

# **PROCESSES AND MINI AND MICROREACTORS**

## **I-19. Mini Reactors for Characterization of Hydrocarbon Oxidations**

### **A. Problem Definition**

The partial oxidations of hydrocarbons in liquid phase, using air and oxygen, are of great industrial importance (i.e. oxidation of p-xylene to terephthalic acid, cyclohexane to cyclohexanol/cyclohexanone, cumene to cumene hydroperoxide etc.). Complicated mechanisms of these reactions, their importance as well as increasing environmental concerns have been the main driving forces for many studies and research (Suresh et al. 2000). In particular, approximately 3 million tons/year of cyclohexane are oxidized, and used in production of Nylon (invented in 1934 and commercialized in 1940). This is one of the most inefficient industrially commercial processes today. Conventional route (tanks in series or staged bubble column) has low conversion (4-10%) due to higher reactivity of intermediates (cyclohexanol and cyclohexanone) than that of cyclohexane (selectivity is 80-85 %) and involves large separation and recycle tasks.

### **B. Research objectives**

It is expected that use of oxygen enriched air or pure oxygen should benefit the oxidation process. However, the concern for potential explosion or deflagration either in the vapor space or the vapor bubbles has been the major reason for not performing the oxidation of cyclohexane even in small lab-scale reactors.

Greene and his collaborators (US 5,780,683 patent, 1998) reported first cyclohexane oxidation with pure oxygen performed in Liquid-phase Oxidation Reactor (LOR). They claimed an increase of selectivity and productivity while reaction temperature and residence time were reduced (to reach 4% conversion of cyclohexane).

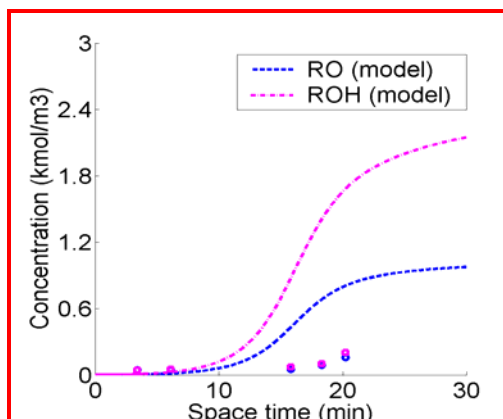
Our objective is to determine the effect of the oxygen availability. Since intermediates are desired products in cyclohexane oxidation, plug flow reactor is the reactor of choice among conventional reactors.

However, in situ removal of products is to be preferred and the information needed to access the feasibility of various reactors with in-situ separation (e.g. reactive distillation) will also be investigated.

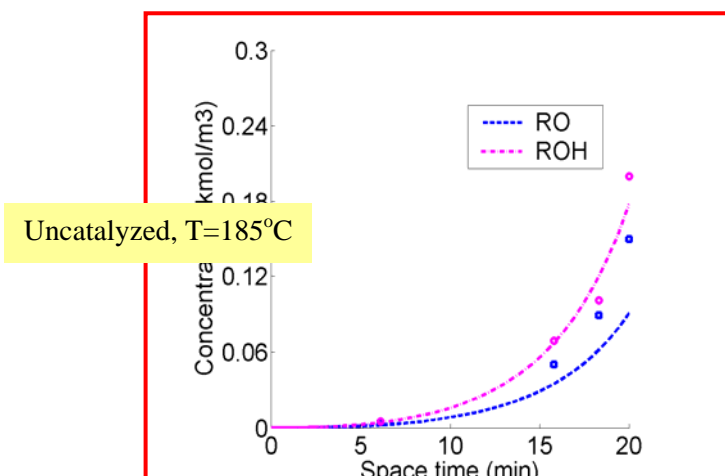
Finally, we want to develop an appropriate reactor model for interpretation of various reactor configurations.

### **C. Accomplishments and Current Work**

Cyclohexane oxidation was performed in two capillary reactors ( $d_1=0.762$  mm;  $V_1=13$ ml and  $d_2=2.159$  mm,  $V_2=50$ ml) at different temperatures ( $T=150-200^{\circ}\text{C}$ ), with and without catalyst (cobalt naphthenate). The experimental results are compared with the plug flow reactor (PFR) model and presented below.



