

CHARACTERIZATION OF MICROMIXING EFFICIENCY BY A NEW CHEMICAL METHOD IN SUPERCRITICAL MEDIUM

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This work deals with the development of a new chemical method of micromixing characterization suitable for supercritical media (more particularly for carbon dioxide which is apolar). The system is based on two competitive reactions:

- The esterification of phenylacetic acid by ethanol using paratoluenesulfonic acid as a catalyst,
- The neutralization of paratoluenesulfonic acid by tributylamin.

The neutralization reaction is faster than the esterification reaction. The test procedure consists in adding in stoichiometric defect paratoluenesulfonic acid to a mixture of ethanol, phenylacetic acid, tributylamin and carbon dioxide under supercritical conditions (15 MPa, 323 K). The quantity of ester formed at the end of the reactions is related to the quality of micromixing.

Preliminary studies concerning solubility or analytic method (GPC) have been achieved in order to allow carrying out reactions' system in batch reactor. The sensitivity to micromixing effects has been investigated in a 0.5 L stirred vessel. The final composition in the vessel has been proved to be dependent on the stirring speed. This new system seems to be very efficient to characterize micromixing effects in a supercritical medium that are particularly important in the Supercritical Anti-Solvent precipitation processes.

INTRODUCTION

Supercritical anti-solvent precipitation is used to produce powders, which can be very fine (nano or micro particles), crystalline or amorphous, composite or not. Precipitation under supercritical conditions produces particles without or with a few solvent traces.

A previous study [1] of the mixing at the vessel scale showed that, whatever the studied conditions, the precipitation vessel behaves like a well-mixed reactor, auto-agitated by the introduction of the supercritical anti-solvent phase and of the liquid phase. However, the characteristics of the particles produced are dependent on the hydrodynamic conditions in the precipitation vessel. The influence of hydrodynamics on the particles morphology may be due to micromixing effect and thus it is necessary to study the hydrodynamics' effects at a smaller scale than the vessel one.

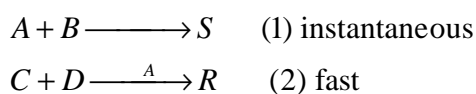
Mixing process is the evolution of macroscopic aggregates to finer structures. The size reduction of fluids aggregates is due to convective viscous deformations and later on to

molecular diffusion. Micromixing state depends on local concentration distributions. From fluid mechanics, the length corresponding to micromixing is not clearly defined. This scale could be the one from which there is competition between mass transfer and chemical reaction: it should thus depend on dissipated power in the vessel and on kinetics of the reactions carried out.

Micromixing plays a great role in product distribution and quality for fast phenomena like polymerisation or precipitation. The precipitation phenomenon in SAS process was proved fast [1, 2] the precipitation time was understood between 1 and 4,9 ms for the system L-PLA – methylene chloride at 10 MPa and 308 K. When crystallisation process goes so fast, nucleation begins before supersaturation is uniform and the precipitation is controlled by mixing. Inhomogeneous supersaturation affects nucleation and growth and thus final characteristics of the particles formed (mean particle size and particle size distribution). In order to produce monodispersed and predetermined size particles, it is necessary to control mixing process. Competition between mixing and nucleation is decisive [3].

The purpose of this paper is to describe a method for micromixing characterisation in the pressure vessel thanks to a new chemical method. The existing chemical systems involved ionic reagents. Unfortunately, supercritical carbon dioxide is a non-polar solvent and it cannot solvate ions. Thus, the existing reactions are not able to characterise micromixing in supercritical media and we had to develop a new chemical system suitable for the characterisation of micromixing in supercritical fluids. This new system has to satisfy some requirements. One of the kinetic steps must be very fast. The reactions have to be carried out simply: reagents of common use, non-toxic. In our case, the implementation is getting complicated because of the supercritical media. Products' analysis has to be comfortable and fast in order to be carried out on line in a continuous study.

