

PROCESSES AND MINI AND MICROREACTORS

I-21. Mini and Micro Reactors Study for Liquid Hydrocarbons Oxidation

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 reaction, their importance as well as increasing environmental concerns have been the main driving forces for many studies and research (Suresh *et al.*, 2000). However, research was mainly focused either on finding new more selective and more effective catalyst (Guo *et al.*, 2003), or on evaluating processes parameters such as mass transfer coefficient, enhancement factor, and reaction rate constant (Pohorecki *et al.*, 2001). Also, as a result of many investigations, some new strategies like photocatalysis, biocatalysis, and oxidation in biphasic systems are emerging. However, no systematic study on the effect of oxygen availability at different temperatures and pressures has been reported to date. Hence, there is still the lack of thorough understanding of fundamental knowledge of hydrocarbons oxidation reaction mechanism and its effect on selectivity.

B. Research Objectives

The overall goal is to examine the effect of temperature and oxygen availability on the rates and selectivities of cyclohexane oxidations in the presence and absence of supercritical CO₂ and expanded solvent (a mixture of supercritical CO₂ and solvent). We intend to assess this at fixed temperature while increasing oxygen concentration, using fixed concentration in air, at different pressure, with and without the presence of CO₂ expanded solvent. Then, we will examine the effect of temperature at each of these oxygen delivery methods. Since safety is one of the most important factors, micro or mini reactor system has been chosen for such experimental study. This project is a part of CEBC (Center for Environmentally Benign Catalysis), and hence, these reactors are designed to run at both subcritical and supercritical condition (or using CO₂-expanded solvents). Cyclohexane oxidation is the reaction system chosen based on its commercial significance to be studied first.

C. Research Accomplishment

The oxidation of cyclohexane was conducted in Mikroglas microreactor setup (Figure 1) at atmospheric pressure (due to equipment constrains), both at room and at elevated temperatures (up to 90°C), with or without catalyst (cobalt naphthenate), and with various oxidants (air, oxygen and ozone). Due to the low residence time achievable (again equipment constriction), no reaction was observed when the microreactor (see Figure 1c.) was used in a continuous mode. The reaction was then conducted in batch mode by circulating the liquid) at atmospheric pressure and at room temperature. The oxidant used was ozone. The first reaction was observed after 4 hours of operation when no catalyst was used. With 2×10^{-3} mol/L of catalyst added, the reaction occurred after 30 minutes. The conversion of cyclohexane was well under 1% and after 4 h of operation with catalyst it reached 2%.

I-22. Modeling the Effects of Temperature, Pressure, and Oxygen Solubility on Liquid Phase the Oxidation of a 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 (CO_2) (expanded solvents) to increase the oxygen solubility.

B. References

1. Kharkova, T. V., Arest-Yakubovich, I. L., Lipes, V.V. (1989). Kinetic model of the liquid-phase oxidation of cyclohexane. I. Homogeneous course of the process. *Kinetika i Kataliz.*, 30(4), 954-8.
2. Pohorecki, R., Baldyga, J., Moniuk, W., Podgorska, W., Zdrojkowski, A., Wierzchowski, P. T. (2001). Kinetic model of cyclohexane oxidation. *Chem. Eng. Sci.*, 56, 1285-1291.
3. Suresh, A. K., Sridhar, T., Potter, O. E. (1988). Mass transfer and solubility in autocatalytic oxidation of cyclohexane. *AIChE Journal*, 34, 55-68.
4. Suresh, A. K., Sharma, M. M., Sridhar, T. (2000). Engineering aspects of industrial liquid-phase air oxidation of hydrocarbons. *Ind. Eng. Chem. Res.*, 39, 3958-3997.

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I-23. Mathematical Modeling and Experiments to Study Effective Diffusivity and Break-Through Curves for Alkylation Processes

A. Problem Definition

The biggest challenge facing the alkylation technology is to commercialize solid acid catalysts in place of traditional hydrofluoric acid (HF) and sulphuric acid (H₂SO₄) 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 economical feasible are by understanding the mechanisms of diffusion and adsorption/desorption of hydrocarbon on solid acid catalysts. This can be achieved by studying tracer response in stirred tank reactor and break-through curves in packed beds. Lyon, 2004 suggested that the rational use of carbon dioxide based supercritical reaction mixtures minimizes the deactivation of solid acid catalysts. So in current study both the cases, one with out supercritical CO₂ and one with super critical CO₂ were considered. The advantage of using a supercritical reaction mixture is the ability to sensitively manipulate the fluid properties, such as density, diffusivity and viscosity.

