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Reactor design for pyridine base production: matching transport phenomena and reaction kinetics

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Highlights

- Reactor design for 2-methyl-5-ethyl-pyridine production
- Detailed kinetic model from experiments in ideal semi-batch reactor
- Determination of influence of mass transfer in continuously operated reactor
- Intensification of mixing by different reactor configurations

1. Introduction

The yield of reactions to produce pyridine bases is affected by various parameters such as concentration, temperature and structure of the catalyst used. 2-Methyl-5-ethylpyridine (MEP) is one of the industrially most important pyridine bases used as intermediate for the production of nicotinic acid (i.e. vitamin B3 or PP). MEP is produced by condensation of acetaldehyde in liquid phase at high pressure and temperature. In our studies [1, 2], we determined the feasibility of the reactions from paraldehyde (PARA) and from acetaldehyde ammonia trimer (AAT) to MEP. The scope of this study is to identify optimal conditions for the reactions and design the optimal reactor for the industrial synthesis of MEP.

2. Methods

At first, experiments were performed in a pressurized autoclave to assess the feasibility of the reactions and to provide data for establishing a kinetic model. In a second step, a continuous setup, consisting of a coil type reactor immersed in an oil bath (thermostat), was employed. HPLC pumps fed two solutions containing the reactant and the catalyst, respectively. The reaction was carried out at 200 °C and 30 bar. The residence time in the reactor was adjusted by modifying the feed rate of the pumps. The reaction mixture was cooled after the reaction and analyzed using GC and NMR.

3. Results and discussion

Initially, the feasibility of the two reaction routes from AAT and PARA to MEP was assessed. The yield of the reaction is similar for the two process routes, but the conversion of AAT is significantly faster than that of PARA. Using a design of experiments approach, we determined the parametric influences on the processes. The parameters with the largest influence on yield are temperature, concentration of reactants and reactant to catalyst ratio. Interaction of these parameters is complex, which makes it difficult to elucidate optimal conditions. For this reason, a detailed kinetic study of the two reactions was carried out in an ideal semi-batch reactor. A kinetic model for the reaction was derived, which allowed for the identification of the optimal operating point for a wide range of process conditions. Furthermore, the kinetic model was used to predict the performance of the two reactions in several different reactor configurations. In order to scale up the reactions studied, the process was simulated and then carried out in a continuously operated coil reactor. This experimental set up can be modified by changing the dimensions of the coils, allowing for the validation of a broad range of fluid-dynamic conditions. The characteristics of the configurations tested are reported in Table 1. The transport phenomena in the reactor are modeled using appropriate correlations to determine the Sherwood number and the global mass transfer coefficient. The results of the mass transfer calculations in terms of time required to fully mix reactant and catalyst solutions are reported in Figure 1. The characteristic time of the reaction is calculated as the inverse of the reaction rate constant determined from the kinetic model. It corresponds to 500 seconds for PARA and 80 seconds for AAT. In the first reactor used for experimental tests (1/8” ID) the flow is laminar (Re=20-30), with a relatively long time required for the two solutions to mix. The mixing time is 164 seconds. This indicates that the reaction from AAT takes place during the mixing phase without control of the reaction conditions. For this reason, the experimental results of the runs with AAT show a lower yield than the corresponding runs performed in an autoclave with perfect mixing. The reaction from PARA does not show this problem because it is kinetically controlled by decomposition, and it is thus operated in the chemical kinetic regime (Figure 2). In order to overcome the mass transfer limitation, the mixing was improved by two methods: (a) direct change of the fluid flow conditions; (b) change of the reactor geometry. In the first case, the flow rate was doubled while maintaining the residence time identical owing to a reactor with double volume (i.e., double length). This approach reduces the mixing time to 140 seconds, which is, however, still higher than the reaction time. Therefore, while a higher yield compared to the original run can be achieved, the results are still not fully in line with the ideal case. In the second approach, a smaller reactor (1/16” ID) is used. This configuration enables good mixing within a time (32 s) smaller than the characteristic reaction time of AAT. The experimental results confirm the improvement in reaction management, so that the yield of the ideal case is reached. A drawback of this solution is the increase of pressure loss. For this reason, a different reactor concept combining (a) and (b) was designed. A static mixer (Fluitec AG) was inserted in front of the reaction zone in the oil bath. This device produces turbulent conditions in the reactor, decreasing the time required to mix the two solutions to a very low value (25 s). Consequently, the reaction yield corresponds to the ideal case, without any further changes in the reactor and at acceptable pressure drop. The results are summarized in Table 1.