**Figure 1.** Concentration of cyclohexanone (RO) and cyclohexanol (ROH) vs time as predicted by model and obtained by experiments ( $T=473\text{K}$ ,  $p=20\text{bar}$ ,  $RH/O_2=6$ , without catalyst)



**Figure 2.** Concentration of cyclohexanone (RO) and cyclohexanol (ROH) vs time as predicted by model ( $T=458\text{K}$ ) and obtained by experiments ( $T=473\text{K}$ ,  $p=20\text{bar}$ ,  $RH/O_2=6$ , without catalyst, smaller capillary)

Kinetic scheme and kinetic constants from Schaefer et al. (2003) and mass transfer correlation for Taylor flow (only Taylor flow was observed) from Bercic and Pintar, (1997) were used in the model.

Concentrations of the products obtained experimentally are an order of magnitude lower (Figure 1) than those obtained by PFR model. Also, conversion at 20 min as predicted by the model is 36% while experimentally achieved conversion is 6%.

If the same experimental data are compared with model results obtained for  $T=468\text{K}$ , the agreement is much better (Figure 2). There is possibility that reaction parameters as reported are not correct or that we had a temperature control problem.

Similar discrepancies between model and experiment were observed when catalyst was used. To examine the effect of the oxygen availability PFR and Stirred tank reactor (STR) model were used as well.

As evident from Table 1 and Table 2, that the effect of oxygen in uncatalyzed oxidation of cyclohexane is not pronounced. In catalyzed oxidation, time to reach 4% conversion of cyclohexane is approximately 4 times shorter if oxygen is an oxidant as opposed to air. Hence, productivity is increased while selectivity is almost the same.

**Table 1.** Oxidation of cyclohexane with air vs oxygen in STR (P=10 bar, T=433K)

	<i>Oxidant</i>	<i>X (%)</i>	<i>Selectivity % (ROH+ RO)</i>	<i>Selectivity % (ROH+RO+ROOH)</i>	<i>t(min)</i>
<b>Catalyzed (STR)</b>	air	4	78	93	7.6
	oxygen	4	57	89	1.8
<b>Uncatalyzed (STR)</b>	air	4	23	96	64.5
	oxygen	4	23	96	61.8

**Table 2.** Oxidation of cyclohexane with air vs oxygen in PFR (P=10 bar, T=433K)

	<i>Oxidant</i>	<i>X (%)</i>	<i>Selectivity % (ROH+ RO)</i>	<i>Selectivity % (ROH+RO+ROOH)</i>	<i>t(min)</i>
<b>Catalyzed (PFR)</b>	air	4	58	87	1.2
	oxygen	4	51	82	0.3
<b>Uncatalyzed (PFR)</b>	air	4	23	96	63.6
	oxygen	4	23	96	61.3

#### D. Future Work and Milestones

In the residence time available in our plug flow system only low levels of conversion of cyclohexane (less than 3 %) were achieved. Our next step is to investigate the use of initiators and better catalyst. Also, we will examine whether laminar flow, which is the type of flow obtained in the capillary reactor, has impacted the reaction negatively and whether some back mixing might be necessary for the formation of free radicals. To understand properly the effect of back mixing on this reaction, a different reactor (stirred tank) is being used. Information gained through this experimental study will help in assessing whether catalytic distillation may work.

- Mini CSTR tested and ready for assessment of hydrocarbon oxidation: June 2006
- Implementation and experimental verification of Gas-Liquid Reactor model prediction: April 2007

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#### E. References

- 1) Bercic, G. and A. Pintar (1997). "The role of gas bubbles and liquid slug lengths on mass transport in the Taylor flow through capillaries." *Che. Eng. Sci.* **52**, 3709-3719.
- 2) Schaefer, R., C. Merten, et al. (2003). "Autocatalytic Cyclohexane Oxidation in a Bubble Column" *The Can. J. of Chem. Eng.* **81**, 741-748.
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## I-20. Modeling the Effects of Temperature, Pressure, and Oxygen Solubility on Liquid Phase Oxidation of Cyclohexane

### A. Problem Definition

Cyclohexane oxidation in the liquid phase is of great industrial importance. Approximately  $10^6$  tpa of cyclohexanone and cyclohexanol (also known as KA oil) are made worldwide and used further in the production of adipic acid and capolactum, which are ultimately used in the manufacture of nylon-6 and nylon-6,6. On the other hand, this process is one of the least efficient of all major industrial chemical processes as large scale reactors operate at low conversions. These inefficiencies as well as increasing environmental concerns have been the main driving forces for many studies and research (Suresh et. al., 2000). However, no systematic study on the effect of oxygen availability at different temperatures and pressures has been reported to date. Hence, there is still a lack of thorough understanding of hydrocarbon oxidation reaction mechanism and its effect on selectivity.

