CRADA No: NFE-20-08393

FINAL REPORT

DFO Computational Modeling Project

Catalytic Upgrading of Bio-based Furfural to 1,5-Pentanediol: A New Renewable Monomer for the Coatings Industry

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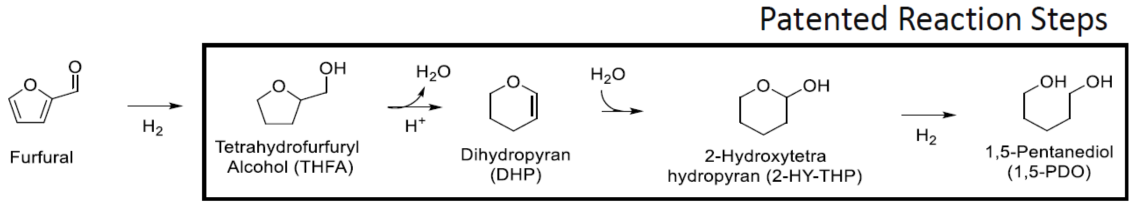
1. Summary

This report summarizes the results of a collaborative effort between Oak Ridge National Laboratory (ORNL) and Pyran™ Inc. to utilize modeling capabilities developed by the CCPC (Consortium for Computational Physics and Chemistry) to assist Pyran in scaling up its proprietary process for thermocatalytic conversion of furfural to 1,5 pentanediol (PDO). Pyran's bio-based PDO is a direct replacement for petroleum-based PDO and 1,6 hexanediol (HDO) currently used in polymers, additives, coatings, adhesives and sealants. The current market is in excess of $1B/yr. According to Pyran, their production process results in 95+% reduction in fossil CO_2 at lower production costs compared to the existing petroleum-based routes for PDO & HDO. Other chemicals based on intermediates from this process have current markets in excess of $10B/yr. [1]



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under Cooperative Research and Development Agreement (CRADA) NFE-20-08393. The project kicked off on February 23, 2021 and was completed in December 2022.

The report here summarizes a packed-bed reactor modeling effort that focused on reactor designs and operating conditions for two of the patented steps shown above: tetrahydrofurfuryl alcohol (THFA) to dihydropyran (DHP) [known as reaction 2 or "R2"] and 2-hydroxytetrahydropyran (2-HYTHP) to 1,5-pentanediol (1,5 PDO) [known as reaction 4 or "R4"]. The combined experimental + modeling studies spanned a range of catalyst beds from 23 grams to 61 kg. Two other reactions in Pyran's process are furfural to THFA (reaction 1 or "R1") _and DHP to 2-HY-THP (reaction 3 or "R3"). Research on the reactions R1 and R3 were of lower priority and are not discussed in depth here.

In this report, the findings are described qualitatively to protect the intellectual property (IP) rights of Pyran. Any specific details found in this report have been shared publicly in prior communications with the permission of Pyran. Detailed results have been shared in monthly steering meetings of the CRADA team and are documented in presentations stored in the shared data house owned by Pyran, accessible only to members of the CRADA team.

2. Work Scope

ORNL's modeling work supported the scale-up exercises and explored reactor configurations and operational strategies to optimize the production of 1,5 PDO from THFA. Model development was supported by Pyran's experimental data obtained from several different lab scale reactors and, later in the project, from the toll manufacturing campaign that took place in the large "pilot-plus" packed bed reactor system located at Refining Process Development Technologies (RPD) in Crosby, Texas. In this unit, the R2 catalyst bed was quite large: 61 kg in total, split between four 14.6 cm diameter, 1.37 m tall reactor tubes connected in series. *(It is worth noting that Adkins introduced Pyran to RPD – a toll manufacturing and development company owned by former KiOR colleagues of Adkins - and assisted on-site in the early setup portion of the campaign.)*

The work plan was as follows:

Task 1: Determine critical model parameters and construct an initial laboratory dataset for Pyran's reactors and catalysts. *Initial reactor data will include parameters such as temperature rise across the catalyst bed, hydrogen availability (for reactions 1 & 4), catalyst deactivation behavior, catalyst regenerability (for reaction 2), and interphase heat and mass transfer limitations. Catalyst characterization data will include catalyst surface area, porosity, and active sites as well as temperature programmed analyses like temperature programmed reduction (TPR).*