B. Research Objectives

The current study evaluates the break-through curves in packed bed reactor and tracer study (pulse response) in stirred tank reactor. A high pressure and high temperature mini packed bed reactor and 1 liter autoclave system are being developed. The physical parameters like bed porosity, dispersion coefficient, film mass transfer coefficient, apparent porosity of the particle, effective diffusivity and adsorption and desorption coefficient will be determined using model dependent numerical algorithm and model independent method of moments.

C. Research Accomplishments

Currently the mathematical model has been developed. The model takes into account the axial dispersion in packed bed coupled with particle level diffusion and adsorption. The experimental set up (Figure 1, 2 & 3) has been designed. The set up components are being specified and ordered. The design incorporates the use of carbon dioxide at supercritical conditions. Figure 1 illustrates the method for making premixed feed. Figure 2 illustrated the feed system and PI & D. Flow control for the hydrocarbon substrates will include HPLC pumps with flow measurement. Figure 3 gives the essential features of the reactor, temperature and pressure control. A backpressure regulator controls the flow from the reactor at a constant pressure. In order to protect the system from exceeding design pressures, one rupture discs is included in Figure 3.

D. Future Work

The experimental set up will be constructed, tested and their results will be validated. The model will be validated using the experimental data available in the literature. Experiments will be conducted for effective diffusivity and adsorption/desorption studies of 1-butene, isobutene and tri-methyl-pentane and for alkylation reactions.

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E. References

Christopher J. Lyon, “Optimization of Activity & Selectivity by Pressure-Tuning during Solid Acid Catalyzed Isoparaffin/Olefin Alkylation in Supercritical Carbon Dioxide” University of Kansas 2004.