A new model for liquid phase oxidation of cyclohexane, including reaction kinetics, mass transfer, and hydrodynamics parameters, is being developed. The comprehensive 9 steps kinetic model by Pohorecki et. al. (2001), multistage free radical chain reaction mechanism and kinetic rate constants determined by Kharkova et. al. (1989), and oxygen solubility in cyclohexane and values of Henry's constant from Suresh et. al. (1988) are used as a starting point. The concentration of free radicals are eliminated using quasi-steady state hypothesis. The influence of temperature, pressure, and oxygen availability on the reaction rate and the selectivity is determined. The new model enables the comparison of different types of reactors, namely, continuous stirred tank, bubble column, and microreactor.

The project also aims of comparing modeling results with the experimental findings, in order to understand and determine the significance of most influencing parameters. Experiments will be carried out in a mini reactor system due to safety with homogenous catalyst (cobalt naphthenate), heterogeneous catalyst, the presence and absence of supercritical media ( $\text{CO}_2$ ) (expanded solvents) to increase the oxygen solubility.

### B. References

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## **I-21. Experiments and Mathematical Modeling to Evaluate Solid Acid Alkylation Processes**

### **A. Problem Definition**

The biggest challenge facing alkylation technology is to commercialize solid acid catalysts in place of traditional hydrofluoric acid (HF) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) homogeneous catalysts. Three decades of research have shown that a number of solid acid alkylation catalysts display good initial alkylation activity, but rapidly deactivates due to build up of heavy hydrocarbons in catalyst pores. Hence, periodic regeneration of solid acid catalysts is required for the successful commercialization of these processes. The first step towards making the solid acid catalyzed processes economically feasible is to enhance our understanding of the mechanisms of diffusion, adsorption/desorption and deactivation on solid acid catalysts. The measurement of transport and equilibrium parameters of liquids in porous solids can be achieved by dynamic tracer methods in a packed bed reactor (M. P. Dudukovic et al (1981), P. Li et al (2004)). The technique of estimating the parameters by modeling the breakthrough curve and comparing with the experimentally generated one is shown by M. P. Dudukovic et al. (1985).

### **B. Research Objectives**

Design and develop a packed bed and a mixed autoclave reactor facility for solid acid catalyst evaluation.

This facility will be employed to:

- Evaluate the catalyst performance, deactivation rate, and product quality
- Estimate transport and equilibrium parameters, like effective diffusivity and adsorption/desorption isotherms, from experimental step responses by using the appropriate reactor and particle scale models
- Investigate and determine the kinetics of solid acid catalyst for alkylation reaction

### **C. Research Accomplishments and Current Work**

A packed bed reactor facility was installed and tested (Figure: 1). Packed bed reactors (5 and 50 ml) were fabricated using titanium alloy to withstand the corrosion effect from any solid acid catalyst. Stainless steel tubing (1/8") was used in process lines. New gas chromatograph was procured and installed for reactor effluent analysis. Mathematical model of the reactor coupled with the catalyst particle was developed for parameter estimation (P. Persson et al. (2005)). Numerical techniques using computational algorithms and moments of solutions were developed to solve the mathematical model (M. P. Dudukovic et al (1981)). In the current work; a step input of iso-butane or 2-butene in helium was made to a packed beta-zeolite bed at different temperatures and pressures. The model dependent numerical algorithm was used to evaluate the tracer response and to estimate transport and equilibrium parameters. The bed is characterized by using a step response of nitrogen. It was observed (Figure: 2) that the adsorption and desorption of iso-butane on beta zeolites was non-linear and follows a Langmuir-Hinshelwood type of adsorption isotherm.

## D. Future Work and Milestones

Task 1: Estimation of the effective diffusivities and adsorption/desorption parameters of 1-butene, iso-butane, and tri-methyl-pentane in the inert gas (Helium) on mesa-porous silica support and beta zeolite in packed bed unit (50 ml). The following conditions will be used:

- Gas Phase: Temperature: 298, 323, 348 and 373 K and Pressure: below vapor pressure  
*Deliverable:* October 31, 2006.

Task 2: Comparing the results for two different reactors (5 and 50 ml) at different operating conditions to give same estimated parameters. This will help for future references

*Deliverable:* October 31, 2006.

Task 3: Estimating the film effect when more than one component is present in gas phase by introducing iso-butane and 1-butene together on mesoporous silica support.

