CHAPTER 3

THEORETICAL CONSIDERATIONS

3.1 Rapid expansion of supercritical solution

The basic concept of RESS was first described by the pioneers Hannay and Hogarth 120 years ago. When the solid is precipitated by suddenly reducing pressure, it is crystalline, and may be brought down as snow in the gas, or on the glass as frost. As stated by Krukonis in 1981, 'One can use this phenomenon as a way of tailoring the size and size distribution of difficult-to-comminute organic materials. However, this concept has not been clearly understood but developed by experience after the pioneering works of Krukonis.

The rapid expansion of supercritical solution consists of saturation of a supercritical fluid with the substrate(s). Depressurization of this solution through a heated nozzle into a low-pressure chamber resulted in an extremely rapid nucleation of the substrate(s). Very small particles, fibers, or films could be manipulated when the jet is directed to the surface with strictly controlled condition.

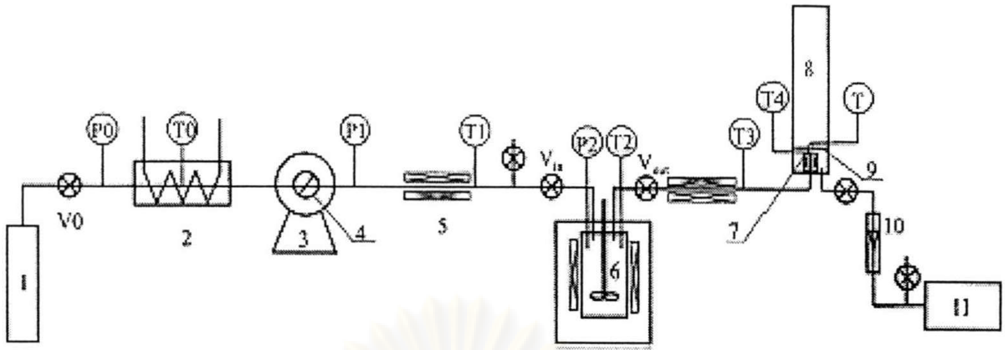

Fig. 3.1 Experimental system of RESS process

1. CO_2 bomb	4. CO_2 flow rate	7. Nozzle
2. Cooler	5. Heater	8. Fluidized bed
3. Pump	6. Extraction column	9. Distributor

The pure carbon dioxide is increased in pressure by a pump and preheated to the extraction temperature of through a heat exchanger. The supercritical fluid is then percolated through the extraction unit packed with one or more substrate (s), mixed in the one or more autoclave in series. In the precipitation unit, the supercritical solution is expanded through a nozzle heated to avoid plugging by the substrate(s) precipitates. The morphology of the resulting solid material depends on the material structure (crystalline or amorphous, composite) and the RESS parameters (temperature, pressure drop, distance of impact of the jet against the surface, dimensions of the atomization vessel and nozzle geometry). It should be noted that the initial investigations consisted of atomization of the pure substrates in order to obtain very fine particles.

3.2 Compressible Flow

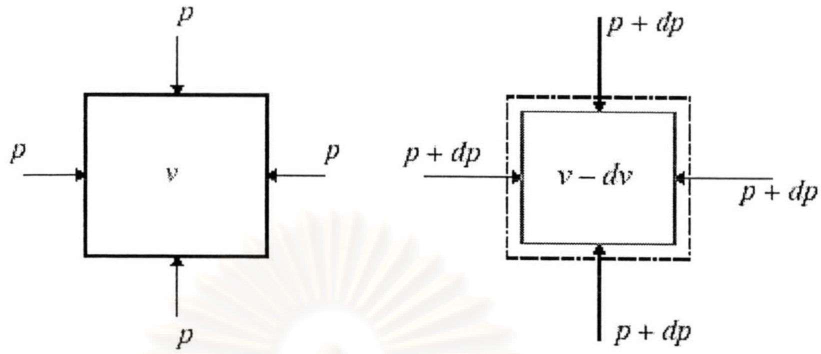

Fig. 3.2 Compressible system

In various situation, the density of a gas can change significantly along a streamline of fluid flow

$$\frac{D\rho}{Dt} \neq 0$$

It is generally known that Mach Number is the ratio of local velocity to speed of sound.

