Condensing CO$_2$ droplets

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Condensing CO₂ Droplets

Condensed contaminant centrifugal separation is an emerging mechanical method to separate carbon dioxide (CO₂) out of contaminated natural gas and combustion effluent. Cooling is achieved by using an expansion device and/or a heat exchanger. CO₂ rich droplets are formed in the cooled gas stream. These CO₂ rich droplets are then separated out of the gas stream by a rotational particle separator. The droplet size is a key parameter for the efficient design of the centrifugal separation unit. This thesis predicts and measures the behavior of condensing droplets formed by continuous expansion cooling. This study also describes the effect of relevant process parameters like feed composition, expansion rate, pressure and temperature.

Measurements of CO₂ rich droplets in CH₄ or N₂ are done for various feed compositions of CO₂ (20-60 mole %) at the experimental test rig in Shell Amsterdam. A novel optical reflectance method is employed under high pressure (up to 30 bar) and semi-cryogenic conditions (down to −60 °C). A scheme to obtain the real droplet diameters from the measured chord lengths is also described and validated. CO₂ rich droplet diameters down to 2 µm are measured. Measurements give the range of condensed CO₂ rich droplets between 2 and 200 µm. 50-80 % of the liquid volume consists of droplets between 2 and 20 µm. Measured number densities are on the order of 10¹⁴ m⁻³.

A theoretical model characterizes the effect of various process parameters on the droplet size. The number density of droplets depends on the expansion rate and surface tension. Droplet size depends on the condensed liquid amount for the given number density. For the typical expansion rates of turbines and valves (10²-10³ s⁻¹), the calculated number densities lie between 10¹²-10¹⁶ m⁻³. The corresponding droplet size range is 0.5-10 µm for a typical liquid volume fraction of 1 %.

The droplet growth model is validated in a steam/air condensation test rig. Laser diffraction measurements of condensed water droplet sizes in air are done for a range of steam in air compositions and flow rates. It is also found that condensation droplet growth is completed within 1 ms for the typical expansion rates of 10² s⁻¹. Thus, the induction time can be shorter than the 0.2 s used in experiments. This enables design of more compact separation units.

We show that CO₂ droplets in a full scale unit will be as small as 1 µm. Thus, a separator needs to be designed to separate all the droplets down to this value in order to achieve 100 % droplet separation efficiency.
Nomenclature

\[ A = \text{area (m}^2\text{)} \]
\[ A_{\text{foc}} = \text{area sampled of the focused beam, eq. 2.8 (m}^2\text{)} \]
\[ A_{\text{fl}} = \text{cross sectional area of flow tube (m}^2\text{)} \]
\[ c_p = \text{molar specific heat at constant pressure (J mol}^{-1}\text{ K}^{-1}\text{)} \]
\[ d = \text{diameter of cluster or droplet (m)} \]
\[ D = \text{diameter of droplet (m)} \]
\[ D_{\text{coeff}} = \text{diffusion coefficient of condensable vapor in carrier gas (m}^2\text{ s}^{-1}\text{)} \]
\[ D_{\text{coeff, ref}} = \text{diffusion coefficient of condensable vapor in carrier gas under standard atmospheric pressure and temperature conditions (m}^2\text{ s}^{-1}\text{)} \]
\[ \text{DOF} = \text{depth of field (m)} \]
\[ D_{\text{foc}} = \text{waist diameter of the focus (m)} \]
\[ \bar{D}_v = \text{volume mean diameter (m)} \]
\[ D_x = \text{percentile drop diameter such that } x\% \text{ of the total liquid volume is in droplets smaller than diameter } D_x \text{ (m)} \]
\[ d_x = \text{percentile drop diameter such that } x\% \text{ of the total liquid volume is in droplets smaller than diameter } d_x \text{ (m)} \]
\[ d(3, 0) = \text{volume mean diameter (m)} \]
\[ E = \text{Heat flux (J s}^{-1}\text{)} \]
\[ f_{\text{liq}} = \text{condensed liquid mole fraction (-)} \]
\[ F_{\text{liq}} = \text{condensed liquid volume fraction (-)} \]
\[ f_r = \text{volume fraction in each bin of the distribution (-)} \]
\[ f(d) = \text{number distribution of droplets (-)} \]
\[ f(d^3) = \text{volume distribution of droplets (-)} \]
\[ G = \text{free energy (J)} \]
\[ h = \text{specific molar enthalpy of gas mixture (J mol}^{-1}\text{)} \]
\[ \Delta H = \text{enthalpy of vaporization (J mol}^{-1}\text{)} \]
\[ J = \text{molar flux (mol s}^{-1}\text{)} \]
\[ k = \text{boltzmann constant (J K}^{-1}\text{)} \]
\[ K = \text{collision frequency (s}^{-1}\text{)} \]
\[ l = \text{arbitrary length along the length of the expander in the flow direction (m)} \]
L = chord length (m)

$L = \text{mean of the measured chord length distribution (m)}$

$L_{\alpha} = \text{volume mean chord length (m)}$

$L_{\alpha} = \text{percentile chord length such that } x \% \text{ of total liquid volume or surface (based on chord lengths) is due to chords smaller than } L_{\alpha} \text{ (m)}$

$L_{\text{exp}} = \text{length of expander (m)}$

m = mass of a molecule (kg)