The following conditions will be used:

- Gas Phase: Temperature: 298, 323, 348 and 373 K and Pressure: below vapor pressure  
*Deliverable:* October 31, 2006

Task 4: Repeating Task 1, 2 and 3 using following conditions:

- Liquid Phase: Temperature: 298, 323, 348 and 373 K and Pressure: above vapor pressure  
*Deliverable:* January 31, 2007

Task 5: Repeating Task 4 using expanded phase at following conditions:

- Expanded Phase: Temperature: 298, 323, 348 and 373 K and Pressure: above vapor pressure

*Deliverable:* April 30, 2007.

Task 6: Using 250 ml autoclave reactor measuring effective diffusivities and adsorption parameters in the liquid phase and expanded phase at the conditions same of Task 4.

*Deliverable:* April 30, 2007

Task 7: Comparing the measured parameters for liquid phase and expanded phase obtained from packed bed unit and autoclave reactor.

*Deliverable:* May 15, 2007

Note: A number of manuscripts for publication should be prepared during this task.

Task 8: Studying Alkylation reaction in autoclave reactor with and without basket and packed bed unit using beta zeolite catalyst for liquid and expanded phases.

*Deliverable:* Initiating work August 31, 2007.

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## E. Acknowledgment

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Figure 1: Packed bed reactor set up

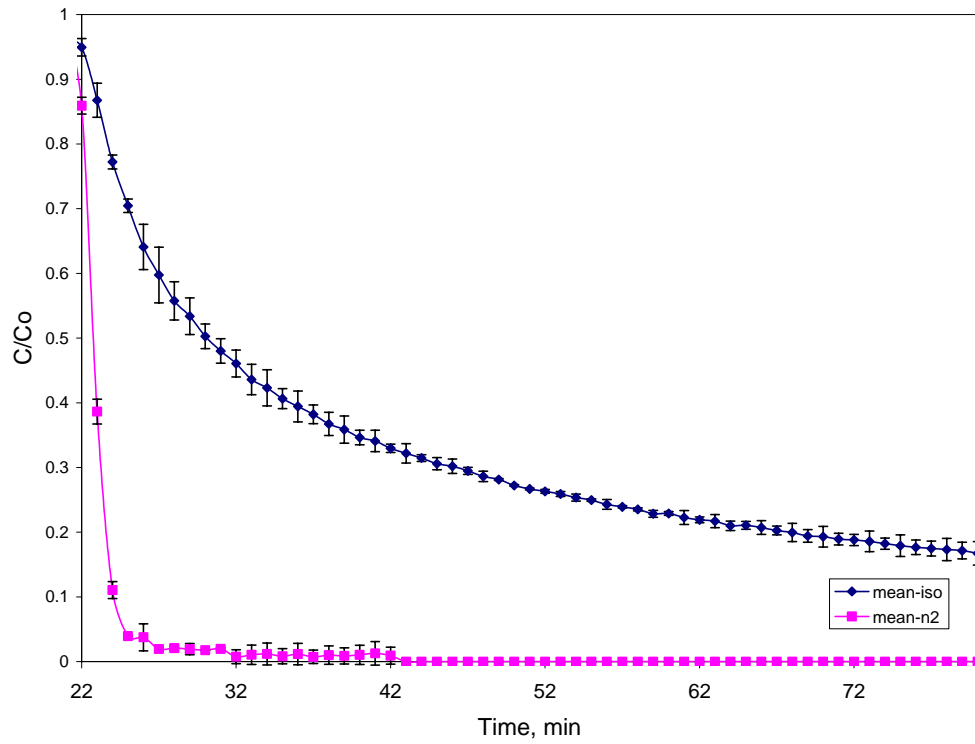
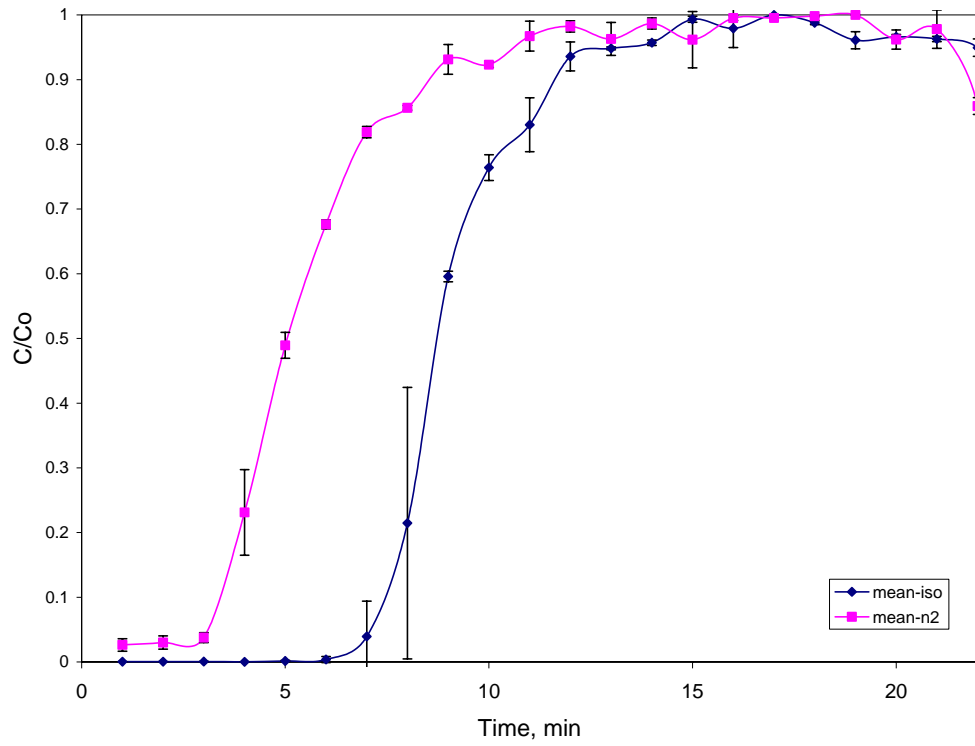


