NATIONAL UNIVERSITY OF ENGINEERING
COLLEGE OF SCIENCES

CHEMISTRY PROGRAM

CQ093 – KINETIC MODELING APPLIED TO CATALYSIS

I. GENERAL INFORMATION

CODE	**:**	CQ093 – Kinetic modeling applied to catalysis
SEMESTER	**:**	9, 10
CREDITS	**:**	05
HOURS PER WEEK	**:**	08 (Theory – Practice – Laboratory)
PREREQUISITES	**:**	CQ252 Physical-chemistry II
CONDITION	**:**	Elective

II. COURSE DESCRIPTION

The subject aims to apply the general principles of heterogeneous catalysis and chemical kinetics to obtain the velocity equation by means of experimental measurements and to establish the kinetic model of better fit according to the mechanistic and non-mechanistic methodology of the reaction. After establishing the model, the course proposes the development of a simulation program of the fixed bed reactor, solving the kinetic equations on the basis of numerical methods (Runge-Kutta method of 4th order).

III. COURSE OUTCOMES

By the end this course the student will:

- Interpret the kinetic equation for simple, multiple and catalyzed homogeneous reactions.
- Analyze the fundamental principles of matter transport between phases, to undertake the study of heterogeneous reaction systems.
- Identify the kinetic equation for non-catalytic and catalytic heterogeneous reactions.
- Plan kinetic models to describe mechanisms of partial and total combustion reactions in a differential and integral reactor, through the SCIENTIST program.
- Describe integral reactors based on the best fitting kinetic model, solving the kinetic equations by numerical methods of Runge-Kutta.

IV. LEARNING UNITS

1. **FUNDAMENTAL CONCEPTS (Part 1) / 4 HOURS.**
Heterogeneous Catalysts / Design Criteria of the Heterogeneous Catalysts / Fundamental Constituents of a Heterogeneous Catalyst: Concepts of Active Phase / Promoter and Support / General Methods of Catalyst Preparation / Effect of activation energies / The active site / Structurally sensitive reactions / Ideal glass models / Concept of Turn Over Frequency (TOF) / Variables of a reaction: effects of solvents / Phenomena of transport / Internal and external

diffusion / Gas-solid reactions / Influence of transport phenomena on the selectivity of reactions.

2. **FUNDAMENTAL CONCEPTS (Part 2) / 4 HOURS.**
   Reaction rate / Reaction order / Elemental reactions and complex reactions / Reaction mechanism / Integrated velocity equations / Concept of spatial time and spatial velocity. Determination of reaction orders / Influence of different variables on the reaction rate: temperature, pressure, concentration / activation energy.

3. **CATALYTIC REACTORS / 8 HOURS.**
   Discontinuous reactors Batch Reactors / Perfect Mixing Reactors / Tank-Agitated Continuous Reactor (Slurry) / Flow-Piston Reactor / Summary of the Ideal Reactor Models / Kinetic Equations for Continuous and Flow-Piston Reactors / Mass Transfer Diffusion Phenomena / Thiele Coefficient.

4. **REACTIONS MECHANISMS / 8 HOURS. .**
   Reactions Mechanisms / Reversible reactions / Parallel reactions / Consecutive reactions. Chain reactions / Approximate methods to solve the speed equation in complex reactions. Approximation of the determining stage of speed and approximation of the steady state / Determination of reaction mechanisms.

5. **MODELING OF KINETIC PROCESSES / 8 HOURS**
   Hydrogenation and combustion reactions / Non-mechanistic models (potential model) and mechanistic models: Mars-Van Krevelen model / Langmuir-Hinshelwood model / Eley-Rydel model. Model discrimination / Statistical discrimination parameters: MSC (model selection criteria), DC (determination coefficient) / Correlation coefficient / Application of the SCIENTIST program for multivariate adjustment of kinetic data / Data convergence / Examples of application in combustion reactions of VOCs (volatile organic compounds).

6. **SIMULATION OF INTEGRAL REACTORS / 8 HOURS**
   Reactor simulation concept / Simulation model hypothesis / Approximate resolution of differential equations / 4th order Runge-Kutta method / Application of programs for the simulation of reactors in FORTRAN language based on the kinetic constants corresponding to the best fitting model / Data interpretation.