M = molar mass (kg mol$^{-1}$)

$M_{\text{avg}} = \text{average molar mass of the gas mixture (kg mol}^{-1})$

N = number density of clusters or droplets (m$^{-3}$ of gas)

NA = numerical aperture of the focusing lens (-)

$N_{\text{tot}} = \text{sampled number of droplets (-)}$

$n_{\text{mole}} = \text{number of moles in a cluster (-)}$

n = number density of molecules (m$^{-3}$ of gas)

$p (y) = \text{probability density of sampling } y \text{ such as diameter } D \text{ or chord length (m}^{-1})$

$p (L|D) = \text{conditional probability density of measuring } L \text{ given the droplet of diameter } D \text{ (m}^{-1})$

P (y) = probability of sampling y such as diameter D or chord length L (-)

P = total pressure (kg m$^{-1}$ s$^{-2}$)

$p = \text{partial pressure (N m}^{-2})$

$P = \text{total pressure of the gas (N m}^{-2})$

$\dot{P} = \text{expansion rate (s}^{-1})$

$q = \text{specific heat energy (J mol}^{-1})$

$Q_{\text{vol}} = \text{volume flow rate (m}^{3} \text{s}^{-1})$

$Q_{f} = \text{feed flow rate (mol s}^{-1})$

r = arbitrary circle radius lying within the radius of droplet (m)

R = radius of droplet (m)

$R_{u} = \text{universal gas constant (J mol}^{-1} \text{K}^{-1})$

S = super saturation (-)

T = temperature ($^\circ$C)

t = time duration (s)
Nomenclature

\(v\) = velocity (\(\text{ms}^{-1}\))

\(v_s\) = scanning velocity of laser relative to the droplet (\(\text{ms}^{-1}\))

\(V\) = volume (\(\text{m}^3\))

\(V_{\text{tot}}\) = sampled volume (\(\text{m}^3\))

\(v^*\) = partial molar volume of \(\text{CO}_2\) in the gas (\(\text{m}^3\ \text{mol}^{-1}\))

\(y\) = molar concentration in gas phase (-)

\(Y\) = amount of water vapor per kg of air (kg of water-vapor/kg of air)

\(Z\) = compressibility factor (-)

**Greek letters**

\(\lambda\) = laser wavelength (m)

\(\tau\) = sample duration (s)

\(\rho\) = molar density (\(\text{mol} \ \text{m}^{-3}\))

\(\mu\) = chemical potential (J \(\text{mol}^{-1}\))

\(\sigma\) = surface tension (N m\(^{-1}\))

\(\gamma\) = adiabatic index of isentropic expansion (-)

**Subscripts**

\(\text{avg}\) = average

\(\text{corr}\) = correction

\(\text{cal}\) = calculated

\(\text{dew}\) = intersection point of expansion path and the dew-point line of the feed gas mixture

\(\text{drop}\) = droplets

\(\text{eff}\) = effective

\(\text{exp}\) = expander

\(\text{eq}\) = equilibrium conditions

\(\text{foreign}\) = foreign particles

\(f\) = feed

\(i, j\) = droplets in distribution

\(j\) = discrete time step

\(\text{in}\) = inlet of expander

\(\text{isen}\) = isentropic

\(k\) = clusters of diameter \(d\) having number density \(N\) formed at each discrete time step \(t_j\)

\(\text{low}\) = lower limit of the sampling bin in distribution

\(\text{liq}\) = liquid phase
m = number of bins
mass = mass
meas = measured
out = outlet of expander
s = saturation conditions
up = upper limit of the sampling bin in distribution
vap = gas phase
vol = volume
valve = J-T valve

Superscripts
i = component in the gas
air = air
H₂O = water-vapor
Chapter 1

Introduction

1.1 Background

Separation of gas mixtures is an issue in various energy related processes [1]. Examples are the separation of H\textsubscript{2}S and/or CO\textsubscript{2} from methane to upgrade sour gas fields [2, 3] and the capture of CO\textsubscript{2} from coal fired power plants to reduce the emissions of greenhouse gases [4]. The mature industrial method for these applications has been the amine absorption technology. The contaminated gas is bubbled through solvent in an absorber column where the solvent absorbs the contaminant. Afterwards the solvent is regenerated by heating and/or flashing to a lower pressure. The process becomes increasingly uneconomical at higher contamination levels due to the intensive energy requirements and large equipment size [5].

An alternative method is to separate on the basis of phase separation. The mixture is cooled to semi-cryogenic temperatures, whereby the contaminant condenses partially and after which the condensate is separated mechanically. Several processes have been developed on this principle, for example the Total Sprex process to remove H\textsubscript{2}S from natural gas [6], Cryocell by Cool Energy to remove CO\textsubscript{2} from natural gas [7], Controlled Freeze Zone by Exxon for sour gas fields [3] and the Alstom anti-sublimation process [8]. A technological challenge is however posed by the feature that rapid cooling of binary or multi component mixtures of gases to temperatures where one, or some of the components preferentially condense, leads to a mist of droplets [9]. The phenomenon is known to occur by aerosol formation in flue gases of biomass combustion installations [10] and condensate droplets resulting from the cooling of wet natural gas [11]. For a process which relies on fast phase change as a means of separation to be economical and practical, it is necessary to have a separation device capable of capturing the condensed droplets of with high collection efficiency at low pressure drop and a small footprint.
1.2 Condensed rotational method