Figure 2: Step up and down responses of Iso-butane on Beta Zeolites at 298 and 323 K and 1 atmospheric

## I-22. Molecular Simulation Studies of Adsorption Isotherms for Solid Acid Alkylation Catalysts

### A. Problem Definition

Microporous materials, such as zeolites, both in powder and thin membrane form, play a major role in solid acid catalysis. The pore sizes of these materials are usually of the same magnitude as the molecular diameters of the adsorbates. This causes rich and interesting transport behavior that is difficult to predict. Molecular simulations have become increasingly popular tools for developing an understanding of the relationship between molecular-level structure and observable macroscopic properties in such systems. The aim of this project is to predict the adsorption properties by using molecular simulations. Such information is important in developing and selection of new catalyst design as it provides a link between the crystallographic zeolite structure and the adsorption properties.

### B. Objectives

The objective of this work is to study important transport properties, such as adsorption isotherms for chemicals that are important in the CEBC alkylation test bed via molecular simulations. These simulations will provide important benchmarks for the experiments. Our aim is to provide a foundation to understand molecular scale phenomena in solid acid alkylation test bed. This will ultimately help us select the best catalyst between different kinds of zeolites or other microporous materials.

### C. Accomplishments and Current Work

In order to study the adsorption curves of several chemicals, a GCMC (Grand Canonical Monte Carlo) simulation program is being developed.<sup>1,2</sup> GCMC simulations have been proven to produce very useful information to study adsorption in zeolites and other microporous materials.<sup>1-5</sup> For this study, beta zeolite (polymorph A), that is being used in the experiments at The University of Kansas and Washington University in St. Louis, is chosen. The GCMC simulation program is first tested with methane. Figure 1 shows the adsorption isotherm of methane in the beta zeolite at 300 K.

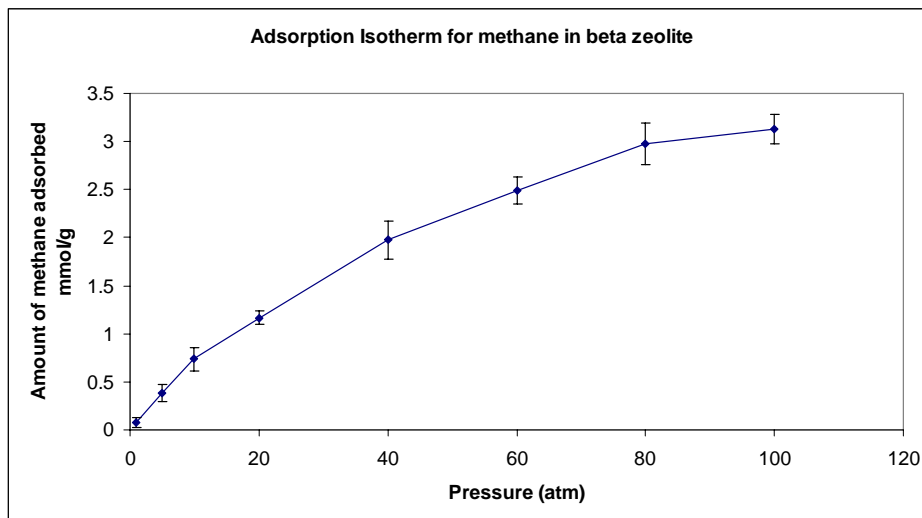


Figure 1. Adsorption isotherm for methane in beta zeolite at 300K.