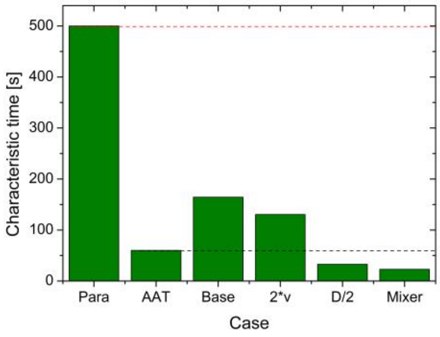

Figure 1. Characteristic time of the reactions and of mixing

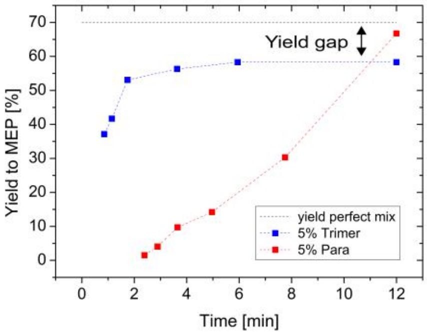

Figure 2. Yield of reaction AAT and para in ideal and real reactor

Case	Perfect mixing	Base	2v	D/2	Static mixer
ID [in]		1/8	1/8	1/16	1/8
Vol [mL]		6	12	6	6
Notes	Autoclave experiments	Standard configuration	Double flow	Half diameter	Mixer before the reactor
Yield [%]	70	60	65	70	70

Table 1. Characteristics of the reactor configurations and respective yield

4. Conclusions

A new reaction route to produce MEP is studied in detail and compared to the conventional process by determining the conditions for optimal yield. A kinetic model derived from lab scale semi-batch experiments guides the design of a new continuously operated industrial reactor. This model enables predicting the performance of various reactor configurations and determining the influence of transport phenomena. The reaction of AAT to MEP is prone to influence by mass transfer, so that particular attention to reactor design is necessary. Thanks to the derivation of rational reactor designs, it is possible to achieve the desired yield by introducing mixing devices in the reactor configuration, thereby avoiding the influence of heat and mass transfer limitations.

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Keywords

“coil reactor”, “mass transfer”, “static mixer”, “reaction scale up”

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EDUCATION

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University of Erlangen - Nuremberg, Germany

Ph.D. in Chemical Reaction Engineering (supervisor: Prof. H. Freund)

Thesis Topic: Rational reactor design for enhanced efficiency

- Conceptual design of new reactors for production of fine chemicals
- Identifying optimal reactor based on kinetic modeling tools

2013 -2015

Politecnico di Torino

M.Sc. in Chemical and Sustainable Processes Engineering

Thesis Topic: Virtual Water, Food and Energy, an analysis of the water-food-energy nexus

2012 -2014

Politecnico di Milano

M.Sc. in Chemical Engineering

Thesis Topic: Kinetic study and Raman characterization of the catalytic partial oxidation of light hydrocarbons

2013 -2014

Alta Scuola Politecnica

Honor school for management of innovation

Specialization courses: Sustainability, design methods, management of technology, entrepreneurship and decision making

2009 - 2012

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B.Sc. in Chemical Engineering