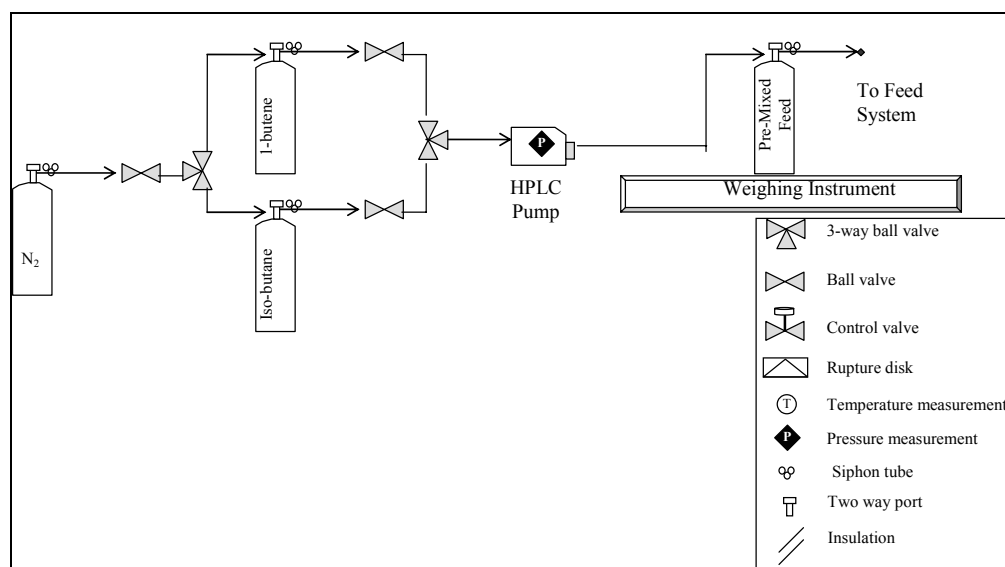


Figure 1: Pre-Mixing Feed P&ID

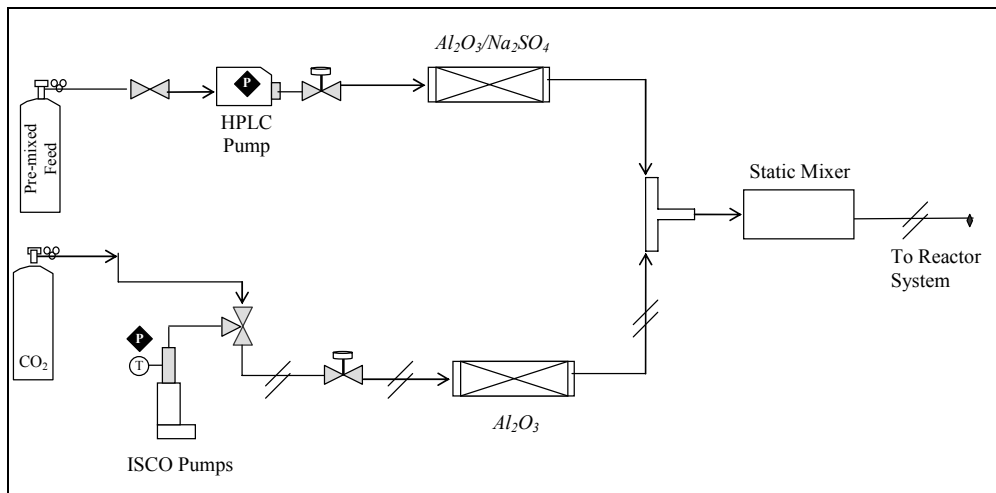


Figure 2: Feed System P&ID

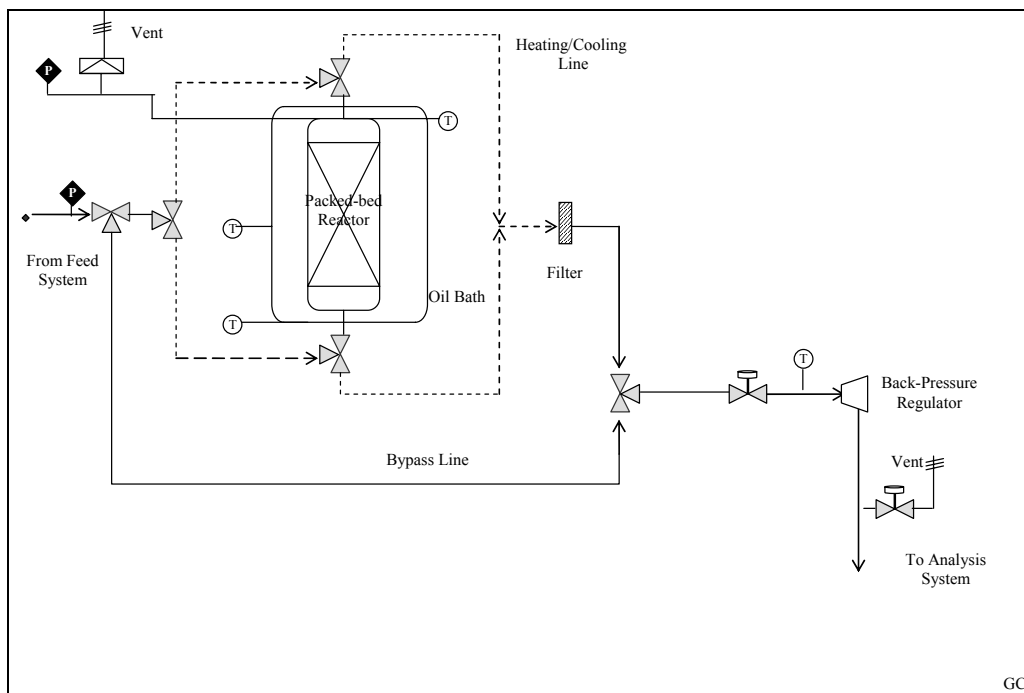


Figure 3: Reactor System P&ID

I-24. The Integrated Struvite-CANON System

A. Introduction

The intent of this project is to design a technology to reduce nitrogen concentration from anaerobic sludge digestion centrate at the New York City Department of Environmental Protection (NYCDEP) wastewater facilities.

B. Research Objectives

The main objective of this project is to reduce nitrogen concentration from 600 to less than 100 mg-N/L in the centrate stream. To add value, we have introduced a pre-treatment step to simultaneously remove phosphorous and ammonia by forcing the precipitation of magnesium ammonium phosphate hexhydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), also called struvite, from centrate. Several factors were taken into consideration for the design as shown below:

- The acceptable effluent concentrations
- Comparison the kinetic modeling result of CANON (Completely Autotrophic N-removal Over Nitrite) system with SHARON (Single reactor system for High activity Ammonia Removal Over Nitrite) system
- The costs, value-added products, and design stability.