#### **D. Future Work and Milestones**

Once the GCMC program is working efficiently, bigger and more complex molecules will be tested in the beta zeolite to obtain the adsorption curves for such compounds. Mixtures of these components will also be tested. The program will also be flexible enough to handle different microporous materials such as Nafion® that is widely used in the alkylation reactions.

**For further information**, please contact Canan Tunca at [tunca@che.wustl.edu](mailto:tunca@che.wustl.edu)

#### **E. Acknowledgements**

We would like to thank CEBC for their support that allowed us to develop the GCMC code.

#### **F. References**

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## I-23. Kinetic modeling and mass transfer effects in Homogeneous Catalytic Hydroformylation of 1-Octene in CO<sub>2</sub> – Expanded Solvent

### A. Problem Definition

CO<sub>2</sub>-expanded liquids (CXLs) represent a continuum of reaction media that combine the reaction benefits provided by organic solvents and the environmental benefits provided by supercritical CO<sub>2</sub> (*sc*CO<sub>2</sub>) in an optimal manner. Homogeneous hydroformylation of 1-octene using an unmodified rhodium catalyst (Rh(acac)(CO)<sub>2</sub>) was successfully demonstrated employing CXLs as reaction media<sup>1</sup>. At 60°C, the turnover numbers (TONs) for aldehydes formation in CO<sub>2</sub>-expanded acetone were significantly higher than those obtained in either neat acetone or supercritical carbon dioxide (*sc*CO<sub>2</sub>), demonstrating that CXLs are optimal reaction media. The higher TON at relatively mild pressures (tens of bars) in CXLs is attributed to enhanced syngas solubility in CXL (compared to neat solvent) while maintaining complete miscibility of the transition metal catalyst complex (due to the presence of the neat solvent). The reported experimental study showed a long induction period of nearly 2 hours, following which reaction occurs. The induction period has been reported previously by several researchers<sup>2,3,4</sup> but a systematic investigation of the cause of such a phenomenon still lacks in the literature. Also, kinetic parameters for hydroformylation of 1-octene in this relatively new class of solvent are currently not available. Estimation of reliable kinetic parameters is essential for scale-up and operation of these reactors.

### B. Research Objectives

The objective of this work is to develop a detailed batch reactor model, incorporating reaction kinetics<sup>5</sup>, mass transfer rates and phase equilibrium to systematically investigate the effects of mass transfer and catalyst activation on induction period in 1-octene hydroformylation in CXL. Complementary experiments in stirred autoclave reactors equipped with an *in situ* ReactIR probe were performed to validate the cause of the induction period predicted by the model. The model is then extended to two-phase semi-batch reactors and the temporal concentration profiles obtained using an *in situ* ReactIR probe is used to estimate the required kinetic constants for the hydroformylation of 1-octene in CO<sub>2</sub>-expanded solvent using an Orthogonal Distance Regression Technique (ODRPACK).

### C. Accomplishments

Figure 1 shows the computed octene-1 and nonanol dimensionless concentrations as a function of dimensionless time at different mass transfer to fastest kinetic step resistance ratio, *Da*. Larger value of *Da* means increased mass transfer limitation compared to the smallest reaction time scale. Clearly, high values of *Da* number lead to large induction times. It thus seems plausible that the induction period (on the order of hours) observed in the original batch experiments<sup>1</sup> is likely due to hydrogen mass transfer limitations in the reactor in which the experiments were carried out. Experiments in gas-sparged and well-stirred autoclave reactors show significantly lower induction time (on the order of minutes)<sup>6,7</sup>. The smaller induction period in well-stirred reactor is attributed to enhanced H<sub>2</sub> availability in the liquid phase that in turn intensifies catalyst hydrogenation rate which must occur before the catalytic cycle begins.

