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Processes Using Supercritical Fluids: A Sustainable Approach for the Design of Functional Nanomaterials*

Cyril Aymonier, Arnaud Erriguible, Samuel Marre, Anne Serani, and François Cansell

Abstract

The concepts of green chemistry and sustainable development are being considered more and more due to the evolution of regulations and mentalities. In this context, the development of supercritical fluid technologies should go on to evolve in the right direction.

Since the nineteen fifties, studies and development efforts have been focused on new ways of separating substances using the specific properties of supercritical fluids. In this context, a mention must be made about the use of carbon dioxide as an extracting agent in many industrial processes (decaffeination of coffee and tea, extraction of hops, spice, aromatic substances, fragrances, pharmaceuticals, etc). Processes using these fluids are particularly attractive at the industrial scale in many fields such as impregnation, analytical and preparative separations, organic synthesis, waste management and material recycling. The industrial development of the supercritical fluid technology is accompanied by numerous research activities, in particular, in the field of inorganic Materials Science for the synthesis of multifunctional nanomaterials.

Today, supercritical fluid technology allows the production, with a reduction of the environmental impact, of well designed nanomaterials with controlled properties for applications in many interesting fields, such as catalysis, electronics, energy, optics, pharmacology, etc. This paper is focused on the interest of using supercritical fluids to overcome the drawbacks of solution chemistry approaches

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for designing multifunctional nanomaterials in term of chemical engineering, sustainable chemistry and control of size, morphology, composition and the structure of nanomaterials.

KEYWORDS: supercritical fluids, nanomaterials, green chemistry, sustainable development

1. INTRODUCTION

Sustainable development is an old concept of the seventeenth's born at the first conference of Stockholm in 1972. From this event, the word "sustainable" is become more and more important in the every day life of people, especially of researchers, engineers, etc.

If a researcher speaks about green or sustainable chemistry or processes, he has to keep in mind that it refers to economy, society and environment (Figure 1).

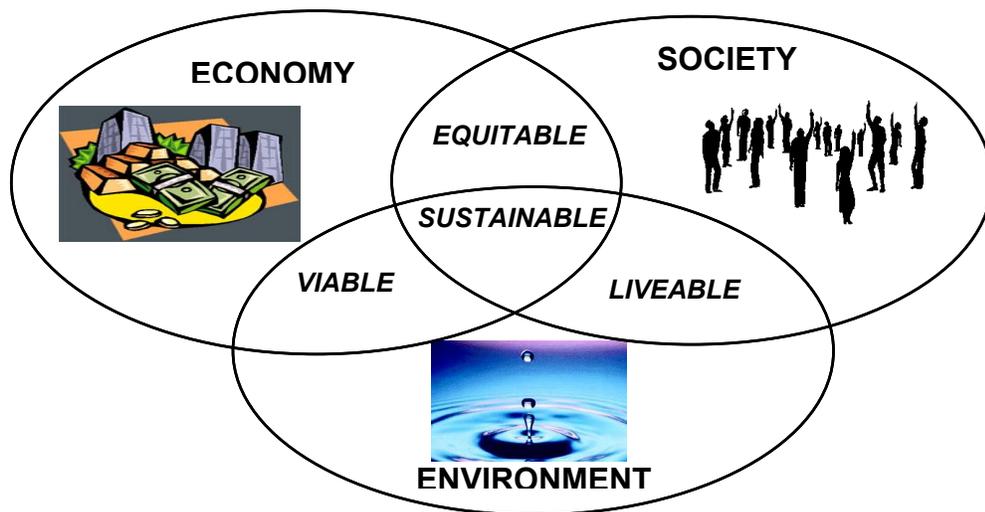


Figure 1. Basis of sustainable development

If you just consider two of them, you are not sustainable. For example, joining economy and society just means an equitable development, economy and environment, a viable development or society and environment a liveable development.

Sustainable development is based on four main regulations at the European level on:

- regulation on air,
- regulation on water,
- regulation on waste,
- regulation on classified facility for the environment.