1.2.1 Working principle

Condensed rotational separation (CRS) method is a recently developed mechanical separation method for upgrading the sour gas fields or CO₂ capture from the combustion effluents [12]. Fig 1.1 shows a schematic of the condensed rotational process. The contaminated gas is rapidly lowered in temperature (typically between −50 °C and −56 °C) and reduced in pressure (typically 30 to 40 bars) by expansion cooling. Chilling can also be provided prior to expansion to reach the separation conditions. After the expansion, a mixture forms which consists of predominantly the gaseous phase with a mist of droplets enriched in contaminant. These droplets are then separated from the product rich gas phase by a rotational separator. The separation process is further enhanced by introducing a second step in the process (not shown in the schematic). In the second step, the collected liquid is flashed to form a liquid/gas mixture typically at 10-20 bars. The liquid is purified, while most of the gas which was dissolved in the liquid evaporates. This gas is re-fed into the gas stream in the first part of the process.

CRS process uses the rotational separator (RPS) which is capable to separate the droplets down to 0.1 µm [13, 14]. The RPS consists of a cylindrical pipe wherein a rotating element is placed. The rotating element is a simple rotating body consisting of a very large number of axial channels of a few millimetres in diameter. In such a channel, the micron-sized droplets are centrifuged to form a liquid film at the channel-wall, which is ripped off at the exit of the channel in the form of droplets; typically 20 µm or larger. These droplets are separated according the working principles of ordinary axial cyclones.

The basic idea behind the CRS process is that expansion cooling is faster compared to cooling by fractional distillation. Furthermore, the CRS unit is based on the rotational particle separator, which unlike cyclones can separate the droplets down to ca. 0.1 µm from the gas stream. Therefore, CRS has an overall shorter residence time and equipment size compared to the fractional distillation.

1.2.2 Process thermodynamics

As an example, in fig. 1.2 (a) shows a phase (pressure-temperature) diagram of 50/50 mole % CH₄/CO₂ system. A solid-dotted line on the top of fig. 1.2 (a) shows a typical process path during the expansion. The label in indicates the inlet conditions to the
1.2 Condensed rotational method

expander in the figure. The incoming mixture with methane concentration $y_{in}^{CH_4}$ (50 mole %) is cooled by expansion to pressure $P_{out}$ (30 bars) and temperature $T_{out} (-50 \, ^oC)$. This point is indicated by $out$ in the figure. The corresponding pressure-concentration diagram is shown in fig. 1.2 (b). Fig. 1.2 also depicts the basic principle of condensed rotational separation. A mist of small droplets is formed with composition $x_{out}^{CO_2}$ (87 mole %) because of binary condensation after the expander. The vapour phase has a composition $y_{out}^{CH_4}$ (83 mole %) and is separated. These CO$_2$ rich droplets are then separated by the RPS to obtain a liquid stream. In practice, the pressure and temperature at the outlet of expander are chosen such that CO$_2$ recovery from the feed gas stream is maximized [12]. For further details of the condensed rotational process refer [12, 15].

**Figure 1.1:** Schematic of condensed rotational separation process
Figure 1.2: (a) Pressure-temperature diagram of 50/50 CO\textsubscript{2}/CH\textsubscript{4} mixture. A solid-dotted line on top of it shows a typical process path during the expansion cooling. Contaminated gas is brought to $P_{\text{out}} = 25$ bars and $T_{\text{out}} = -50^\circ \text{C}$ after the expansion. After the expansion, liquid-vapor phase co-exists. (b) Corresponding pressure-concentration diagram of CO\textsubscript{2}/CH\textsubscript{4} mixture at outlet temperature $T_{\text{out}} = -50^\circ \text{C}$. It depicts that after the physical separation of the liquid-vapor phase, product vapor phase become rich in CH\textsubscript{4} and liquid phase become rich in CO\textsubscript{2}.
1.3 Goal and outline

For an efficient CRS process design, it is essential to know the condensed CO₂ droplet size before the separator. In this thesis, the focus is on CO₂ removal from the contaminated natural gas or combustion effluents. The objective of this work is to find out the size of condensed CO₂ rich droplets formed by the expansion cooling of CO₂/CH₄ or CO₂/N₂ mixtures.

In chapter 2, measurements of condensed CO₂ rich droplet sizes in methane or nitrogen atmosphere are reported at varying feed CO₂ concentrations. An optical reflectance method is used and developed to measure the condensed CO₂ rich droplets at semi-cryogenic and high-pressure environments. The number density of the condensed CO₂ rich droplets is also measured.

In chapter 3, a numerical model is formulated to understand the droplet formation process during the expansion cooling. This model predicts the distribution of the homogeneously condensed CO₂ droplets in N₂ or CH₄ atmosphere for the given process conditions. The important process parameters affecting the droplet number density and the size are identified.

In chapter 4, a simple analytical model is formulated for predicting the condensed CO₂ droplet size. The input process parameters are expansion rate, pressure and temperature before the expander and feed composition of CO₂.