Task 2: Develop preliminary spreadsheet models for Participant's demonstration scale reactors. *Participants will focus on obtaining laboratory scale data for this step. Preliminary spreadsheet models will be produced for reactions 2 (THFA dehydration) & 4 (2-HTHP hydrogenation) for demonstration scale.*

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Task 3: Develop COMSOL reactor models for Participant's upscaled reactors. *ORNL will use reactor and catalyst data obtained by Pyran in Obj. 1 to design fixed-bed reactor process models in COMSOL for reactions 1, 2, & 4. Reactions 1 & 4 are exothermic hydrogenations with greater technical challenges and complex reactor requirements and will therefore be the focus of this objective. It is desired to complete a detailed COMSOL model for reaction 2 (THFA dehydration) if time and resources allow, but this is not* *regarded as critical for the progression of this project or Participant's scale-up needs.*

Task 4: Validate COMSOL reactor process models with experimental data and generate base-case simulations for upscaled operation. *Pyran will collect additional data in lab and demonstration scale equipment to validate the reactor models developed in Obj. 3. Using this validation data, ORNL will generate base-case simulations for Pyran's toll scale reactors. A validation dataset will be obtained from toll scale reactors for reactions 2 & 4. As reaction 1 will not be included in toll scale experiments, additional laboratory data will be collected for this step to validate the COMSOL model.*

Task 5: Completion of CRADA final report. *Target date is one calendar year after project kickoff.*

During the project, ORNL performed computational modeling, and Pyran provided process and reactor information, provided critical experimental data, and performed scale up of their technology at RPD in Crosby, TX. Frequent steering team meetings were held to facilitate technical exchange and ensure the project remained on track. As common for research projects of high level of complexity, task priorities and technical challenges evolved over the duration of the project. Specific notes on project flow of interest follow:

- R2 became the highest priority in the project, followed by R4. R2 proved to be the most difficult step requiring the most time and effort and demonstrated the biggest scaleup difficulties and commercial-scale reactor design challenges. In the large reactors at RPD, the exothermicity of R1 and R4 proved to be much less challenging than the endothermicity of R2, plus additional phenomena were observed in R2 that were not seen in the lab-scale reactors.

- In substitution of the temperature programmed characterization method, a detailed shape characterization was performed for the R2 catalyst using optical microscopy capabilities at ORNL. This provided the best estimate for pellet SED (spherical equivalent diameter) for our modeling work.

- Some spreadsheet models were completed for (a) estimating pressure drop for known product slates and reactor temperature profiles, and (b) for thermodynamic verification of heat balance. The latter proved to be a critical project addition, as some of the newer COMSOL features required accurate heat balances to verify correct software settings were used. However, creation of ROMs (reduced-order models, or "spreadsheet models") from most of our completed reactor models proved elusive, given the timing of the toll campaign and unforeseen modeling difficulties. (The exception is the transient coke deactivation models, for which ROMs were built.)

- It was originally proposed that the work would be finished one year after kickoff, however, the longer-than-expected toll campaign at RPD necessitated extending the project. The CRADA was extended but no additional funds were requested or needed to complete the work scope.

- The use of ORNL's COMSOL models in Tasks 3 and 4 went extremely well and provided an excellent framework for achieving the targeted scale up of Pyran's technology. The team's experience in (a) developing a lab-scale model with preliminary data, (b) collecting additional lab-scale data for validation, and (c) extending the model to larger scale with specific experiments and adjustments followed by large-scale validation, was a textbook example of computational-guided technology scaleup.

3. Pyran's Process and Specific Scaleup Challenges

In typical packed-bed catalytic reactors, catalysts pellets are loaded into cylindrical tubes, and reactants are fed through the reactor inlet. Lab and pilot scale reactors make use of both inlet and wall heating (or cooling), but for commercial scale reactors, wall heat input or removal is difficult because of large conduction distances in the bed. Many commercial reactor designs exist to improve heat transfer in packed beds, such as shell and tube reactors used for highly exothermic or endothermic reactions like steam-methane reforming (SMR) or partial oxidation (EPO), or quench boxes common in hydrotreating. Of course, these features increase the reactor cost.

The composition of the product mixture at the reactor outlet is analyzed at regular intervals. Deactivation is reflected by loss of conversion with time and is typically compensated by increasing temperature. (For that reason, deactivation rates in industrial packed bed reactors are commonly expressed as "TIR", i.e., temperature increase required.) The most common cause of deactivation is coke formation, which is usually reversible, but many types of irreversible deactivation can also occur. Coke formation is usually studied by characterizing the physical distribution of coke (by bed segmentation and pellet sectioning) along with chemical analysis. Such measurements have great value in developing coke deposition models, which are very useful for optimizing processes using catalysts that experience rapid coke deactivation.