In this context, a mention must be made on the use of supercritical fluids for sustainable chemistry and the development of green processes. Since the nineteen fifties, studies and development efforts have been focused on new ways of separating substances using the specific properties of supercritical fluids (Schmieder et al., 1996). In particular, supercritical carbon dioxide is used as extracting agent in many industrial processes replacing conventional organic solvent (decaffeination of coffee and tea, extraction of hops, spice, aromatic substances, fragrances, pharmaceuticals, etc). Processes using these fluids are also particularly attractive at the industrial scale in many fields such as impregnation, analytical and preparative separations, organic synthesis and waste management and material recycling. The development of this green technology is accompanied by numerous research activities, in particular, in the field of inorganic Materials Science for the synthesis of multifunctional nanomaterials (Aymonier et al. (a), 2006). After a brief description of supercritical fluids, we report in this paper on the chemistry and process using supercritical fluids for the design of multifunctional nanomaterials in underlining the green and sustainable aspects of this method. This will be illustrated by few examples of nanomaterials processed using supercritical fluids.

2. SUPERCRITICAL FLUIDS

In 1822, Cagniard de la Tour described his observation of the liquid phase disappearing when various liquids were heated in a closed vessel (Cagniard de la Tour, 1822). This study is considered to be the first publication describing the phenomenon of the supercritical domain. A fluid is said to be “supercritical” when its temperature and pressure exceed the critical temperature (T_c) and pressure (p_c). Figure 2 represents a phase diagram of a pure fluid in the p, T space.

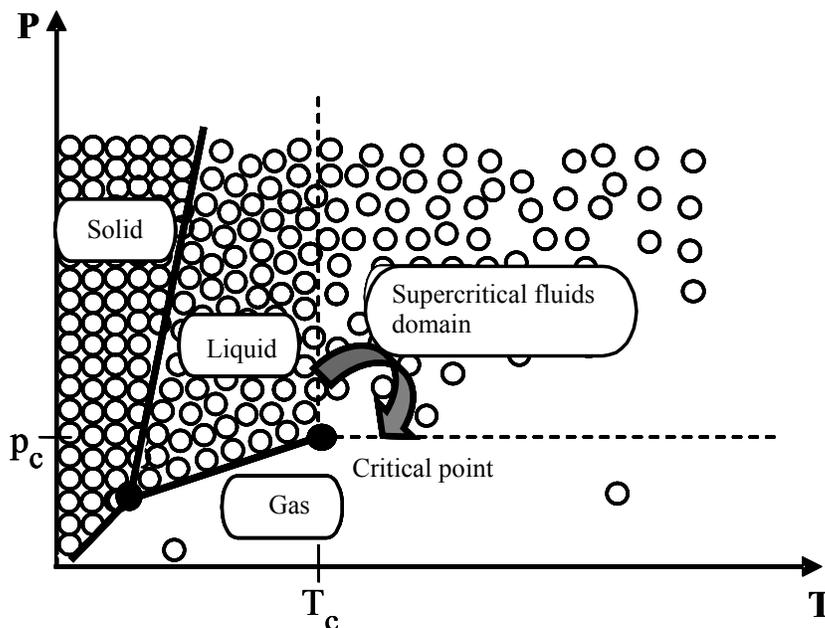


Figure 2. Phase diagram of a pure fluid in the space p, T

The most important feature of figure 2 is the indication that, within the supercritical region, there is no phase boundary between the gas phase and the liquid one. This means that there is a continuity in the physical properties of the fluid between the gas and the liquid states. The consequence is that supercritical fluids have properties, which are “hybrids” of those normally associated with liquids and gases, and which are continuously adjustable from gas to liquid with small pressure and temperature variations. Thus, the viscosities and diffusivities are close to those of the gas while the density is closer to that of a liquid. It is this combination of properties which has continued to fascinate chemists for over 150 years and have led to the current scientific and industrial interest in supercritical fluids.

In the field of nanomaterial synthesis using supercritical fluids, two green solvents are mainly used, carbon dioxide ($p_c=7.38$ MPa, $T_c=31.2^\circ\text{C}$, $\rho_c=468$ kg.m⁻³) and water ($p_c=22.1$ MPa, $T_c=374.1^\circ\text{C}$, $\rho_c=317$ kg.m⁻³). There is no better solvent than supercritical water (H₂O) and supercritical carbon dioxide (CO₂); carbon dioxide is considered as non toxic, non flammable, cheap and environmentally friendly. With CO₂, the idea is the development of processes with a recycling loop of the solvent.