In chapter 5, size measurements of heterogeneously condensed water droplets in air are performed to validate the diffusional growth part of the model used in chapter 3 and chapter 4. In addition, a time scale to complete the heterogeneous condensation growth during expansion cooling is obtained.
Chapter 2

CO₂ Droplets Condensed from Natural Gas or Flue Gas

2.1 Introduction

The size of condensing CO₂ rich droplets is a key parameter for the design of the centrifugal separation units (CRS units). The droplets need to grow to a specific size in order to be separated efficiently out of the natural gas. To achieve 100 % efficient separation and thus the desired purity of the contaminated gas, these condensed droplets need to be removed completely out of the CH₄ or N₂ rich vapor phase.

Despite its current relevance, very few studies of condensation of CO₂ have been reported. Condensation and sublimation of CO₂ in a helium atmosphere has been studied in a pre-cooled expansion chamber, but the study was only restricted to the reporting of threshold values of expansion ratios for the onset of the phase change [16]. The data for onset of condensation and pressure variation during expansion in supersonic nozzles has also been reported [17]. Two studies of CO₂ condensation from the super-critical phase have been reported, mainly studying hydrodynamics and heat transfer [18, 19]. There has been no work on the measurement of condensing CO₂ droplet sizes at the semi-cryogenic conditions specifically associated with mechanical separators.

The liquid regime of pure CO₂ exists between the triple point (P = 5.2 bar and T = −56.4 °C) and the critical point (P = 73.8 bar and T = 31.1 °C). For mixtures of CO₂/CH₄ or CO₂/N₂, the vapor-liquid regime exists between the dew-point curve and bubble-point curve. In this liquid/vapor coexistence region, condensed rotational separations are performed [21, 22]. To give an example, for a mixture of 50 mole % CO₂ in CH₄ at 30 bar, a liquid-vapor coexistence region exists between −60 °C and −30 °C. At a pressure of 50

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* Cryogenic generally refers to temperatures below −150 °C [20]. For the present measurements, we use ‘semi-cryogenic’ because temperatures involved during the measurements can be as low as −65 °C.
bar, the liquid vapor region extends over the temperatures between $-65^\circ C$ and $-20^\circ C$. Therefore, the measurements of condensed CO$_2$ enriched droplets need to be done at the pressures above which the liquid-vapor coexistence region exists and at semi-cryogenic temperatures (down to $-65^\circ C$).

The most commonly used droplet measurement methods like video/photography; diffraction and phase-Doppler need wide spatial optical access for detection [23]. These methods are difficult to apply under the semi-cryogenic conditions used for the CO$_2$ droplet size measurements in this chapter. It is not feasible to provide wide optical access for measuring condensing CO$_2$ droplets under discussion here because small droplets would evaporate due to heat ingress from the surroundings. Techniques like phase-Doppler and laser diffraction can be applied to systems at ambient temperatures where heat ingress is less of a problem, for example: measurement of water/oil/ higher hydrocarbon (C$_5$+) mist at ambient temperatures in natural gas/air [24, 25]. However, for our semi-cryogenic systems, especially the test unit discussed here which has much higher surface to volume ratios than full scale commercial units, the optical access should restrict heat ingress to an absolute minimum.

In this work, we describe a method with constrained optical access for measurements which thus minimizes the heat ingress. Section 2.2 describes the optical reflectance method used for the present measurements of CO$_2$ droplets formed by condensation. Section 2.3 describes the experimental test rig. In Section 2.4, the analysis to reach the real droplet diameter from the raw measurements has been explained. In Section 2.5, validation of the analysis scheme has been done with light diffraction measurements on calibration liquid droplets at room temperature. In Section 2.6, results of condensing CO$_2$ droplets in a methane or nitrogen atmosphere are presented and discussed.
This study makes use of a non-intrusive device called an optical reflectance probe to measure condensing CO$_2$ rich droplets. A schematic of the optical reflectance probe used for the droplet measurements is shown in fig. 2.1. The device is based on a modified (Process analytical technology, PAT) sensor manufactured by Sequip S& E GmbH [26]. A 4 mm diameter laser beam of wavelength 680 nm from a 25 mW semiconductor diode laser is focused through a sapphire glass window into the flow of condensing droplets. The flow section as part of the condensing droplet measurement system is described in the next section. The focus can be positioned into the flow of condensing droplets (up to 2mm) from the sapphire glass window. The working principle is illustrated in fig. 2.1.

A back reflected/scattered signal as a function of time is generated when a droplet passes across the focus. This back reflected/scattered signal travels back along the incident light path through the optical fiber and is transmitted at a partially reflecting mirror and then detected by a photodiode. Thus, no wide angle transmission scattering collection optics are required. As long as the droplet passes across the focus, back reflected/scattered light is detected by the photodiode (detector). A pulse of the back reflected/scattered light is seen by the detector and then converted into an electronic signal. The electronic signal pulse of duration ($\Delta t$) is thus related roughly to the size of droplet (D) and is given by:

$$D \approx \Delta t \times v_s$$

(2.1)

where $v_s$ is the scanning velocity of the laser relative to motion of the liquid droplet in the gas stream. The focus is stationary inside the flow tube and the scanning velocity $v_s$ refer to the average bulk velocity $v_{avg}$ of the gas phase which entrains small droplets and given as:

$$v_{avg} = \frac{Q_{vol}}{A_f}$$

(2.2)

where, $A_f$ is cross-section area of the flow tube where droplet size measurements are carried out (see next section). $Q_{vol}$ is the volume flow rate through the flow tube.