In scaleup, the dimensions of the reactor tube, fluid distributors, internal and external heat transfer equipment, bed grading and catalyst bed properties (loading methods) are all subject to change. Importantly, scaleup is often accompanied by larger gradients in temperature and composition resulting from pellet-scale and reactor-scale mass and heat transfer limitations, as well as dispersion from maldistribution (flow patterns deviating from plug flow) that can result in nonuniform residence time distributions. Except for the simplest cases, computational scaleup models usually offer the best means to compensate for these phenomena. Not surprisingly, scaled-up reactors usually differ considerably from their lab-scale counterparts in both physical and operational aspects.

Pyran's R1, R2 and R4 steps are carried out in packed bed catalytic reactors. The R3 step is a simple noncatalytic reaction carried out in a CSTR reactor and was never part of this project. Appropriately for a dehydration reaction, R2 is a single (gas) phase reaction at relatively high temperature and low pressure, while R4 is carried out at high pressure in the presence of excess hydrogen and is a two-phase (trickle bed) reaction. (ORNL confirmed R4 to be a two-phase reaction system through thermodynamic calculations). Strictly from the perspective of modeling, R4 is considerably more difficult than R2. However, the R2 catalyst suffers from deactivation from coke on a relatively short timeframe (0.5-2 days) and requires regular oxidative regeneration, whereas the R4 catalyst is much more stable and requires very infrequent regeneration, as is typical for most hydrotreating processes with relatively high hydrogen partial pressures. Thus, R2 is more complex from the viewpoint of the operational cycle. We will return to this point later.

One of the most important efforts both on Pyran and ORNL side was kinetic model development. The initial reference for R2 chemistry failed to describe the rate constants and units were not consistent [7], and the range of operation conditions given in the paper was limited. A new Design of Experiments (DoE) was created for kinetic model validation, and additional experiments were carried out by Pyran. The kinetic expression was rewritten using the LHHW convention, and the rate constants were readjusted using the full set (old and new) of isothermal reactor data. As the data expanded, Chemical Kinetic (CK) models were fine tuned in progression, starting with version CK-1 and culminating with version CK-5. CK-5 was especially important for RPD R2 operations, where higher temperatures were required than in the isothermal lab work.

4. The Computational Modeling Frameworks

One- and two-dimensional axisymmetric packed-bed reactor modeling frameworks were developed using COMSOL™ Multiphysics software, for Pyran's R2 and R4 reaction steps. Both frameworks model the fluid flow and heat and mass transfer occurring in beds of porous catalyst(s). For R2, the models included accurate chemical kinetics (CK-1 through CK-5), but for R4, the models developed in this project have progressed only to the stage of incorporating multiphase equations of state. R4 kinetic model development requires additional work.

A 2D axisymmetric framework was used for all steady state models and nonreacting transient models (heat transfer studies), while a 1D axisymmetric framework was used exclusively for transient models with full chemistry and deactivation by coke deposition, which were computationally intractable in 2D form (especially at RPD scale). Obviously, the 1D form cannot predict radial variations in any computed properties, but a wall heat transfer boundary condition is available.

Both model frameworks solve for heat transfer (conduction and convection) and mass transfer (advection and diffusion) occurring in the void spaces of the beds, while simultaneously solving for mass and heat transfer and chemical reaction inside the catalyst pellets. The pellet calculations are carried out with the aid of the "extra dimension" feature in the *Packed Bed* model, which is part of the *Reaction Engineering* module in COMSOL v6.0+. This extra dimension is used to model a 1D intrapellet domain, for which the fundamental heat transfer, mass transfer, thermodynamic and chemical reaction equations are solved simultaneously with those in the 2D reactor domain. Since the intrapellet domain is one-dimensional, catalyst pellets are represented as spheres having the same surface to volume ratio as the real pellets. Discrete pellet conservation equations ensure that heat and mass fluxes in each grid cell accurately represent the actual number of real pellets.

This approach basically places a virtual catalyst pellet in each grid cell, so gridding determines the resolution of pellet-to-pellet variations. We use an important parameter called the "pellet number" which represents the number of real pellets represented by the average virtual pellet. Variations in pellet packing can be easily incorporated provided experimental guidance exists (there is no DEM-type modeling of pellet packing). Importantly, mixed systems of any number of pellet types can be modeled, but again, experimental data is needed to describe the overall packing system. Stacked beds of different catalysts can also be modeled.