The synthesis of nanomaterials using supercritical fluids have been reviewed several times over the last three years (Aymonier et al. (a), 2006; Cansell et al., 2003; Holmes et al., 2003). The next sections are focused on the interest of using supercritical fluids to overcome the drawbacks of solution chemistry approaches, especially from a process point of view, from a control of the nanomaterial characteristic point of view and from the sustainable development point of view.

3. PROCESSES OF PRODUCTION OF NANOMATERIALS USING SUPERCRITICAL FLUIDS

The synthesis of inorganic nanomaterials with processes involving supercritical fluids is achieved through two distinct processes. The difference depends on the driving force of particle formation, which can thus be based on either a physical transformation or a chemical reaction.

Several papers present a good overview of the state of the art concerning the first kind of processes (Fages et al., 2003; Hakuta et al., 2003; Jung et al., 2003); the driving force of nanoparticle nucleation and growth is a physical transformation: Rapid Expansion of Supercritical Solutions (RESS), Supercritical Anti-Solvent (SAS), Particles from Gas-Saturated Solutions/Suspensions (PGSS). Numerous other processes were patented from these three concepts of particle design using supercritical fluids with a physical transformation. These processes are mainly applied to the processing of organic nanoparticles with applications, for example, in pharmacology (Ibuprofen, Insulin, Griseofulvin, etc). These processes of nanoparticle design involving a physical transformation and using supercritical fluids are not really suited for the formation of inorganic functional nanoparticles; the second family involving a chemical reaction in supercritical fluids is more adapted for synthesizing inorganic multifunctional nanomaterials.

The synthesis of nanomaterials in supercritical fluids, from a chemical reaction, has received considerable attention since the nineteen's. In such methods, supercritical fluids are used as reaction media to synthesize a number of materials (metals, semiconductors, nitrides, oxides, etc) from the micrometer down to the nanometer scale. Different chemical reactions, which take their inspiration from solution chemistry, are performed in supercritical fluids for nanomaterials synthesis:

- 1- Hydrothermal reactions in supercritical water, based on a two-steps mechanism, namely the hydrolysis and dehydration of metal salts and metal – organic precursors (reaction extensively used to form various nanoparticles of metal oxides),
- 2- Thermolysis reactions from metal – organic precursors described with the thermal decomposition of metal – organic precursors (synthesis of different natures of nanomaterials such as oxides, metals, nitrides and semiconductors),
- 3- Red/Ox reactions corresponding to the reduction of metal salts or metal – organic precursors, generally in the presence of hydrogen (formation of metals),
- 4- Sol/gel reactions based on the well-known two-steps mechanism, namely the hydrolysis and condensation (mainly for the formation of oxide nanoparticles).

Taking care of sustainable development, these reactions are performed in a green media as explained previously and the reagents are chosen to reduce the formation of by-products at the end of the reaction.

From the point of view of chemical engineering, these reactions can be carried out using batch or continuous reactor technologies. Figure 3 shows a flow chart of a continuous facility of nanomaterials processing in supercritical fluids. This facility is composed of three main parts:

- 1- The injection with high pressure pumps (1) of a solvent, co-solvent(s), if necessary, and reagents; the feed solutions can be preheated (pre-heater). The pressure is the same in the whole set-up and is adjusted with a back-pressure regulator,
- 2- The reactor (2) where the chemical reaction takes place; different geometries of reactors can be used (from tubular to stirred vessel technology). The reactor technology allows the control of the hydrodynamics and kinetics of reaction influencing crucially the nucleation and growth of nanoparticles,
- 3- The recovery of nanoparticles (3) and/or (3') is considered with two approaches depending on the solvent nature. For solvents with high critical data (for example water), the nanoparticles are recovered in a filter system (3) or in solution (3') as a function of the application. If the synthesis is performed in a supercritical fluid with low critical data (for example, carbon dioxide), a dry nanopowder can be recovered by turning around the critical point.

