Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

KINETIC MODELLING OF A POLYPHASIC REACTOR BY PRE-DETERMINATION OF PHASES EQUILIBRIA INVOLVED

A.J. Bougrine, C. Duriche, H. Delalu

Laboratoire Hydrazines et Procédés
UMR 5179 Université Claude Bernard Lyon 1 – CNRS – Isochem/SNPE
43, Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France
anne-julie.bougrine@univ-lyon1.fr

1. Summary

During the process of synthesis of a hydrazine, a transient miscibility gap appears. An experimental determination of the properties of the liquid-liquid equilibria involved permits to develop a predictive kinetic model for this polyphasic reactor. In fine, this study allows then to predict the behavior of the reaction mixtures in a plug-flow reactor according to the degree of conversion of the reaction whatever the operating conditions used.

Keywords **:** Hydrazine, kinetic modelling, polyphasic reactor, phases equilibria

2. Extended Abstract

The know-how of our laboratory focuses on the development of integrated original processes, including the synthesis, extraction, purification and stability of solid or liquid hydrazines. The methods of preparation are selective and clean (chemistry in water with no use of organic solvent) and permit to produce and extract, by use of the particularisms involved in the phase diagrams, a hydrazine in conformity with the particularly restricting specifications (pharmaceutical or spatial applications as propellants).

Within the framework of the development of a process of synthesis of a hydrazine of pharmaceutical interest (hypoglycaemic drug), this work deals with the modelling of a plug-flow reactor which presents, in steady state conditions, a double diphasic and monophasic segment. This case arises in the second step of the elaboration of N-N bonding, by action of monochloramine with an excess of amine in strongly alkaline medium.

First step : $NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$ (monophasic medium)

Second step : $NH_2Cl + R_1R_2NH \rightarrow R_1R_2NNH_2 + HCl$
$HCl + NaOH \rightarrow NaCl + H_2O$ (diphasic + monophasic medium)

In this configuration, amine and sodium hydroxide are responsible of a transient miscibility gap. The partial neutralization of excess NaOH by formed HCl leads, at the time $t = t'$ and for the degree of conversion of the reaction $\xi = \xi'$, to a breaking of the polyphasic state and the continuation of the reaction in a homogenous medium.

The developed method consists in predicting the variation of the diphasic system according to ξ. The successive preparation of mixtures (ξ = 0 ; ξ = 0.1 ; ξ = 0.2 …; ξ = ξ') allows to determine the variables $C_i^\alpha, C_i^\beta, v^\alpha, v^\beta$ as a function of ξ, by physico-chemical analysis of the two phases in equilibrium. Then, it is possible to determine the value ξ' from which the medium becomes homogeneous.

Taking into account the distribution of the reagents between the phases in equilibrium, the evolution of the system is described by the following equation :

$$\frac{dC_i^\alpha}{dt} = -(k^\alpha . C_i^\alpha . C_j^\alpha) + \left(\frac{C_i^\alpha}{v^\alpha} . \frac{dv^\alpha}{dt} \right) \qquad \text{with } C_{i,j}^\alpha = f(C_i^0, C_j^0, \xi, T) \text{ and } v^\alpha = g(\xi, T)$$

The first term in brackets indicates the effect of the chemical transformation, whereas the second results from the variation of the volume v.

The presented work permits to establish the residence time of the diphasic and monophasic segments whatever the experimental conditions.