

# PROCESSING OF ENERGETIC MATERIALS FINE POWDERS USING FLUID ANTISOLVENT METHOD.

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The antisolvent effect is a process known to extract solute from saturated solution. The use of an antisolvent fluid as CO<sub>2</sub> expects several advantages compare to conventional industrial methods. The size and the dispersion of the powders are generally small. The concentration of the solution and the nature of the solvents play an important role on the feature of the powders. The possibility of recycling CO<sub>2</sub> fluid decreases the use of organic solvents and improves the quality of the process towards the environmental problems. The first application of supercritical antisolvent micronization of nitroguanidine was proposed by Gallagher et al[1]. with different liquid solvents and two different antisolvents were tested: chloro-difluoromethane and CO<sub>2</sub>. They observed various morphologies: spheres, large crystals, snowballs and starbursts. Particles dimensions ranged from 1µm to hundreds of micrometers. The principle of antisolvent effect is to broke the saturation of a saturated solution by the wanted powder by the introduction of a second solvent witch moves the equilibrium of solubility and causes the precipitation of the solute. In the present communication, the crystallization and the characterisation by SEM of an energetic powder has been carried out with CO<sub>2</sub> as gas antisolvent at 313,15 K. Some articles[2-4] about this energetic powders like RDX and HMX treat experimental conditions of the process. New results on the determination of the parameters of fine powders of HNIW by antisolvent process are presented. Indeed, this product shows growing interest in the field of rocket fuel and this process can be achieve in high conditions of security.

## **Introduction**

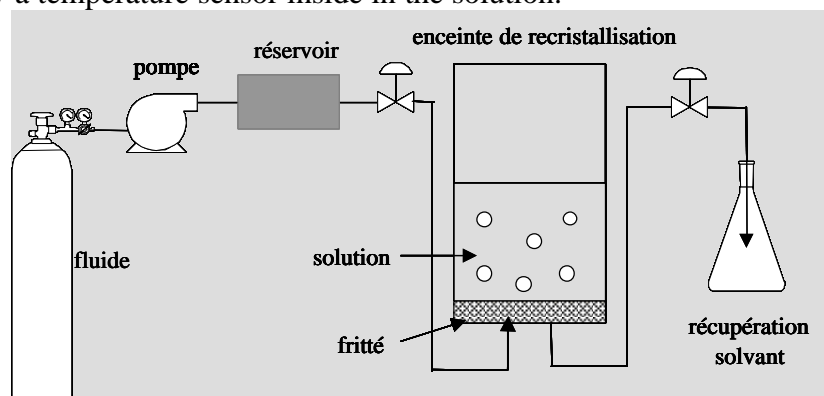
The antisolvent recrystallisation process is known to extract solute from saturated solution. The use of an antisolvent fluid as CO<sub>2</sub> expects several advantages compare to conventional industrial methods: the precipitation of the solute can be controlled by the pressure-temperature parameters, in particular the morphology, the fineness and the purity of the powders. On the other hand the size and the dispersion of the powders are tunable. The antisolvant effect brings into play three made up: a main organic solvent, a solute to be extracted and one antisolvant. The antisolvant it is non solvent of the solute. In the present process, the interaction of the fluid antisolvant with organic solvent causes an expansion in volume of the solution and a displacement of the balance of solubility in favour of the precipitation of the wanted solute. The denomination of Anti-Solvent Gas (GAS) or Anti-Solvent Supercritical (SAS) comes from the thermodynamic field (critical or not) where is the antisolvant fluid. The relevant parameters to optimise the process are :

- the temperature;
- the nature of organic solvent;
- the ratio volumes solution/volume recipient;
- the concentration of the solute in the initial solution;
- the flow of the injection.

Recrystallization using antisolvent effect is a good way to design sensible compounds, like explosives because their efficiency depends on the fineness and size distribution of the particles. We proposed to achieve fine particles of HNIW using an antisolvent recrystallization process and to define the adequate parameters.