Thus, the control of the physicochemical properties of nanomaterials (size, morphology, structure, and composition) is achieved by choosing specific operating parameters for controlling the thermodynamical properties of the media and the reaction kinetics: solvent nature, pressure, temperature (adjusted with pre-heaters and reactor),

reagent nature and concentration, reactor technology, residence time in the reactor. The control of these parameters is performed as follow:

- 1- pressure (p) with a back pressure regulator,
- 2- temperature in the reactor (T_4) with the pre-heaters (T_1 , T_2 and T_3), the system of reactor heating and the chemical reaction heat,
- 3- residence time in the reactor (t_s) with the pump mass flow rates (Q_{m1} , Q_{m2} and Q_{m3}), the reactor volume and the temperature,
- 4- reagent concentrations with the pump mass flow rates (Q_{m1} , Q_{m2} and Q_{m3}) and the initial concentration of feed solutions.

The control of T_5 is also very important to recover the powder with the desired characteristics.

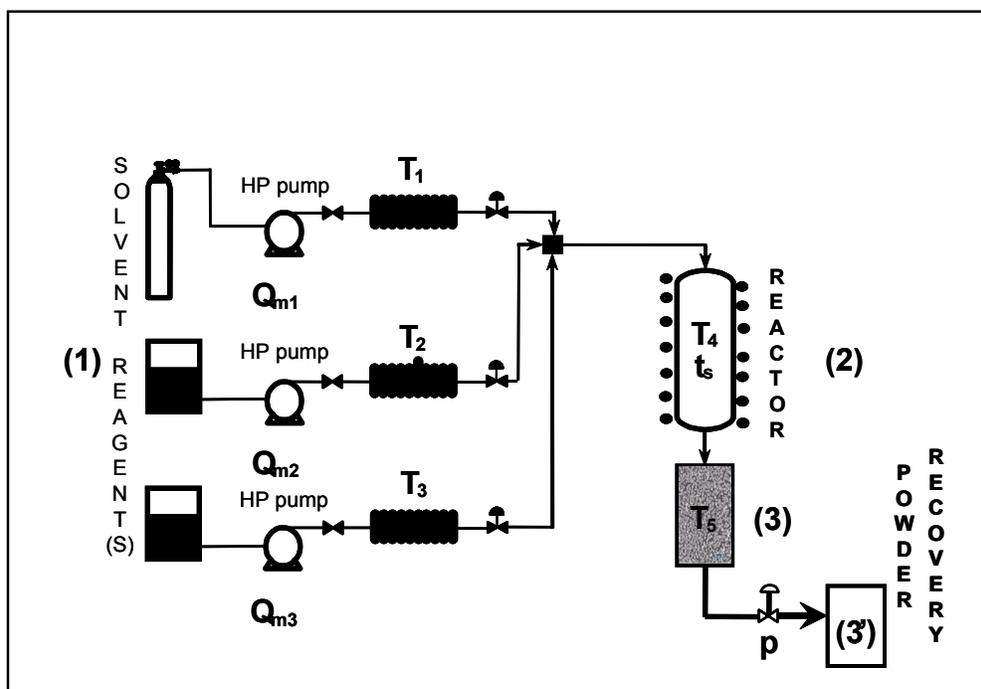


Figure 3. Flow chart of a continuous facility of synthesis of nanomaterials using supercritical fluids

Today, the aforementioned chemical reactions are well known and material scientists are working on the modeling of the nucleation and growth phenomena (Aymonier et al. (a), 2006) in connection with chemical engineers.

The development of simulation tools is one of the ways for improving the process as a sustainable one. In particular, key points of the supercritical fluid technology are to well control the heat transfer and the recycling of the fluid in minimizing the depressurization and pressurization steps.

The modelling of the formation of nanoparticles in such reactors is based on a population balance equation which has to be solved in order to predict particle size and aggregate formation. The phenomena that occur in the reactor are the nucleation and the growth of particles including the collision, the coalescence and the aggregation. Regarding fine spherical particle synthesis, we can assume in a first approximation that the particle size distribution is monodisperse. If N represents the number of particles/aggregates, the population balance equation in a batch reactor for a monodisperse distribution can be described classically by (Kruis et al., 1993):

$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2 + I \quad (1)$$

$$\frac{dV}{dt} = Iv_0 \quad (2)$$

where V is the volumetric concentration of particles, v_0 is the monomer volume, I represents the production (nucleation) of monomer due to fluid-phase reactions and β is the collision kernel function which is estimated by the Fuchs interpolation expression for brownian coagulation in the free molecule and continuum regime (Kruis et al., 1993). Non spherical particles can be taken into account by adding to the system one equation describing the coalescence phenomenon (Kruis et al., 1993; Lethinen, 1997).