C. Research Accomplishments

An integrated struvite-CANON system offers multiple advantages over other system designs, such as classic nitrification/denitrification and a single reaction system for high activity ammonia removal over nitrite (SHARON). A comparison between the three is given in Table 1.

Integrated Struvite-CANON	Nitrification/Denitrification	SHARON
<ul style="list-style-type: none"> • Single tank system • Minimal O₂ addition • No Carbon source addition • Trace NO₃⁻ in effluent • >90% Phosphorous removal • Profitable struvite produced 	<ul style="list-style-type: none"> • Two tank system • Highest O₂ requirements • Required methanol addition • NO₃⁻ rich effluent • No Phosphorous removal • No marketable product 	<ul style="list-style-type: none"> • Single tank system • Median O₂ requirement • Required methanol addition • Median NO₃⁻ effluent • No Phosphorous removal • No marketable product

Table 1: Integrated Struvite-CANON comparison to conventional Nitrification / Denitrification and SHARON systems.

Struvite precipitation reduces the concentration of phosphorous and ammonia from the waste stream while concurrently creating a marketable product. Without struvite precipitation, the CANON process may reach allowable TKN levels, but it cannot achieve the regulated minimum ammonia concentrations of 40 mg-N/L. In addition, the magnesium hydroxide

added to the struvite precipitation decreases buffer requirements in the CANON process needed because of the formation of protons during the biological process. Incomplete nitrification to nitrite in combination with ANAMMOX (anaerobic ammonium oxidation), to convert ammonia directly into nitrogen gas, reduces costly aeration by 63% when comparing a CANON system to classic nitrification/denitrification. Methanol usage as an organic carbon source for microbial activity is completely eliminated. In contrast, methanol is needed for both classic nitrification/ denitrification and SHARON. Overall, the coupling of struvite precipitation and CANON processes reduces costs by producing a marketable product, decreasing the overall aeration requirements, reducing the formation of detrimental struvite, and eliminating the need of an added carbon source.

The integrated Struvite-CANON system (Figure 1) is a cost effective method to achieve greater than 85% TKN removal from a centrate stream. The integration of struvite precipitation and CANON maximizes nitrogen reduction by removing nitrogen through the production of struvite and biological conversion.

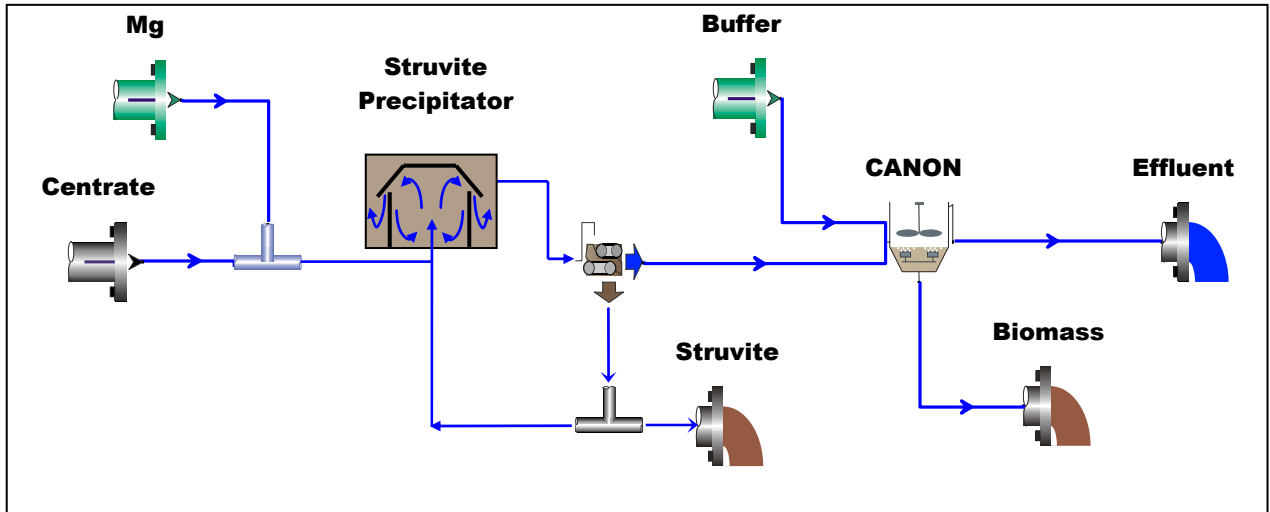


Figure 1: Process Flow Diagram for Integrated Struvite-CANON system drawn in BioWin; Struvite modeled in BioWin, CANON modeled in Matlab with mathematic equations from Hao et. al. (2002).