Prior to COMSOL v6.0, the *Packed Bed* feature was called *Reactive Pellet Bed*, and while many variables could be functions of radial position inside pellets, temperature could not. In other words, pellets were always treated as isothermal entities. So, when using the *Reactive Pellet Bed*, heat transfer models were restricted to essentially bed-level heat transfer, with equivalent thermal conductivities defined according to a number of physical solid-fluid interspersion models. These models were dubbed *LTE*, for *Local Thermal Equilibrium*. With the release of *Packed Bed* in v6.0, microscopic heat balances equations were introduced in the pellet domain, allowing nonisothermal pellets, with discrete modeling of heat transfer within the pellet and at the pellet-fluid interface. This was a non-trivial development, as it requires two interspersed temperature fields. The version of this model incorporated in v6.0 is called *LTN-PB*, for *local thermal nonequilibrium packed bed*.

A major shortcoming of *LTN-PB* is that no pellet-pellet heat transfer is modeled. Recently we carried out a large study of actual heat-up data from the individual 16-kg R2 catalyst beds at RPD and proved that *LTN-PB* gave insufficient heat transfer to match the experimental data. Notably, we were able to develop a hybrid *LTN-PB/LTE* model which combines intrapellet, pellet-fluid and pellet-pellet heat transfer, and tune it to accurately fit the experimental data. This model is useful for scoping new catalysts and reactions, where the Biot number might not give an unambiguous answer regarding particle isothermality. The hybrid model is computationally expensive and complex, so we plan to use it only when needed. One or more publications on the heat transfer studies and development and application of the hybrid model are in preparation.

On the chemical reaction side, the models can include elementary surface reaction microkinetics as well as lumped kinetic models that include some steps where coverages are governed by adsorption-desorption equilibria, such as LHHW. The gas-phase species thermodynamic properties are defined in NASA-type (quartic) polynomials taken from the Burcat database [3]. The transport properties are adapted from the Chemkin database [4].

For additional details on the COMSOL features used in these modeling frameworks, see ref. [5].

5. R2 Models

The vast majority of modeling work was for R2. In total 35 different models were constructed, with slightly more than 2,000 simulations in total. An Excel run log was created for each model, and all simulations were logged in detail sufficient to re-create the models from scratch using the appropriate version of COMSOL. Probe tables and other results were imported into the Excel run logs, and detailed analysis was carried out in a variety of ways ranging from simple graphical analysis to multivariate regression. PowerPoint presentations were prepared summarizing the relevant features and findings of each model. A summary table of all 35 models was also created, with many details, explanations, and findings. All these materials are available to members of the CRADA team.

The R2 models can be summarized as follows:

- **PR2-5 through PR2-7 (242 simulations)**: **steady-state 2D models of lab-scale** single-bed and multiple bed reactors with and without diluents (Al-Dahhan method [2]) and inerts, in isothermal, adiabatic and heat transfer versions. Pyran's starting kinetics were tweaked, resulting in kinetics version CK-3, and models were validated against Pyran's original lab data.

- **PR2-8 through PR2-20 (524 simulations): transient 1D models of deactivation by coke deposition at lab scale** with and without diluents and inerts, with several different chemical, physical and kinetic postulates for coke formation. The results have been analyzed in ways suitable for comparison with physical data (pore sizes, intrapellet carbon profiles, bed carbon profiles etc.) and ROMS were constructed for fitting deactivation times. So, while no validation has yet occurred, only a (reasonably) small amount of data is needed for model for model down-selection and further refinement.

- **PR2-21 through PR2-25 (169 simulations): initial attempts at modeling the large RPD reactors** in both 2D steady-state and 1D transient forms. In spite of many attempts utilizing various numerical strategies, these were largely unsuccessful.

- **PR2-26 and PR2-27 (76 simulations): successful modeling of large RPD reactors in 2D steady-state form**. These models were the culmination of considerable numerical work started in the previous group. They were the first to test some of the options in COMSOL heat transfer models. <u>These models constituted the first successful validation of our scaleup models with RPD data,</u> in that several key observations from RPD operations were predicted correctly, not the least of which was the steady-state "fresh" THFA conversion at the actual WABT (weight-average bed temperature) and feed flowrate. These models were also the first to have confirmed heat balances based on manual thermodynamic calculations – a development which proved very important for validating correct choices of COMSOL modeling options.

