catalyxx), is suggested to reduce the impact of mass transport limitations. The flow rate has a strong impact on the mass transfer limitations and the product compositions. At relatively low flow rate, the mass transport limitations are insignificant. Increasing flow rate increases the mass transport limitations. There is a trade of between the Butanol selectivity and conversion with increasing flow rate. High flow rates increase the Butanol selectivity, but conversion is decreased. A specific flow rate, temperature, and pressure, H_2/EtOH ratio condition is suggested to maximize the yield and minimize the internal mass transfer limitations. Also, the new pilot-scale reactor provides a new unique opportunity to reduce the inlet H_2 fractions which can reduce the operational costs. Based on the simulation results, the H_2/EtOH can be decreased up to 50% with some expectations for decreasing process OPEX and CAPEX. The product composition Butanol and hexanol are strongly affected by the pellet size. While bigger pellets increase the mass transfer limitations and decrease the overall yield, when the pore size of the pellets are increased, the bigger pellets increase the local residence time. As a result, EtOH conversion and hexanol selectivity increases. A maximum of 20% increase in the hexanol yield can be achieved. The details of the catalyst properties, flow and pressure regimes have been delivered to Catalyxx.

- **Scale-up methodology for commercial scale reactor operation: 5-ton reactor concept**

Based on the defined range of operating conditions, the reactor modeled was extended to the 5-ton scale. This scale is beyond the initial milestone of 200 kg. Despite the size and complex reactor geometry the reactor model was able to show full 5-ton scale with detailed heat and mass transfer in 2D. The projected results show that the from 4 kg scale, the operating ranges can be linearly scaled to 5 ton by avoiding the heat and mass transfer limitations. The model also defines the ideal reactor diameter and length for a stable operation. The model results have been shared to predict the net carbon selectivity for each product, yield as function of temperature and pressure. The ideal pellet size and porosity have been also defined.

- **Innovative reactor concept: 12 kg scale reactor with side inlet**

Catalyxx wanted to explore the benefit of a new reactor geometry and feed control strategy. By changing the axial feed point of the H_2 feed, a possible benefit on the alcohol yield was projected.

Catalyxx had a 12 kg scale reactor operation with a side inlet configuration. ORNL developed a new reactor geometry and modeled the possible effects of side inlet configuration. The effects of temperature, pressure, and fraction of side inlet H_2 feed to the total feed were explored.

- **Innovative reactor concept: H_2O removal**

A novel innovative reactor concept was presented. The ORNL team modeled a packed-bed reactor model with in-situ H_2O removal. The results suggest that the EtOH conversion and alcohol yield can be increased. Model conceptualizes in-situ H_2O removal in a packed-bed reactor configuration in a lab-scale (4 gram) reactor. ethanol conversion and butanol yield linearly increase with increasing H_2O removal rate. Model results suggest that the butanol yield and formation rate can be increased up to 30%, when 60% of the H_2O is removed. The model does not specify the H_2O transport mechanism assuming there is no H_2O transport limitation occurs. The yield increase depends on the H_2O amount removed from the system. The practical application of the H_2O removal concepts has been proposed. An invention disclosure (ORNL Disclosure Record Number: 81938384) has been submitted. The Invention disclosure summarizes the practical ways of H_2O removal in a packed-bed reactor geometry. The patent disclosure explains two possible methods of designing and operating a membrane reactor.

Acknowledgements

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