Topic: Industrial fluid flow, Mixing

MIXING INFLUENCE ON ε-CAPROLACTAM QUALITY - AN INDUSTRIAL APPLICATION OF CFD SIMULATION

AUTHORS: P. Santucciu, [1]C. Aragonese, P. Andrigo e K. Rame

EniChem, Corporate R&D Centre, via G. Fauser, 4, 28100 Novara, Italy; Tel. +39.0321.447.571,
Fax +39.0321.447.233, e-mail :Patrizia_Santucciu@hq.enichem.geis.com;
[1] CRS4, Centre for Advanced Studies, Research and Development in Sardinia, VI strada ovest, Zona Industriale Macchiareddu, 09010 Uta, Cagliari Italy; e-mail:cosimo@crs4.it

Abstract: CPL production is a mixing sensitive system and for this reason it is used as test case for a CFD code including micromixing phenomena description. The code CFX-4 is used for simulating the behaviour of a rotor-stator mixer, considered as a reactor. Specific properties like kinetic laws and viscosity functions have been experimentally estimated and here reported. The preliminary results of fluid dynamic validation are here reported.

The production of ε-Caprolactam (CPL) from Cyclohexanone Oxime (OX) by Beckmann rearrangement involves a fast exothermic main reaction and other side reactions that affect the product quality. Preliminary tests were performed in a lab-scale loop reactor; they showed a significant product quality dependence on mixing conditions. The most attractive among side reactions was the production of 1,2,3,4,6,7,8,9-octahydro-phenazine (OHP). In order to simulate with CFD code this phenomenon the knowledge of both kinetic and chemical-physical properties has to be known.

The existing ***kinetic model*** of the main reaction (Cavalieri d'Oro *et al*., 1991) must be improved including the kinetics of side reaction. In order to study kinetics of fast reactions is important to carry out experiments in which mixing time is sensibly lower than reaction time; to reach this goal two ways were followed: at first, experiments were performed with a chemical quenching apparatus but in this case technical constraints like corrosivity of medium and viscosity lead to perform experiments with a batch reactor. In this second case concentration of reagents were changed in order to increase the reaction time with respect to mixing time. The data collected were used for the estimation of kinetic parameters.

The chemical mechanism for both reactions (main and side) is very complex; since CFD code requires kinetic model as much simple as possible, a very simple empirical model was written:

r_1 OX $\rightarrow$ CPL $r_1 = k_1(H) * [OX]$

r_2 OX $\rightarrow$ OHP $r_2 = k_2 * [OX]^n$ n=1,2

where H is an acidity function.

The best fitting with experimental data has been obtained when both reactions are of first order with respect to OX.

In order to describe the overall process of mixing, it is important to have a kinetic model able to predict r_1 over a wide range of acidity; so the main reaction kinetic model was reformulated using both experimental data collected over the last ten years and literature data at different conditions.

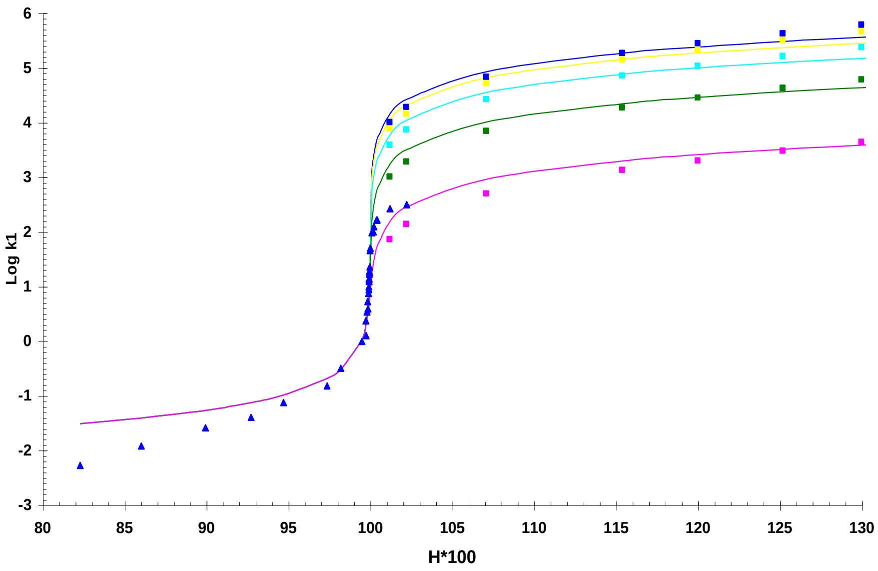


Fig.1 - acidity influence on main reaction

In fig.1, log k_1 versus acidity is plotted and a good consistency of these data is evident; the shape suggests the data will fit with a log-like expression similar to the one used for the titolation of a strong acid with a strong basis:

$$\log k_1 = -\log\left(-A \cdot x + \sqrt{(Ax)^2 + K_w}\right)$$

Two parameters A and K_w have to be calculated; a transformation of x is needed to explicit the acidity functionality and conversion of K_w as function of the ratio of reagents.