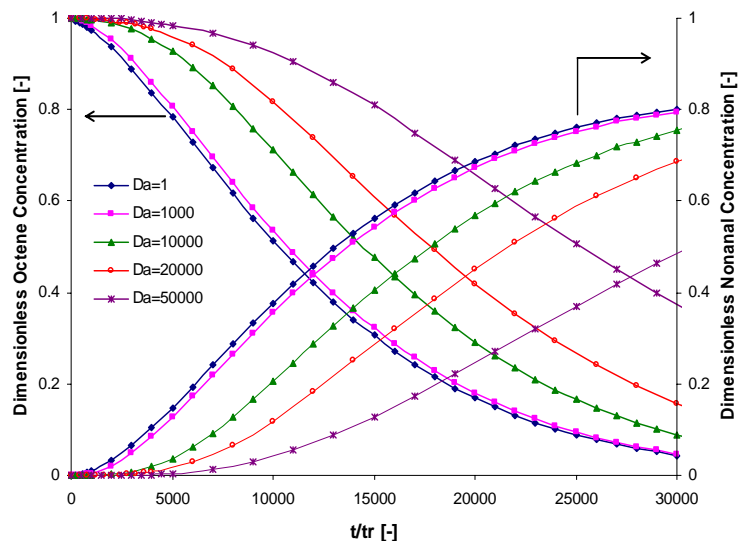


Fig.1: Dimensionless 1-Octene and Nonanal Concentration Profiles for varying  $Da$

For further information, please contact Debangshu Guha at [dguha@wuche.wustl.edu](mailto:dguha@wuche.wustl.edu)

#### D. References

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## I-24. Membrane Steam Reforming Reactor for Pure Hydrogen Production

### A. Problem Definition

A new very promising hydrogen production process has been identified. It utilizes fossil fuels (natural gas, but also naphtha, LPG methanol, ethanol etc) to produce a pure hydrogen stream (90% molar) and a pressurized concentrated stream of CO<sub>2</sub>. In this way, CO<sub>2</sub> produced is suitable for sequestration or EOR (Enhanced Oil Recovery) without need for re-compression (like conventional process would require). Hydrogen product is fit to be used as a clean fuel to run fuel cells, H<sub>2</sub> turbines or H<sub>2</sub> internal combustion units.

This is achieved in Membrane Steam Reforming Reactor operating at ca. 500°C and 30 bars. The reactor is packed with supported nickel catalyst and equipped with perm-selective Pd-alloy membrane that separates hydrogen from the remaining gases as they pass through the catalyst bed (Figure 1). In this way, lifted equilibrium limitations (due to hydrogen removal) allow use of lower temperature and higher pressure. Lower temperature also favors the formation of CO<sub>2</sub> at the expense of CO while (according to initial investigation of the temperature effect) the catalyst is still active enough to provide acceptable reaction rates. Reacting system is heated with Flameless Distributed Combustor (Shell Patent) to provide isothermal conditions, which in turn, will allow better utilization of the catalyst.

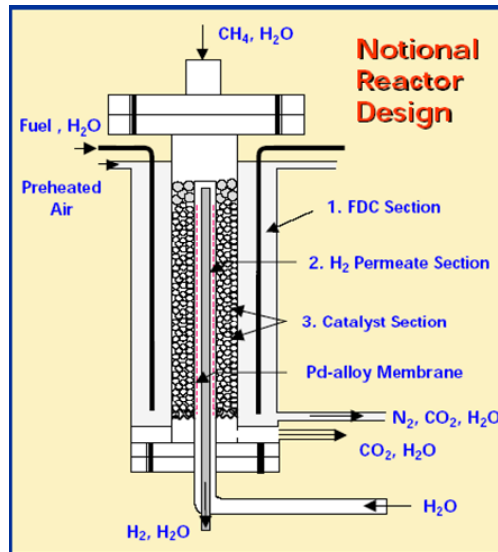


Figure 1. Membrane Steam Reforming Reactor

### B. Objectives

The objective of the present work is to build a CFD model of the actual configuration with all the steps involved in the process: reaction, mass transfer and diffusion through the membrane column. This will be accomplished in two parts:

1. Build a 2-Dimensional model based on the simplification of two concentric tubes, but computing the gas phase species concentration profiles in the radial direction
2. Build a 3-Dimensional model using the actual reactor configuration

### C. Accomplishments and Current Work

2-Dimensional, steady state, axi-symmetric model has been developed (Figure 2). This simplified configuration consists of two concentric tubes, the area of the external tube quantifies the total area of the heat source tubes and the internal tube quantifies the total area of the membrane tubes. The gap between these concentric tubes is filled with catalytic particles. The flow direction of the gas is parallel to the tubes (axial direction) and the hydrogen diffuses from the gas phase through the membrane column perpendicular to the gas flow direction (radial direction). Model equations are continuity (1), heat (2), and component mass balances (3). Boundary conditions are given by equation (4). Hydrogen transport through the membrane is modeled using Sievert's law (eq. 5). Pressure drop is estimated using Ergun's equation. The kinetics used is given in Xu et al. 1989.