$$M = \frac{v}{c}$$

Compressibility of a fluid becomes important for High Speed Flows when $M > 0.3$

- $M < 0.3$ – Subsonic & incompressible
- $0.3 < M < 0.8$ – Subsonic & compressible
- $0.8 < M < 1.2$ – transonic flow – shock waves appear mixed subsonic and sonic flow regime
- $1.2 < M < 3.0$ – Supersonic – shock waves are present but NO subsonic flow
- M > 3.0 – Hypersonic Flow, shock waves and other flow changes are very strong
- Significant changes in velocity and pressure result in density variations throughout a flow field

- Large Temperature variations result in density variations.

It should be noted that flow regimes are strongly dependent to the fluid velocity. Following are some basic knowledge involving with the mentioned flow.

1. Choked Flow – a flow rate in a duct is limited by the sonic condition
2. Sound Wave/Pressure Waves – rise and fall of pressure during the passage of an acoustic/sound wave. The magnitude of the pressure change is very small.
3. Shock Waves – nearly discontinuous property changes in supersonic flow. (Explosions, high speed flight, gun firing, nuclear explosion)
4. A pressure ratio of 2 : 1 will cause sonic flow

In the real world, some applications shown below are involving with RESS

1. Nozzles and Diffusers and converging, diverging nozzles
2. Turbines, fans & pumps
3. Throttles – flow regulators, an obstruction in a duct that controls pressure drop.
4. One Dimensional Isentropic Flow – compressible pipe flow.

3.3 Equation of State (EOS)

The properties of fluid can be assumed when its temperature, pressure and other state properties remain unchanged. A suitable PVT equation of state can be used to evaluate many important properties of pure substances and mixtures, including the followings:

- Density of liquid and vapor phase.
- Vapor pressure.
- Critical properties of mixtures.
- Vapor – liquid equilibrium relations.

- Deviation of enthalpy from ideality.
- Deviation of entropy from ideality.

At present no single equation of state is universally suitable for all these properties of any large variety of substances. In this study, the interested fluid is carbon dioxide. Carbon dioxide is a symmetrical molecule and its dipole moment value equals 0 debye. However, it has 2 opposed dipoles which imply low polarity compounds with its compressibility of 0.274. Therefore, the suitable equation of state for calculating the properties of carbon dioxide is Peng-Robinson EOS or Soave Redlich-Kwong EOS.

3.3.1 Peng-Robinson Equation of State

Standard form:
$$\frac{P}{(V-b)} = \frac{(RT-a)}{V^2+2Vb-b^2} \tag{3.1}$$

where
a = $0.45724R^2Tc^2/Pc$
b = $0.07780RTc/Pc$
α = $(1+(0.37464+(1.5422\omega)-(0.26992\omega^2))(1-(T/Tc)^{0.5}))^2$
ω = $(0.2905-Zc)/0.085$
Zc = 0.307

3.3.2 Soave Redlich-Kwong Equation of State

Standard form:
$$\frac{P}{(V-b)} = \frac{a\alpha}{V(V+b)} \tag{3.2}$$

where
a = $0.42747R^2Tc^2/Pc$
b = $0.08664RTc/Pc$
α = $(1+(0.48508+(1.5517\omega)-(0.15613\omega^2))(1-(T/Tc)^{0.5}))^2$
ω = $(0.2905-Zc)/0.085$
Zc = 0.333

To investigate the suitable equation of state for estimating the thermodynamic properties of carbon dioxide several models were investigated by comparison between calculated results from the Peng-Robinson EOS and the Soave Redlich-Kwong EOS with the experimental results for verifying their suitability.