Furthermore, when the precipitated struvite is sold on the open market, its revenue will supersede the cost of chemical additions to the integrated Struvite-CANON system by an estimated \$5000 per year (Table 2)^{1, 8, 9}. A comparison of methanol costs estimates between Integrated Struvite-CANON, Nitrification/Denitrification, and SHARON reveal that the elimination of methanol usage alone will grant a considerable reduction in costs. The design group anticipates the building cost of the Integrated Struvite-CANON system to be similar to a SHARON system, because the overall HRT of our design is similar to a SHARON system with a comparable level of complexity.

	<i>Usage kg/day</i>	<i>Cost \$/tonne</i>	<i>Cost \$/year</i>
Integrated Struvite-CANON			
MgOH	137	159	38,580
NaOH	19.5	315	2,242
Struvite	505	(135)	(45,804)
Methanol	0	236	0
Total			(4,982)
Nitrification/Denitrification			
Methanol	3391	236	292,410
SHARON			
Methanol	2034	236	175,394

Table 2: Operational chemical cost summary for the Integrated Struvite-CANON system and methanol costs for Nitrification/Denitrification and SHARON systems based upon Matlab modeling. Bracketed costs indicate revenues.

D. Future Work

Lab-size experiments are recommended and the process will be investigated to improve the kinetic model and estimate the model parameters.

E. References

1. Ueno Y, Fujii M. Three Years Experience of Operating and Selling Recovered Struvite from Full-Scale Plant. *Environmental technology*. 2001 2001;22(Part 11):1373-1381.
2. Wu Q, Bishop PL, Keener TC. A Strategy for Controlling Deposition of Struvite in Municipal Wastewater Treatment Plants. *Water Environment Research*. March/April 2005 2005;77(2):199-207.
3. Industries KW. Denitrification: High-Speed Processing Can be Realized by Microorganisms. *Water and Wastewater Newsletter*. Vol 6; 2004.
4. Jetten MS, Wagner M, Fuerst J, van Loosdrecht M, Kuenen G, Strous M. Microbiology and application of the anaerobic ammonium oxidation ('anammox') process. *Current opinion in biotechnology*. 2001 2001;12(3):283-288.
5. Hao X, Heijnen JJ, Loosdrecht MCMv. Sensitivity Analysis of a Biofilm Model Describing a One-Stage Completely Autotrophic Nitrogen Removal (CANON) Process Published online 6 December 2001. *Biotechnology and bioengineering*. 2002 2002;77(3):12.
6. Egli K, Langer C, Siegrist H-R, Zehnder AJB, Wagner M, Meer JRvd. ENVIRONMENTAL MICROBIOLOGY AND BIODEGRADATION - Community Analysis of Ammonia and Nitrite Oxidizers during Start-Up of Nitrification Reactors. *Applied and environmental microbiology*. 2003 2003;69(6):10.
7. Regy S, Mangin D, Klein JP, Lieto J. Phosphate recovery by Struvite Precipitation in a Stirred Reactor March-December 222/06/02 2001.

8. Pitt M. Chemicals Cost Guide 2002 [Website]. February 26, 2002. Available at: <http://ed.icheme.org/costchem.html>. Accessed April 9, 2005, 2005.
9. Williams A. *Recovery of Nitrogen and Phosphorous from Anaerobically Treated Wastes Using Struvite Precipitation* [Masters']. Ames: Civil Engineering, Iowa State University; 1997.
10. Kaldnes. The Compact Solution for Biological Wastewater Treatment. *Kaldnes North America Inc.* [pdf]. Available at: <http://www.h2flow.com/Website2003/Products/kaldnes/KNA.pdf>. Accessed April 12, 2005.