The chosen reactions' system does not follow a known chemical scheme for the micromixing characterisation. There are two competitive reactions; one of the reagents of the first one is also the catalyst of the second one. The first reaction, the faster one, is an acid-basic neutralisation. The acid used for the first reaction is the catalyst of the second one, the esterification that is the slower one. The reaction scheme is the following (also see figure 2):



With :

- A: paratoluenesulfonic acid
- B: tributylamin
- C: phenylacetic acid (APA)
- D: ethanol
- S: Salt
- R: ethyl phenyl acetate

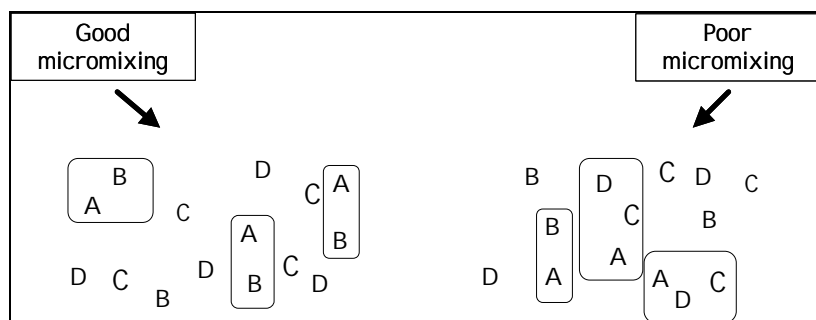


Figure 1 : Chemical method for micromixing characterization.

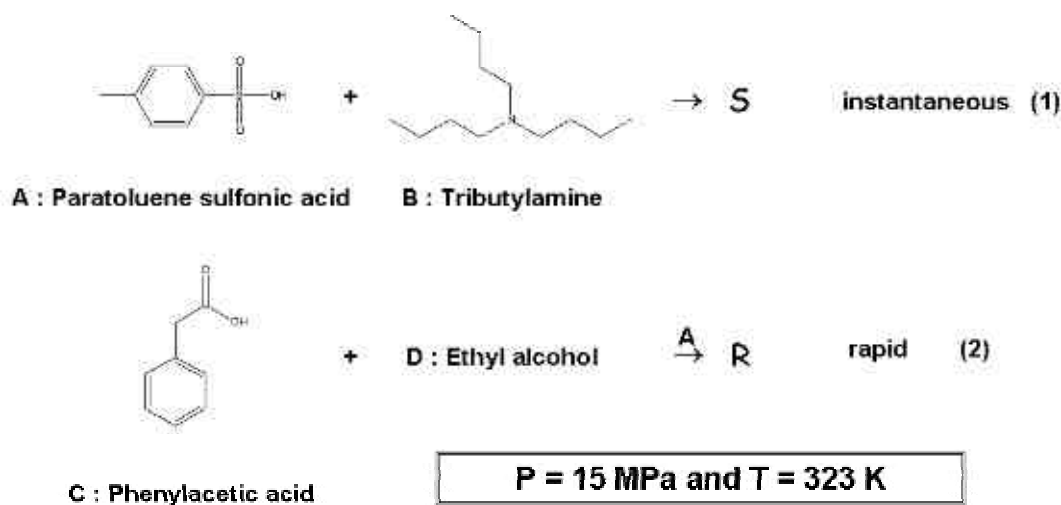


Figure 2 : Reactions' system used for micromixing characterization.

The test system is carried out by introducing the reagent A by stoichiometric defect compared to the reagent B. If micromixing is well done, no ester is produced. On the contrary, if the micromixing is bad, ester can be formed. The reaction products distribution is related to the micromixing efficiency (cf. figure 1).

Before applying the micromixing characterization test to precipitation processes or other supercritical processes such as reactions, it is necessary to prove its sensitivity to micromixing efficiency. This is carried out in batch reactor with a controlled mechanical stirring. Some preliminary studies such as analysis, solubility or catalyst efficiency were necessary before carrying out chemical system reactions.

I. PRELIMINARY STUDIES

I. 1. ANALYSIS

Among all the analytical techniques, Gas Phase Chromatography was chosen to quantify reaction products. The column is a Mega fused capillary column designed for the analysis of carboxylic acids. The film thickness is 0.25 μm and the internal diameter is 0.32 mm. The

column length is 25 m. The chromatograph is a Chrompack apparatus (CP 9001) equipped with a flame ionisation detector. The temperatures used were:

- Injector: 503 K
- Detector: 513 K
- The temperature of the column was 398 K during 3 minutes, it rised from 398 to 463 K at 5 °C. min⁻¹.