## I- Apparatus

A schematic diagram of the apparatus is shown in Figure 1. Experiments were carried out in a wide range of CO<sub>2</sub>'s density and always at constant temperature (313,15K) to be sure to have no gas-liquid transformation of CO<sub>2</sub> during the application of pressure. A stainless steel reservoir with a known volume (11,5 cm<sup>3</sup>) is fill up with CO<sub>2</sub> and heated. A volume of a mixture, containing the dissolved compound in a solvent, is introduced into a sapphire cell. This cell was realised to do experiments near and over the CO<sub>2</sub>'s critical pressure (0<P<150bars). All of the system, reservoir and cell, is heated up to 313,15 Kelvin by an heating regulator WATLOW series 986. Carbon dioxide is injected slowly and the mixture is stirred. Pressure and temperature are given respectively by a pressure sensor downstream of the cell and by a temperature sensor inside in the solution.



**Figure 1 :** Schematic illustration of fluid antisolvent recrystallisation setup.

When precipitation took place, the solvent supernatant is aspirated through one filter at the bottom of the sapphire cell while an excess of fluid is injected to be always with saturation of fluid and to avoid of the powder dissolving. This one is then dried by a current of fluid. It is possible to achieve powders about five microns.

The characterisation of the product was made by SEM with a microscope LEICA S440.

## II- Results

### *Temperature*

Except the condition of constant temperature of the antisolvent it in the fluid state, the experiments carried out at various temperatures, showed that it did not have any influence on the recovered product.

### *The nature of the organic solvent*

Various organic solvents were used in this study: acetone, ethyl acetate, toluene and a mixture toluene/ethyl acetate (60/40 %vol). Indeed, they answer the first two requirements imposed by the principle of the antisolvent phenomenon, namely they are solvents of HNIW and they have a good miscibility with CO<sub>2</sub>. The results are described in the following table:

	size	size distribution	yield
<b>acetone</b>	9 $\mu$ m	5,7-24,2 $\mu$ m	45%
<b>ethyl acetate</b>	< 2 $\mu$ m	large	30%
<b>toluene</b>	2 $\mu$ m	-	-
<b>toluene/ethyl acetate (60/40)</b>	3,5 $\mu$ m	2-6 $\mu$ m	75%

**Table 1 :** Evolution of the shape of HNIW as a function of the nature of the organic solvent used in the process.

The experiments with acetone obtained crystals with a rhomboedral form with a weak thickness. The crystals are as large as those obtained by conventional methods, like grinding, evaporation.

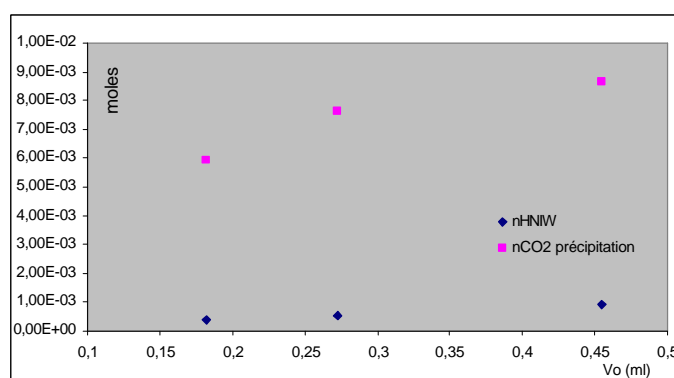
Ethyl acetate has a good interaction with CO<sub>2</sub> and it is a very good solvent for HNIW, this is why the particles obtained are very small but the yield is poor. Indeed, at the time of the elimination of the solvent, this one involves most of the product precipitated in spite of the CO<sub>2</sub> excess and for the period of drying of the powder, other crystals are formed by evaporation of remaining solvent.

Toluene is a poor solvent of HNIW (< 2 mg of HNIW/ml at 313K). The quantity of recrystallized product is so weak that one can regard toluene as a bad solvent for this process.

The mixture toluene/ethyl acetate is a good arrangement for HNIW (80 mg/ml) in the present study and gives a good yield in the antisolvent recrystallisation. It gives crystals with a shape of bipyramidal truncated at the tops. Particles are small and size distribution is fine. It seems to be the best adapted for this process and will be used like organic solvent in the continuation of the study.

### *The ratio volumes solution/volume recipient*

The morphology of the particles depends on the initial volume of the solution organic solvent-HNIW. Three initial volumes were tested: 2, 3, 5 ml. On the following curves, are reported (in red) the quantity of CO<sub>2</sub> injected at the moment of the precipitation as a function of the ratio volume of initial solution/volume of the cell (11 ml). In blue, the points represent the quantity of HNIW in the solution. As a saturated initial solution, this quantity is proportional to 80 mg/ml.