The minimum diameter detectable by the probe is limited by the waist diameter of the focused beam. The diameter of the focal point $D_{foc}$ is given by [23]:

$$D_{foc} = \frac{\lambda}{2NA}$$

(2.3)

where $\lambda$ is the wavelength of the laser beam and $NA$ is the numerical aperture of the focusing lens. (i.e. the ratio of lens radius to focal length).
The diameter of the focal point defines the resolution (in our case ca. 2µm) of an optical probe used for the present measurements. It was also confirmed by ruled diffraction grating (frequency: 200-600/mm, THOR-LABS) calibration experiments. The depth of field DOF is approximated by [23]:

\[ \text{DOF} = \frac{\lambda}{2NA^2} \]  

(2.4)

In our study this was ca. 10 µm.

A typical raw signal recorded with the oscilloscope (Dewetron, Sampling rate: 10 Giga-samples/s) during live measurement is shown in fig. 2.2. This raw signal is then processed through various steps to infer the final size of droplet. The analogue signal output from the photodiode is first digitized and then a number of operations including noise removal and removal of multiple peak signals are carried out in a micro-processor. The peak base widths (\(\Delta t\)) after thresholding are calculated in time. These widths are then multiplied by the scanning velocity \(v_s\) to generate a histogram corresponding to the droplet size distribution.

The optical reflectance method can cope with high droplet densities because it collects signals in the back scattered domain in contrast with devices based upon low angle scattering. This method based upon back scattered/reflectance has been extensively applied in the study of liquid/liquid emulsions and solid/liquid crystallization [27-30]. To our knowledge, it has never been applied for the measurements of droplet sizes in condensing gas-gas mixtures or indeed for the semi-cryogenic studies used here.
2.2 Optical reflectance probe

**Figure 2.1:** (a) Schematic of the optical reflectance probe illustrating the working principle of probe (b) Details of focused beam showing the focus height corresponding to depth of field DOF and the focus width which corresponds to diameter of focus $D_{foc}$. 
CO₂ Droplets Condensed from Natural Gas or Flue Gas

**Figure 2.2:** Recorded analogue signals of back scattered/reflected light of different base widths (Δt) after threshholding.

### 2.3 Experimental test rig

A schematic of the test set up used for present measurements is shown in fig. 2.3. Contaminated natural gas or flue gas, methane (CH₄) or Nitrogen (N₂) in varying ratios with carbon dioxide (CO₂), is first compressed to high pressures (typically up to 150 bar) using a diaphragm compressor (Burton Corblin, 12 kW, 60 Nm³/hr) and then cooled with a water chiller to take out the heat of compression while remaining above the dew point. This compressed and cooled mixture is then expanded isenthalpically in a Joule-Thomson (J-T) valve to pressures and temperatures (typically down to 30 bar and −60 °C), where contaminants condense in the form of fine micron sized CO₂ rich droplets. A circular section tube (“induction pipe”) of 13 mm inner diameter and 1 m length is connected to the low pressure side of the J-T valve. The time for flow through the induction pipe (“residence time”) provides for the growth of CO₂ rich droplets to a separable size. For the present measurements, the induction pipe corresponds to a residence time of approximately 0.2 s based upon the maximum possible flow rates (0.02 kg/s). The induction pipe is connected to a stainless steel rectangular channel (“flow tube”) where droplet measurements are carried
2.3 Experimental set up

The flow tube has a cross-sectional width and depth of 33 mm and 5 mm respectively at the measurement section. The optical reflectance probe for measurement of droplets is installed in the flow tube (see fig. 2.4). A sapphire glass window for the optical probe is located flush with the upper wall of the flow tube to minimize flow disturbances. The focus of the laser beam is positioned 2 mm below the surface of the sapphire glass window inside the flow tube. Flow tube, induction pipe and optical reflectance probe are well insulated during the measurement to minimize heat penetration.

Downstream from the flow tube, there is a particle separator (rotational particle separator) which separates small CO$_2$ enriched liquid droplets from the methane or nitrogen enriched vapor phase. The rotational particle separator consists of a collection of metal channels rotating around a common rotational axis. Within the separator, the liquid CO$_2$ droplets are spatially separated from the methane or nitrogen enriched vapor phase under the action of centrifugal force on these liquid droplets. After the separation, the product stream is enriched in CH$_4$ or N$_2$ and the waste stream consists of the separated liquid enriched in CO$_2$. The waste liquid stream is collected in a storage vessel. It is then evaporated, remixed with the product stream and then fed back to the compressor in a closed loop. Further, details of the gas loop can be found elsewhere [22].