We verified that all the products are collected at the end of the reaction by mass balance.

I. 2. SOLUBILITY OF THE REAGENTS IN SUPERCRITICAL PHASE

In order to carry out the reactions in a single phase, the homogeneity of the medium was tested. We used the experimental apparatus represented in the figure 3 [4] It makes it possible to determine visually the transition pressure between a monophasic medium and a biphasic medium for constant temperature and composition. The volume and thus the pressure of the cell are modified by moving manually a piston.

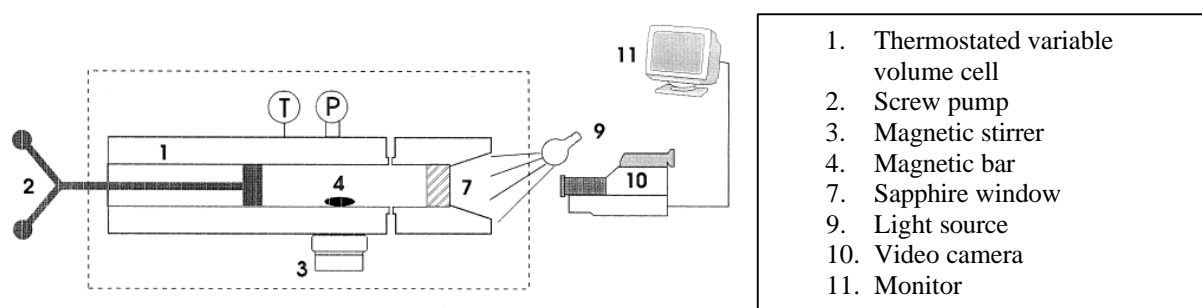


Figure 3: High-pressure variable volume view cell.

A well-defined mixture of the reagents was introduced in the cell. Carbon dioxide was introduced thanks to a sampling cylinder; the quantity introduced was measured by weighing. The system was allowed at least one hour to reach the equilibrium.

The experiments enabled us to define suitable conditions to carry out micromixing characterisation in supercritical media at 15 MPa, 50°C:

- [B] = 6.48 .10⁻² mol.L⁻¹
- [C] = 7.34 .10⁻² mol.L⁻¹
- [D] = 8.6 .10⁻¹ mol.L⁻¹

I. 3. CATALYST EFFICIENCY

It was necessary to check that the ester was not formed without the catalyst (A). Although this was observed in liquid media, it had to be tested in supercritical medium (in the same operating conditions than for the characterisation of micromixing) which has some specific properties concerning chemical reactions [5]. The reagents (B, C and D or C and D) were contacted during 2 hours in the high-pressure vessel at 15 MPa and 323 K. The analyses of the products show that no ester was formed. Thus, during the micromixing characterisation, the ester production will be due to the action of acid catalyst.

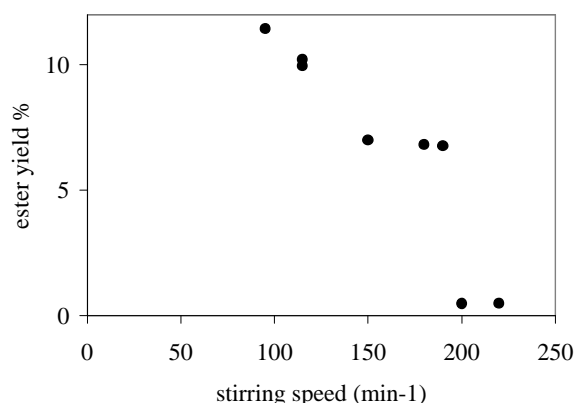


Figure 5: Variation of ester yield with mechanical stirring speed.

CONCLUSION

The new reaction system developed is suitable for the micromixing characterisation in supercritical media. The test conditions have to be improved with the aim of making an easy tool for mixing characterisation. The micromixing study is of first importance for precipitation processes and for fast phenomena in general. With some complementary studies such as kinetics characterization of the reactions, it will be possible to know local dissipated power in the vessel. Another application of this new test is the chemical reaction: micromixing has a determining influence on the product quality, selectivity and yield for some organic synthesis or polymerisation reaction. It gives a tool to make a diagnosis of the reactor under supercritical conditions.

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