**Figure 2 :** Evolution of quantity of CO<sub>2</sub> injected at the moment of the precipitation as a function of the concentration of HNIW in the initial solution.

The quantity of CO<sub>2</sub>, to achieve the precipitation, is very significant compared to the quantity of HNIW and it increases in a significant way until arriving at a maximum where the quantity of CO<sub>2</sub> does not change any more whatever the initial volume of the solution.

The principal characteristics of the powders obtained are summarized in the following table:

Vo (ml)	size	size distribution	yield
2	3,5µm	1,6-9,6µm	70%
3	3,5µm	1,8-6,5µm	75%
5	1,5µm	0,9-12,8µm	70%

**Table 2 :** Size and size distribution of HNIW as a function of the initial volume of the organic solvent used in the process.

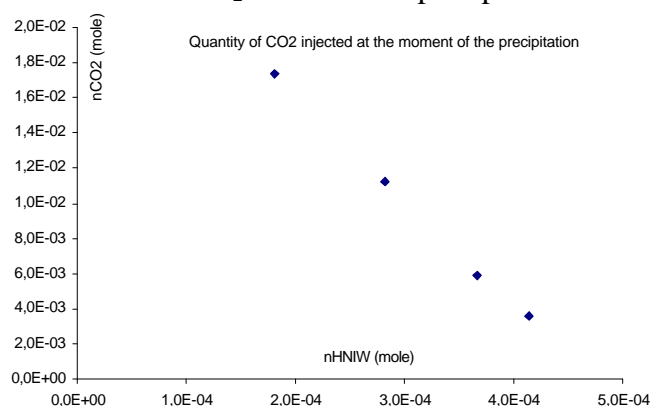
### *The concentration of the solute in the initial solution*

This part of this study was performed with 2 ml of initial solution because the handled quantities reach the limits as regards safety at the laboratory scale.

[HNIW] (mg/ml)	size	size distribution	yield
39,6	2,5µm	1,8-10,5µm	30%
61,7	1,9µm	0,8-6µm	60%
80,4	3,5µm	1,6-9,6µm	70%
90,6	3,5µm	1,5-7,6µm	75%

**Table 3 :** Evolution of the shape of HNIW as a function of the concentration of HNIW in the initial solution.

The concentration has a little influence on the size and the distribution in the faces of the particles. But the quantity of CO<sub>2</sub> injected at the moment of the precipitation is inversely proportional to the initial quantity of HNIW in the solution. Indeed, more the concentration in HNIW is weak and more one needs CO<sub>2</sub> to be able to precipitate it.



**Figure 3 :** Quantity (in mole) of CO<sub>2</sub> injected at the moment of the precipitation as a function of the quantity of HNIW in the initial solution.

### *The flow injection of CO<sub>2</sub>*

The influence of the flow of the antisolvent injection is not significant on the particles size. But the size distribution is more fine when CO<sub>2</sub> is injected slowly into the solution. The bipyramidal shapes of the particles are more homogeneous. When CO<sub>2</sub> is injected quickly, the particles are fine, but there are more polydisperse and have no precise form.

<b>VCO<sub>2</sub> (g/min)</b>	<b>size</b>	<b>size distribution</b>	<b>yield</b>
3,68E-02	2,5µm	1,6-9,6µm	70%
2,47E-02	2,5µm	1,6-10,6µm	-
1,06E-02	2,5µm	1,7-7,0µm	35%

**Table 4 :** Evolution of the shape of HNIW as a function of the the flow injection of CO<sub>2</sub>.

### **Conclusion**

This study allowed highlights the significant parameters of process GAS and to follow the evolution of the powder produced according to these parameters. For the development of an industrial process, the adapted parameters would be:

A mixture toluene/ethyl acetate (60/40 %vol for example) as organic solvent, because it seems to give a good yield at the end of the process.

The initial volume of the solution is important in the fact that it must allow the phenomenon of swelling of the solution causes the displacement of the balance of the solubility of the solute in the new solution.

For effectiveness reasons, the suitable concentration is the saturation, in order to be on being always with the same concentration if one would consider a continuous process.

Finally, the flow injection of CO<sub>2</sub> is important. Muhrer et al. showed that if the speed of injection is more significant, the particles are smaller, and the size distribution is finer.

With this process, it is expected to achieve particles of HNIW about 2 microns and to recover them dry, under expected conditions of safety better than the conventional processes.

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