The measurements of CO$_2$ enriched liquid droplet sizes using the optical reflectance probe are done just before the particle separator. Droplet sizes are sampled over a period $\tau$. We assume steady state conditions when pressure and temperature (before and after the expander), feed concentration of CO$_2$ in CH$_4$ or N$_2$ and feed flow rate through the expander were not changing by more than ca. 2 % over a period of few hours. Pressures (before and after expander) are measured using piezo-electric type pressure transducers which are accurate to within 0.01 bar. Temperature measurements are done with resistive type thermocouples (PT100) and are accurate to within 0.1 °C. Feed flow rate is measured by a Coriolis type flow meter (Endress-Hausser PROMASS 83M, accuracy: ± 5 %). For feed concentration measurements, 4 channel gas chromatography is used. Feed concentration measurements are accurate to within ± 2 mole %.
CO₂ Droplets Condensed from Natural Gas or Flue Gas

**Figure 2.3:** Schematic of the experimental test rig

**Figure 2.4:** Photograph of the optical reflectance probe installed in the flow tube
2.4 Analysis

The size given by eq. 2.1 is not necessarily the diameter $D$ of the detected droplet. The focus of the laser beam can traverse the droplet at different locations, mostly not through the center (see fig. 2.1). The intersected length from one surface to another of the droplet is thus detected as a chord of length $L$. Thus, the optical reflectance measurement does not measure the distribution of diameters directly. It rather measures the distribution of chords. The measured distribution of chords needs to be converted to the distribution of diameters of droplets.

Previous work on converting chord measurements to diameters can be broadly classified into two types. The first type covers empirical approaches in which the correlations between the diameters (which are measured by using other techniques e.g. light diffraction, direct imaging, sieving etc.) and the measured chords are found. In the second type of study, the theoretical models to convert the measured chord distribution to the actual diameter distribution or vice-versa are described.

Many empirical studies have been reported in the past to find the correlation between the measured chords and the actual diameters. Surface median chord lengths $L_{50}$ were found to be in agreement with volume median diameters $D_{50}$ measured by light diffraction for polyvinyl chloride suspensions in water (90-300 µm) [31]. Heath et al. also reported a similar agreement between surface median chord lengths $L_{50}$ and volume median diameters $D_{50}$ measured by laser diffraction and sieving for aluminum suspensions (50-100 µm) [32]. However, Alfeno et al. reported an agreement between the mean of measured chord length distribution $\bar{L}$ and the volume mean diameter $\bar{D}$ measured by laser diffraction for aggregated silica suspensions (20-180 µm) [28]. In another study, volume mean chord lengths $\bar{L}$ were found to be in agreement with volume mean diameters $\bar{D}$ measured by sieving for kaolin suspensions (0.3-663 µm) [33]. No single correlation, which relates the measured chord distribution to the corresponding actual diameter distribution, has been established.

A theoretical model has been proposed for translating the measured chord length distributions to actual diameter distributions and also validated by the sieve analysis for spherical amberlite particles (200-850µm) [29]. In another study, a model for transforming the chord length distributions to the diameter distributions has been validated with light diffraction measurements for calcinated silicate suspensions in water (1-100 µm) [30]. Another different study describes a model to infer the actual diameter distributions from the
measured chord length distributions and also the model is validated using photographic measurements for oil/water suspensions (500-5000 µm) [34]. The principle form of the models to transform the measured chord distributions to the actual diameter distribution is the same in all of the reported studies mentioned above. In this paper, we consider the problem to infer the diameters from the measured chords for our application using the reported study of Hu and Panguita as our basis [34]. We validated the scheme of conversion with light diffraction measurements on non-cryogenic calibrated liquid droplets (see section 2.5) in the size range (2-10 µm) of our interest. The conversion scheme to obtain real diameters from the detected chords is described for two cases (a) Monodisperse distribution of droplets (b) polydisperse distribution of droplets

2.4.1 Monodisperse case

We start by considering a collection of identical droplets of diameter D. A distribution of chord lengths is measured rather than a single chord length. The size range for this measured chord length $L_i$ distribution lies between 0 and D. In this case, the simplest analysis can be done by relating the mean of measured chord length distribution $\bar{L}$ to the diameter of a droplet D. The droplet diameter is found to be 3/2 times the mean of chord length distribution $\bar{L}$ measured by the optical reflectance (Appendix 2A). The probability density of obtaining a chord length $L_i$ when measuring a droplet of diameter D is:

$$p(L_i|D) = \frac{2L_i}{D^2}$$

which is the extension of eq. 2A8 and represents the conditional probability density that a droplet of diameter D is sampled to yield a chord length $L_i$.

2.4.2 Polydisperse case

In reality, there is a fine mist of polydispersed condensed CO$_2$ enriched liquid droplets in the CH$_4$ enriched vapor phase. There is thus a range of diameters for the droplets rather than only one diameter D as in monodisperse systems. A chord length $L_i$ can be measured from all the diameters $D_j \geq L_i$ within the distribution. For example, the chord length $L_i = 5$ µm can be detected/sampled from all the droplets diameters $D_j \geq 5$ µm. However the chance of sampling the chord length $L_i$ is not the same for each droplet diameter $D_j \geq L_i$. In other words, the probability of measuring the particular chord $L_i$ depends upon the droplet diameter $D_j$ but has the same form as eq. 2.5. The chance of sampling a particular chord $L_i$ in a
2.4 Analysis

A *polydisperse* system is then given by the sum of conditional probabilities averaged over all the droplets $D_j$:

$$P(L_i) = \sum_j (P(L_i | D_j) \times P(D_j))$$  \hfill (2.6)

The final factor to be included is the fact that optical reflectance measurements are biased to sample large droplets more than the small ones. This is because the chance of hitting a larger droplet is larger. This sample biasing is directly proportional to the capture cross-sectional area of the droplets in the sampling volume, i.e. $D_j^2$ of the droplets in the polydisperse system. For example, the chance of sampling the chord length $L_i$ from a diameter $D_j = 10 \mu m$ droplet is 100 times more than from a diameter $D_j = 1 \mu m$ droplet. Thus, the probe scans more chord lengths from the large droplets than from the smaller droplets. We need to correct the measured raw chord distribution for this biased sampling. The raw chord measurement can be corrected for this biasing if we multiply the right side of eq. 2.6 by the cross-sectional area of the droplet:

$$P(L_i) = \sum_j (P(L_i | D_j) \times P(D_j)) \times D_j^2$$  \hfill (2.7)

After renormalization, eq. 2.7 is the same as eq. 2.6 but corrected for the sampling bias of optical reflectance probe and valid for discrete droplet size distributions.