  At the same time, the results of these models clearly pointed to the next level of refinements needed to take the scaleup exercise to the next level (i.e. to evaluate new reactor designs and startup procedures and optimize the full swing cycle, including catalyst regeneration), taking into account (a) some observations that were never seen at lab scale that are currently being researched at Pyran, and (b) the true level of deactivation, which was much higher than at lab scale, and (c) the temperature variations across the bed for the given wall heating scenarios.

- **PR2-28, 30,31 (441 simulations): first full test of heat transfer options available in COMSOL v6.0**, including the new *LTN-PB* pellet-resolved heat transfer model, at 100 g hypothetical scale. This was the first demonstration that heat flows in *LTN-PB* are determined by intrapellet and pellet-fluid heat transfer and relatively independent of bulk parameters, as would be expected based on the mathematical formulation (see section 4).

- **PR2-32 (36 simulations): first full test of *LTN-PB* in RPD reactors**. Confirmed the 100 g findings concerning *LTN-PB*.

- **PR2-29 (21 simulations): transient 1D models of deactivation by coke deposition in RPD reactors**. This model demonstrated that the approach to coke deactivation modeling worked at large scale.

- **PR2-33 through PR2-40 (319 simulations): highly detailed 2D transient heat transfer study for the RPD reactors**, using heat-up (nonreacting) data with highly refined wall and inlet temperature maps and five bed thermocouples in each reactor. Findings include (a) for the *LTE-VA* model, an optimum value of pellet effective thermal conductivity and average bed probe penetration depth (essentially the same for all reactors), (b) a clear demonstration that in all cases, *LTN-PB* produced insufficient heat transfer to match the bed thermocouples, and (c) a hybrid model of our own creation, in which the fluid thermal conductivity is replaced with an *LTE-VA* type effective thermal conductivity and combined with the *LTN-PB* pellet-scale model, which could accurately fit the bed thermocouple data in all cases tested. The hybrid model is especially significant as it essentially allows for intrapellet, pellet-fluid and tunable pellet-pellet heat transfer. A publication summarizing this highly successful study is in preparation.

- **PR2-41 (84 simulations): a final model testing our "best-in-class" heat transfer (*LTE-VA* with fitted parameters) and kinetic (CK-5) models.** This model uses bed and wall temperature data and THFA conversion measured at reaction conditions and includes a comparison of WABT (weight average bed temperature) and ABTT (average bed thermocouple temperature), which differ by as much as 20°C under modeled heat transfer conditions. Use of these models culminated in a quantitative estimate of the average extent of startup deactivation seen in the RPD R2 reactors – something that was realized by Pyran, but not possible to quantify before. Thus, this tool is now available for evaluating different reaction designs and startup conditions, in the attempt to minimize the startup deactivation and extend the time between regenerations. More importantly, these results proved that our R2 models are indeed ready to go to the next level - i.e., to evaluate new reactor designs and startup procedures and optimize the full swing cycle, including coke deactivation (pending validation) and catalyst regeneration (based on Adkins' previous work [6]).

- **PR2-42**. This designation has been reserved for a future iteration based on PR2-41, wherein the actual bed and wall temperature profiles are used instead of ABBT and average wall temps. The idea here is to try to estimate the activity profile across the bed. This model would be extremely helpful for optimizing and validating the coke deactivation model (making the reasonable but to-be-confirmed assumption that most of this startup deactivation comes from rapid coking).

6. R4 models

The final reaction step of 2-HY-HTHP hydrogenation to 1.5 PDO operates as a multi-phase reactor. The high-pressure, low temperature operation results in co-existing liquid and gas-phase species. Although the reaction can operate at stable conditions, the reaction network is complex. Pyran provided a 4-step reaction pathway to describe products and bi-products. However, the overall reaction contains 7 gas-phase and liquid-phase species (@ STP), and some of these species are not well known in the literature. So, the thermodynamic and transport database of these species were extracted from ASPEN. The reactor model uses the Soave-Redlich Kwong equation of state to model the gas-phase and liquid phase properties.

The R4 model contains a vapor-liquid-equilibrium (VLE) feature. Depending on the range of operation (*T,p*) and the species concentration, the model can provide the state of the component i.e., liquid, gas or saturated liquid. Thus, based on the composition and temperature profile in the reactor, the model can detect the phase change.

7. Acknowledgements

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8. References

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