The model for the batch reactor can be adapted to the continuous reactor. To solve such a problem, we need more information as the velocity of the fluid, the evolution of the temperature into the reactor and the turbulent dissipation rate in order to take into account the collision due to the turbulence phenomenon. These parameters can be obtained by solving the Navier-Stokes equations for the fluid, this one is a rigorous method to get information of the fluid phase. Furthermore, the evolution of the particle and the fluid are strongly coupled so the numerical resolution of the complete problem of the particle growth in the continuous reactor can be achieved by coupling two programs, one for the particle size distribution and other for the fluid dynamic.

A fine control of the operating conditions allows to get a great quality of the product and a decrease of the energetic cost. Generally the operating cost of processes using supercritical fluids are less expensive than basics ones.

4. DESIGN OF NANOMATERIALS USING SUPERCRITICAL FLUIDS

Supercritical fluid technology allows today to produce well designed materials, mainly among the families of oxides, metals and semiconductors but also nitrides, carbides or carbons, with controlled properties for applications in many interesting fields for the society: electronics, energy, optics, chemistry, pharmacy, etc.

Figure 4 describes some examples of kinds of nanomaterials or nanostructured materials which can be processed using reactors operating in supercritical conditions. Numerous nanopowders of nano-sized inorganic particles (3 to 105 nm) have been produced, mainly by hydrothermal reactions in supercritical water or thermal decomposition reactions in different solvents (AlOOH, Fe₂O₃, Fe₃O₄, Co₃O₄, NiO, TiO₂, BaFe₁₂O₁₉, ZrO₂, CeO₂, LiCoO₂, BaTiO₃, CeO₂, ZrO₂, Fe₃O₄, CoFe₂O₄, NiFe₂O₄, Ni_xCo_{1-x}Fe₂O₄, ZnFe₂O₄, La₂CuO₄, Ce_{1-x}Zr_xO₂, Zr_{1-x}In_xO₂, Ce_{0.1}Y_xZr_{0.9-x}O₂).

Figure 4a shows a transmission electron microscopy (TEM) picture of Ba_{0.5}Sr_{0.5}TiO₃ nanoparticles (about 26 nm) (Reveron et al., 2006). This nanopowder was produced by a sol-gel reaction in a mixture ethanol / water in continuous (150-380°C, 26 MPa). The use of this supercritical process presents advantages regarding conventional sol-gel approach. In fact, a pure, well crystalline and stoichiometric nanopowder can be produced without formation of carbonates in relatively short reaction times (few minutes).

As shown in figure 4b, supercritical fluids can also be employed to synthesize hybrid nanoparticles inorganic / organic. Figure 4b represents a TEM picture of hybrid nanoparticles of Pd /organic functionalizing agent synthesized in supercritical CO₂ (Aymonier et al. (b), 2006; Moisan et al., 2007). The control of the synthesis is based on the arrested precipitation concept; it was applied from solution chemistry. Supercritical fluids are employed to replace conventional solvent. This is also the case for the synthesis of hybrid nanoparticles with reverse micelles. For example, using water-in-CO₂ (W/C) microemulsions, researchers have transferred the chemistry performed in water-in-alcane microemulsions in the frame of the development of the green chemistry. Metal and semiconductor nanoparticles have been prepared with this approach, such as silver (5 to 15 nm), copper (5 to 15 nm), palladium, silver halide (3 to 10 nm), cadmium sulfide (1 to 2 nm), zinc sulfide (1.6 nm) and copper sulfide (4 to 6 nm).