The measured chord lengths by optical reflectance probe are not truly discrete but distributed in successive size intervals (bins) over the complete range. Each bin contains a fraction of the total number of detected chord lengths, sampled in time $\tau$. The fraction of the total detected chord lengths in each bin represents the probability of detecting a chord length in the corresponding size interval. Thus, for each size interval (bin) of the measured chord length distribution, eq. 2.7 can be written in the integral form as:

$$\int_{L_{\text{low}}}^{L_{\text{up}}} p(L) dL = \int_{L_{\text{min}}}^{L_{\text{max}}} \int_{D_{\text{min}}}^{D_{\text{max}}} p(L | D) p(D) D^2 dD dL$$  \hfill (2.8)

where $L_{\text{low}}$ and $L_{\text{up}}$ are the lower and upper limit of the size interval of the sampling bin. $D_{\text{min}}$ and $D_{\text{max}}$ are the minimum and maximum diameter in the droplet diameter distribution. $D_{\text{min}}$ and $D_{\text{max}}$ are chosen equal to the minimum and maximum detected chord lengths respectively for the whole droplet diameter distribution. Eq. 2.8 is same as the eq. 2.7 in its discrete form. The chord length $L_i$ in eq. 2.7 corresponds to the middle of the sample bin of the chord length in eq. 2.8. Similarly the diameter $D_j$ in eq. 2.7 is the discretised version of the continuous
diameter variable in eq. 2.8. Eq. 2.7 can be cast into the matrix form. This is solved to obtain the droplet diameter distribution as follows:

\[
\begin{bmatrix}
P(L_1) \\
P(L_2) \\
\vdots \\
P(L_m)
\end{bmatrix} =
\begin{bmatrix}
P(L_1 | D_1) \times D_1^2 & P(L_2 | D_2) \times D_2^2 & \cdots & P(L_m | D_m) \times D_m^2 \\
P(L_1 | D_1) \times D_1^2 & P(L_2 | D_2) \times D_2^2 & \cdots & P(L_m | D_m) \times D_m^2 \\
\vdots & \vdots & \ddots & \vdots \\
P(L_1 | D_1) \times D_1^2 & P(L_2 | D_2) \times D_2^2 & \cdots & P(L_m | D_m) \times D_m^2
\end{bmatrix}
\times
\begin{bmatrix}
P(D_1) \\
P(D_2) \\
\vdots \\
P(D_m)
\end{bmatrix}
\]

(2.9)

Eq. 2.9 can be concisely written as:

\[
[Y]_{mx1} = [Z]_{mxm} \times [X]_{mx1}
\]

(2.10)

Where, \(Y\) is a matrix containing the probabilities of detecting the chord length \((L_i)\). \(X\) is a matrix having the probabilities of droplets having the diameter \((D_j)\). \(Z\) is a matrix containing the conditional probabilities of detected chord lengths multiplied by the corresponding bias correction factor and \(m\) denotes the number of bins. The droplet diameters are inferred from the measured chord distributions by solving the inverse of eq. 2.10 as:

\[
[X]_{mx1} = [Z]^{-1}_{mxm} \times [Y]_{mx1}
\]

(2.11)

After solving eq. 2.11, the number of droplets in each size interval is obtained by multiplying the probability of detecting a droplet of diameter in the given interval by the total number of sampled droplets \(N_{tot}\) in time \(\tau\) as:

\[
N(D_j) = P(D_j)N_{tot}
\]

(2.12)

The number of droplets \(N_{tot}\) is the same as the total number of measured chords in sample time \(\tau\). This is because each signal width \((\Delta t)\) corresponds to a chord length which is detected from a single droplet. The volume in each bin is subsequently obtained by multiplying the number of droplets in each bin by \(D_j^3\):

\[
V(D_j) = N(D_j)D_j^3
\]

(2.13)

So, the volume fraction in each bin is:

\[
f_v(D_j) = \frac{V(D_j)}{\sum_j V(D_j)}
\]

(2.14)

The total liquid volume \(V_{liq}\) sampled in time \(\tau\) is then obtained as:

\[
V_{liq} = \sum_j V(D_j)
\]

(2.15)
2.5 Validation

The conversion scheme described above for the poly-disperse case (section 2.4.2) is validated by comparison with light diffraction measurements on non-cryogenic calibrated droplets. A stream of droplets of heavy oil component (Diethyl hexa sebacate, DEHS) in nitrogen (N\textsubscript{2}) at room temperature and atmospheric pressure is generated with an aerosol generator (TSI-CMAG). It is set to generate droplets of different size ranges between 1 and 10 µm. This stream of droplets is then measured by a laser diffraction instrument (Malvern Master Sizer X) and then compared to the optical reflectance measurements.