Thesis topic: Study of anodic spark deposition oxidation on titanium

PROFESSIONAL EXPERIENCE

2017-present

EPFL, Sion, Switzerland

Assistant researcher

- Development of the Sabatier reaction
- Design of an industrial reactor for optimal heat management of the reaction

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Lonza AG, Visp, Switzerland

Early Stage Researcher at Life Science Ingredients, Research and Technology

- Optimizing synthesis routes of fine chemicals
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PUBLICATIONS

2017	**E. Moioli, F. Salvati, M. Chiesa, R.T. Siecha, F. Manenti, F. Laio, M.C. Rulli,** Analysis of the current biofuel production under a water-food-energy nexus perspective**,** *Advances in water resources,* paper submitted
2017	**E. Moioli, L. Schmid, P. Wasserscheid, H. Freund,** A new reaction route for the synthesis of 2-methyl-5-ethylpyridine**,** *Reaction Chemistry & Engineering*, DOI: 10.1039/c7re00100b
2017	**E. Moioli, L. Schmid, P. Wasserscheid, H. Freund,** pH effects in the acetaldehyde-ammonia reaction**,** *Reaction Chemistry & Engineering*, DOI: 10.1039/c7re00006e
2016	**E.Moioli, F. Manenti, M.C. Rulli,** Assessment of global sustainability of bioenergy production in a water-food-energy perspective, *Chemical Engineering Transactions*, 50
2016	**D. Pagani, R. B. da Silva Jr., E. Moioli, A. Donazzi, A. Lucotti, M. Tommasini, C. Castiglioni, S. Teixeira Brandao, A. Beretta, G. Groppi,** Annular reactor testing and Raman surface characterization of the CPO of i-octane and n-octane on Rh based catalyst**,** *Chemical Engineering Journal*, 294, 9-21

CONFERENCE CONTRIBUTIONS

2017	**E. Moioli, L. Schmid, P. Wasserscheid, H. Freund,** Kinetic study of reactions to produce 2-Methyl-5-Ethyl-Pyridine, *Jahrestreffen reaktionstechnik 2017* (Poster)
2017	**E. Moioli, L. Schmid, P. Wasserscheid, H. Freund,** A New Reaction Route for the Synthesis of 5-Ethyl-2-Methylpyridine**,** *NAM 25*, Denver (Lecture)
2016	**E. Moioli, L. Schmid, P. Wasserscheid, H. Freund,** Guidelines for proper reactor design for aldehyde-ammonias production**,** *CHISA 2016*, Prague (Lecture)
2016	**E. Moioli, L. Schmid, P. Wasserscheid, H. Freund,** Guidelines for optimal dosing strategies for reactions of aldehydes and ammonia**,** *ISCRE 2016*, Minneapolis (Poster)
2015	**E.Moioli, F. Salvati, F. Manenti, M.C. Rulli,** Quantification of the water-food-energy nexus as a guiding instrument for enhanced energy production and sustainability, *World Sustainability Forum*, Basel (Lecture)
2015	**E. Moioli, S. Aghalale, L. Schmid, F. Enzenberger, P. Wasserscheid, H. Freund,** Influence of pH and acid type on the reaction of acetaldehyde with ammonia**,** *ECCE 10*, Nice (Poster)
2015	**E. Moioli, S. Aghalale, L. Schmid, F. Enzenberger, P. Wasserscheid, H. Freund,** Study of pH effect on acetaldehyde-ammonia reaction**,** *ESCRE 2015*, Furstenfeld (DE) (Poster)

AWARDS

2015	Mario Puccioni Award – Special award for MSc thesis in the course studies of chemical engineering at Politecnico di Milano

LANGUAGE SKILLS

Italian	Native Language
English	Fluent – C1 (IELTS Score: 7.5)
French	Intermediate – B2 (DELF B2)
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IT SKILLS

Proficient	MS - Office, Aspen Plus, Matlab programming, Kinetic modeling: Presto-Predici
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PERSONAL INFORMATION

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