In order to model micromixing phenomena, it is necessary to know ***dynamic viscosity*** and its correlation with fluid composition, temperature and shear stress. Measurements were taken with a rotational rheometer at fixed test temperatures (70-90°C) and varying shear stress; pure OX, whose melting point is 90°C, was characterised in the range 90-110°C.

In table 1 the compositions of solutions examined and the their behaviour at the highest frequency investigated (100 rad/s) are presented: some solutions showed a Newtonian behaviour, while others exhibited a non-Newtonian one. Solution viscosity, in general, became higher for temperature close or below 70°C, according to Andrade expression.

SAMPLE	WEIGHT COMPOSITION					PHYSICAL BEHAVIOUR
	%OX	%CPL	%H_2SO_4	%SO_3	%H_20	
1	13.71	54.85	30.18	0.0	1.26	**Newtonian**
2	10.70	42.79	44.65	0.0	1.86	**Newtonian**
3a	0.0	55.25	31.33	13.43	0.0	**Newtonian**
3b	0.0	44.9	38.57	16.53	0.0	**Newtonian**
CPL	0.0	100	0.0	0.0	0.0	**Non-Newtonian**
OX	100	0.0	0.0	0.0	0.0	**Non-Newtonian**

Table1

Conditions more close to the experimental ones are represented by solutions 3a and 3b which presented a Newtonian behaviour within experimental conditions; we can therefore model the fluid dynamic of the mixer assuming an ideal behaviour.

The usual expression for liquid mixture can not be used, due to salification phenomena; and a new expression has been developed using data from solution 3a and 3b, considering them as pseudocomponents.

$$\ln(\eta_{mix}) = \left(\frac{R-1}{0.5}\right) * \ln(\eta_{3b}) + \left(1 - \frac{R-1}{0.5}\right) * \ln(\eta_{3a})$$

$1 \le R \le 1.5$ R= reagents ratio

The plant (fig.2) under study is a ***loop reactor equipped with a Rotor Stator Mixer*** (Silverson, mod.In-line); it is a dynamic mixer built up of a four blade rotor and a high shear screen with square holes and is typically employed when very intensive mixing is required. Oleum is fed before the pump while melt pure Cyclohexanone Oxime is fed in the mixer chamber together with the recycle, which is a mixture of Oleum and CPL.

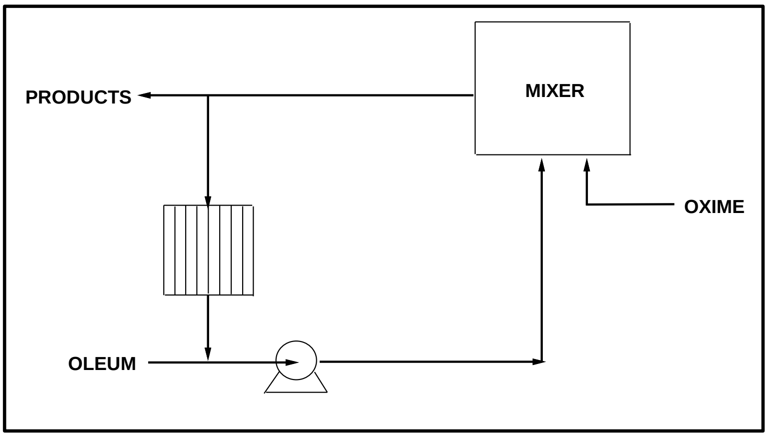
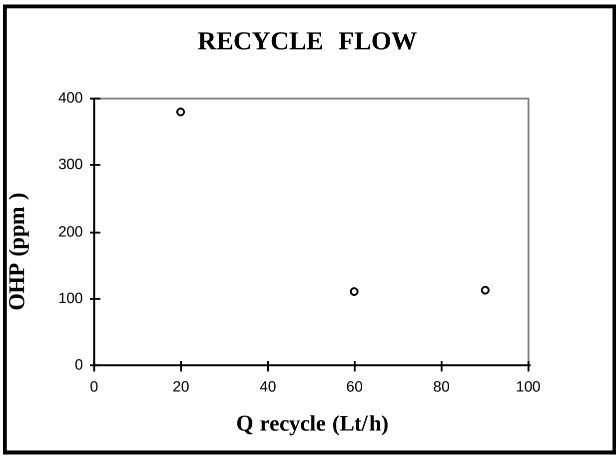


Fig.2 - loop reactor sketch

Mixing experiments are performed in order to evaluate the effect of mixing variables on CPL quality in terms of OHP amount produced.
The parameters which control OHP amount are mainly related to rotator speed and recycle flow; all tests have been performed at a fixed temperature and $\%SO_3$ and they can be collected within 3 groups: two of them investigate the recycle flow at different recycle ratio (in other words linear velocity inside dynamic mixer) while the last investigates the effect of rotator speed mainly in the zone inside the shear screen. Fig. 3,4 show that the effect of mixing is important: more intensive the mixing, lower the content of OHP.