Based on the know how developed on the production of nanopowders, more complex systems can be design using supercritical fluid processes of nanomaterial formation. Two examples are shown in Figures 4c and 4d. Figure 4c represents a TEM picture of silica spheres decorated with copper nanoparticles (Marre et al., 2006). This is a model system studied for the design of multifunctional materials, based on the combination of different materials; this is today a real challenge in Materials Science. As everyone knows, nanomaterials exhibit interesting

intrinsic properties, which can be different of those of bulk materials such as optical, magnetic or electrical ones. One of the challenges lies also in the organization of nanoparticles onto the surface of materials with a control of size, morphology and amount of coverage. Processes using supercritical fluids are an interesting alternative to modify surfaces of materials, especially particles, with nanomaterials. Among the different methods involving supercritical fluids, the Supercritical Fluid Chemical Deposition (SFCD) is very convenient for the design of surfaces with inorganic nanoparticles. Through SFCD, silica spheres, used as model support, were coated by copper nanoparticles (5-17 nm) with a tuneable amount of coverage (40-80%). This fundamental study was applied to the nanostructuring of the surface of magnesium particles with catalysts (Ni and Pd) to develop advanced materials for hydrogen storage, knowing that Hydrogen is now one of the potential vectors of energy for the future (Bobet et al., 2007). The SFCD method was also applied to the synthesis of core-shell structures as recently with the modification of surface properties of particles by nanoparticles until a homogeneous shell (figure 4d) (Aymonier et al. (c), 2005).

Other methods using supercritical fluids are successful in producing nanostructured materials; for example, the specific properties of supercritical fluids can be performant for impregnating polymer matrixes or porous, mesoporous materials with inorganic nanoparticles.

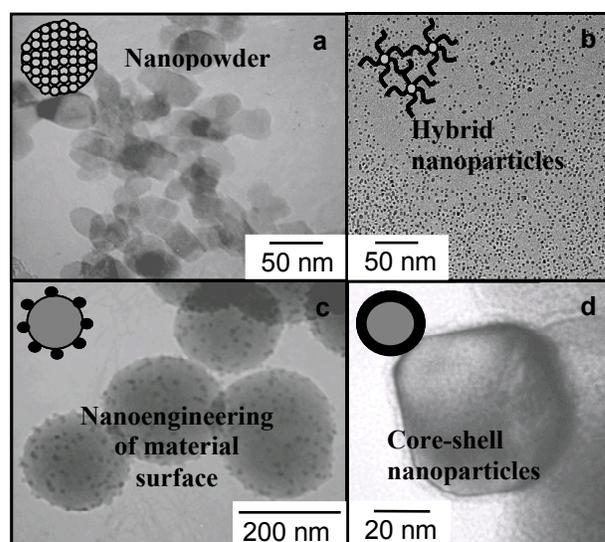


Figure 4. a) Nanopowder of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ for microelectronics, b) Hybrid nanoparticles of Pd /organic functionalizing agent for catalysis, c) Silica spheres decorated with Cu nanoparticles as a model system for new families of materials, d) Core shell nanoparticles of $\text{BaTiO}_3@\text{Al}_2\text{O}_3$ for microelectronics.

5. CONCLUSION

In industry and research laboratories in the field of chemistry, the concepts of green chemistry and sustainable development are more and more considered due to the evolution of regulations and mentalities. In this context, the development of supercritical fluid technologies should go on to evolve in the right direction. Among the different fields of application of supercritical fluids, the controlled synthesis of inorganic nanomaterials is a promising way. The control of the physicochemical properties of nanomaterials (size, morphology, structure, and composition) is achieved by choosing specific operating parameters: solvent nature, pressure, temperature, reagent nature and concentration, reactor technology, residence time in the reactor, additive agents (co-solvent, catalyst, surfactants ...). For example, nanopowders, hybrid nanomaterials or still new multifunctional materials based on the material surface nanostructuring can be produced. There are today numerous kinds of inorganic materials and nanomaterials which can be produced using supercritical fluids. The development of simulation tools is today one of the priorities for improving the “sustainable” side of the process. In particular, key points are to well control the heat transfers and the recycling of the fluid in minimizing the depressurization and pressurization steps. The transfer of supercritical fluid technology of materials processing from laboratory to industry is a challenge for the near future in

combining economical efficiency, environmental respect and society education, that is to say sustainable development.

NOTATIONS

I	nucleation term, $\text{m}^{-3}\text{s}^{-1}$
N	number of particles/aggregates, m^{-3}
V	volumetric concentration
v_0	monomer volume, m^3

Greek letters

β	collision kernel function, $\text{m}^3.\text{s}^{-1}$
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