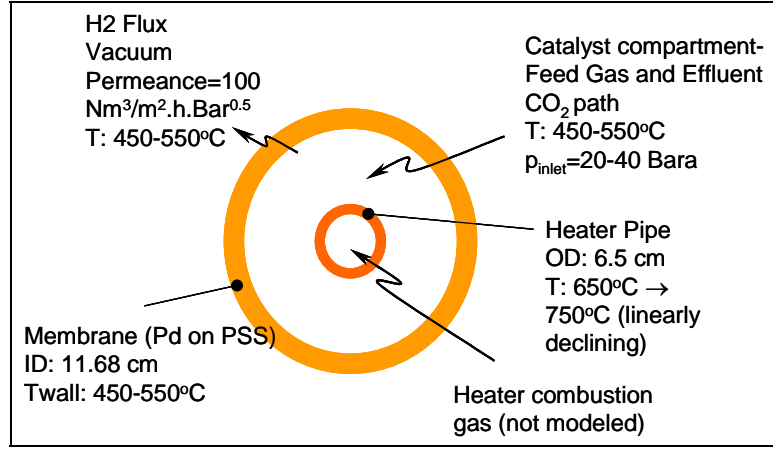


Figure 2. 2-D Model Layout

$$\frac{1}{r} \frac{\partial(\rho_g r v_r)}{\partial r} + \frac{\partial(\rho_g v_z)}{\partial z} = 0 \quad (1)$$

$$k_{eff} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right] + \frac{10}{36} (1 - \varepsilon_B) \rho_{cat} \sum_{i=1}^3 r_i \Delta H_i = \frac{1}{r} \frac{\partial}{\partial r} \left[ r v_r \left( \rho_g \bar{C}_p (T - T_0) \right) \right] \quad (2)$$

$$+ \frac{\partial}{\partial z} \left[ v_z \left( \rho_g \bar{C}_p (T - T_0) \right) \right]$$

$$- \left[ \frac{1}{r} \frac{\partial}{\partial r} (r \rho_g \omega_j v_r) + \frac{\partial}{\partial z} (\rho_g \omega_j v_z) \right] + D_j \left\{ \left( \frac{\partial \rho_g}{\partial r} \frac{\partial \omega_j}{\partial r} + \frac{\partial \rho_g}{\partial z} \frac{\partial \omega_j}{\partial z} \right) + \rho_g \left( \frac{\partial^2 \omega_j}{\partial r^2} + \frac{\partial^2 \omega_j}{\partial z^2} \right) \right\} \quad (3)$$

$$+ \frac{(1 - \varepsilon_B)}{3600} \rho_{cat} M_j \sum_{i=1}^{NR} \nu_{i,j} r_i = 0$$

$$\begin{aligned}
r = R_1, \quad \frac{\partial w_j}{\partial r} = 0, \text{ for all } j, \quad T(R_1, z) = -100z + 750 \\
r = R_2, \quad \frac{\partial w_j}{\partial r} = 0, \text{ for all } j \neq H_2, \quad -k_{\text{eff}} \left( \frac{\partial T}{\partial r} \right)_{r=R_2} = U(T_{r=R_2} - T_{\text{permeate}}) \\
r = R_2, \text{ for } j = H_2, \quad \left( \frac{v_r \rho_g w_{H_2}}{M_{H_2}} \right)_{r=R_2} = \frac{P_m}{\delta} \left( \frac{w_j}{M_j} \frac{P}{\sum_{i=1}^5 \frac{w_j}{M_j}} - p_{H_2} \Big|_{r=R_2, \text{membrane side}} \right) \quad (4)
\end{aligned}$$

$$z = 0, \quad w_j = w_{j0}$$

$$z = L, \quad \frac{\partial w_j}{\partial z} = 0$$

$$J_{H_2} = \frac{P_m}{\delta} (p_{H_2, \text{feed}}^n - p_{H_2, \text{permeate}}^n) \quad (5)$$

#### D. Future Work and Milestones

In the nearest future, a numerical scheme for solving 1D model (which is not shown here due to limited space) will be developed. The results obtained using this model will later be used as a validation tool for more complex, 2D model. This (i.e. 2D) model will be setup by the summer of 2007.

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#### F. References

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