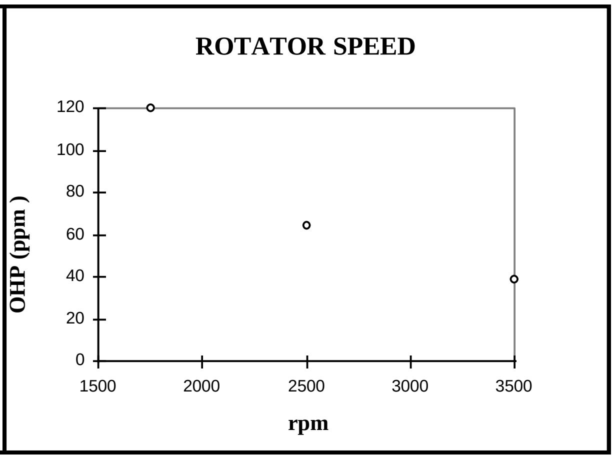


Fig. 3 - recycle flow effect on CPL quality fig.4 - rotator speed effect on CPL

quality

Code validation The simulation work with the CFX-4 code (AEA) was planned using a step by step procedure: 1) the test of the fluid dynamic simulation with LDA measurements (LSTM) in order to verify that flowfield is correct; 2) the test of the reactive simulation with extended Bourne Reaction System (BHR) data in order to validate micromixing modules (PFD); 3) the comparison of the simulation of the loop reactor for CPL production with laboratory loop reactor tests, above reported, in order to check CFX-4 performances.

The geometry of the dynamic mixer is very complex and, considering the symmetry of the mixer, the grid has been generated in cylindrical co-ordinates, only a quart of the mixer is simulated in order to save CPU time. The sliding grid approach has been used to describe the system and due to small clearance between shear screen and blades, the simulation could be very heavy especially at very high rotator speed.

The first step is the simulation of LDA measurements (LSTM) performed in a modified dynamic mixer; some parts were constructed in Duran glass in order to have optical access. Measurements were collected within radial range 10-14 mm and 19-26 mm and axial range 0-20 mm. The data show a very complex flow field: radial inflow and outflow were observed depending on the blade position and they change significantly along axial position.

The flow field coming from CFX-4 simulation has a very similar profile showing also recycle around shear screen as shown in fig.5. Further validation steps are in progress.

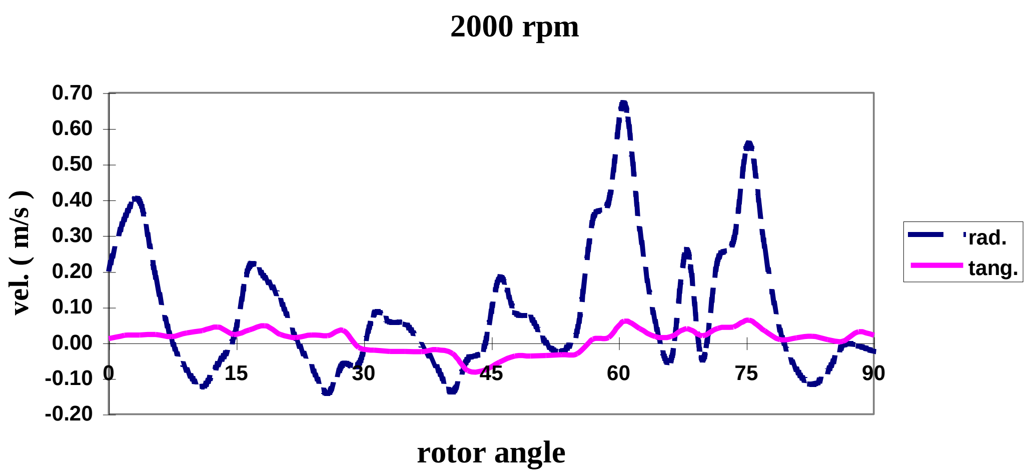


Fig.5 - velocity profiles outside shear screen

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Reference

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