7. **DEACTIVATION KINETICS/ 8 HOURS**
   Introduction / Types of deactivation / Kinetics of deactivation by coke deposition / Operation strategies in the presence of deactivation / Kinetic study of deactivation from temperature-time sequences / Comparison of the proposed methods.

8. **ENZYMATIC KINETICS / 8 HOURS**
   Introduction / Enzyme concept / Protein types / Body-antigen selectivity / Classification of enzymes by their functionality / Application of the Michaelis-Menten model to enzymatic kinetics / Basic and linear equation / Lineweaver-Burk plotting / Examples of enzymes.

V. LABORATORIES AND PRACTICAL EXPERIENCES

Laboratory practices

1. Use of the SCIENTIST program for kinetic applications.
2. Potential model and determination of the activation energy and order of a reaction. Reliability of the results.
3. Model of MVK (Mars-Van Krevelen) applied to catalytic reactions.
4. Langmuir-Hinshelwood model applied to catalytic reactions.
5. Discrimination of kinetic models from the statistical point of view. Experimental determination of a kinetic model.
6. Notion of reactor simulation.

Topics of seminars and projects.

1. Catalytic reforming. Methane production. Methane demand in the industry. Methane consumer countries. Environmental impacts
2. Special configurations of a catalytic reactor: fluidized bed, membrane, monolith,
3. Monoliths used as a catalytic converter in automobiles.
4. Biofuels: catalytic production of the biodisesel.

VI. METHODOLOGY

The subject is developed in theory and laboratory sessions. In theory sessions, the teacher makes a descriptive presentation of the basic theory of chemical kinetics and application of the kinetics of catalytic reactors to specific problems (elimination of volatile compounds, oxidative dehydrogenation reaction of ethane, etc.).The students actively participates in solving problems individually and / or in groups. In the laboratory and seminar sessions, the student applies the knowledge learned to obtain the best fitting kinetics and simulation of the reactor based on the obtained model.

VII. EVALUATION FORMULA

Calculation of the final grade: PE (weight 1) + FE (weight 1) + Practices average (weight 1)
PE: Partial Exam – FE: Final Exam.
Note: The practices are carried out in the Physical–Chemistry Research Laboratory - LABINFIS (R2-409).

VIII. BIBLIOGRAPHY

- Janssen F. J. J,, Van Santen R.A. Environmental Catalysis. Series Editor Gram. J. Hutchings
- Trovarelli A., Catalysis by Ceria, Series Editor Gram. J. Hutchings
- Guisnet M., Gilson J. P., Zeolites for Cleaner Technologies, Series Editor Gram. J. Hutchings.
- Anderson J. A., Garcia M.F., Supported Metals in Catalysis, Series Editor Gram. J. Hutchings.
- Bond G. C., Louis C., Thompson D.T., Catalysis by Gold, Series Editor Gram. J. Hutchings.

Recommended books in Applied Science

- González Velasco, J.R.; González Marcos, J.A.; González Marcos, M.P.; Gutiérrez Ortiz; J.I.; Gutiérrez Ortiz, M.A.; , Cinética Química Aplicada, Ed. Síntesis, Madrid (1999).
- Levenspiel, O. , Ingeniería de las Reacciones Químicas. 6ª Edición. Ed. Reverté. Barcelona. (1990).
- 3.R.W. Missen, C. A. Mims, B.A. Saville,, Chemical Reaction Engineering and Kinetics, John Wiley & Sons, Inc., New York (1999).
- H.S. Fogler,, Elements of Chemical Reaction Engineering, 3ª Edición. Ed. Prentice-Hall International, Inc. New Jersey (1999).
- Froment, G.F. and Bischoff, K.B., Chemical Reactor Analysis and Design. 2ª Edición. Ed. John Wiley & Sons, Inc. New York (1990).

- Smith, J.M.: Chemical Engineering Kinetics, 30 Edici\n, McGraw-Hill (1981).

- Levenspiel, O.: El omnilibro de los reactores químicos. Reverté (1986), Traduccion de J. Costa López y L. Puigjaner Corbella.

- Scott Fogler, H.: Elements of Chemical Reaction Engineering, Prentice-Hall (1992) 20 ed.