Unlike the CO\textsubscript{2} droplet system which is the target of our study the DEHS droplets are stable at room temperature. There are thus no problems with heat ingress using large angle optical access methods. This means that the light diffraction method can also be used. Volume distributions based on the diameters are measured by these light diffraction measurements. The median diameter D\textsubscript{50}, D\textsubscript{90} and D\textsubscript{10} are then obtained from these measured volume distributions using light diffraction. The spread is then the difference between the top and bottom decile fractions D\textsubscript{90}–D\textsubscript{10}.

The stream of generated aerosols is then also passed through the flow tube (used above for CO\textsubscript{2} droplet measurements) with the optical reflectance probe. The chord length distributions are recorded and then converted to the diameter distributions by the scheme mentioned in section 2.4.2. The volume distribution is further generated from these diameter distributions (derived from the measured chord length distribution). The median diameter D\textsubscript{50} and spread (D\textsubscript{90}–D\textsubscript{10}) based on this generated volume distribution are then compared with the corresponding values measured by the light diffraction. Fig. 2.5 shows the comparison of light diffraction measurements with optical reflectance measurements. A good agreement is found within 10 % between the two techniques.
2.6 Results and discussions

2.6.1 Diameters vs. Chords

The measurements of condensed CO₂ rich droplets in a CH₄ or N₂ rich vapor phase are done in the experimental test rig using the optical reflectance method. The corresponding process conditions, pressure and temperature after the expander, feed concentration of CO₂ and feed flow rate, are tabulated in table 2.1 and table 2.2. Fig. 2.6(a) shows the volume distribution based upon the measured chord lengths for the feed concentration of 55 mole % CO₂ in CH₄. The volume median chord length L₅₀ lies at 15 µm. However, these chords are not the actual droplet sizes as we have discussed above. These raw chord length measurements are converted to the actual diameters as described in section 2.4. We want to point out that the real diameters are larger (by factor 1.5) than the detected chords for the case of mono-disperse droplets (see section 2.4.1). This needs not to be true in case of poly-disperse distribution of droplets. For the poly-disperse case, there is a size range of droplets.
2.6 Results and discussion

rather than a single droplet size. The same chord length (e.g. \( L_i = 2 \mu m \)) can be detected from the larger diameter droplets (e.g. \( D_j = 10 \mu m \)) as well as from the smaller diameter droplets (e.g. \( D_j = 2 \mu m \)) in the distribution. The real diameters should be obtained using the conversion scheme described in section 2.4.2 and validated in section 2.5. Volume distributions are generated based upon these derived diameters rather than the measured chord lengths.

Fig. 2.6 (b) shows the volume distribution based on the derived droplet diameters for the feed concentration of 55 mole % \( \text{CO}_2 \) in \( \text{CH}_4 \) after the growth (residence) time of 0.2 sec. The volume median droplet diameter \( D_{50} \) now lies at 7 \( \mu m \). This contrasts with the volume median chord \( L_{50} \) of 15 \( \mu m \) as depicted by the volume distribution based on the measured chords as shown in Fig. 2.6 (a). \( D_{90} \) of the volume distribution lies at 30 \( \mu m \), so most of the liquid volume load is due to droplets having diameters between 2 and 30 \( \mu m \). This means that all the droplets (as small as 2 \( \mu m \)) need to be separated out of the \( \text{CH}_4 \) rich vapor phase to attain the required purity of natural gas. The removal of these fine condensed \( \text{CO}_2 \) rich droplets using standard cyclones would be difficult and inefficient at the high throughputs of gas processing plants. This consequence is discussed further in section 2.6.4.

Figure 2.6: Comparison of (a) cumulative volume distribution based on the measured chord lengths with (b) cumulative volume distribution based on the droplet diameters (b). The feed concentration \( \text{CO}_2 \) in \( \text{CH}_4 \) is 55 mole % and corresponding process conditions are tabulated in table 2.1.
Table 2.1: Process conditions during the measurement of CO₂ rich droplets in CH₄

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Feed concentration (mole %)</th>
<th>Pressure inlet (bara)</th>
<th>Temperature inlet (°C)</th>
<th>Pressure outlet (bara)</th>
<th>Temperature outlet (°C)</th>
<th>Flow (kg/hr)</th>
<th>No. of counts (s⁻¹)</th>
<th>Flash calculated condensed liquid amount (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21</td>
<td>120</td>
<td>−2</td>
<td>−61</td>
<td>35</td>
<td>62</td>
<td>550</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>96</td>
<td>2</td>
<td>−34</td>
<td>28</td>
<td>69</td>
<td>500</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>98</td>
<td>3</td>
<td>−36</td>
<td>29</td>
<td>76</td>
<td>800</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 2.2: Process conditions during the measurement of CO₂ rich droplets in N₂

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Feed concentration (mole %)</th>
<th>Pressure inlet (bara)</th>
<th>Temperature inlet (°C)</th>
<th>Pressure outlet (bara)</th>
<th>Temperature outlet (°C)</th>
<th>Flow (kg/hr)</th>
<th>No. of counts (s⁻¹)</th>
<th>Flash calculated condensed liquid amount (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32</td>
<td>139</td>
<td>−7</td>
<td>31</td>
<td>−47</td>
<td>71</td>
<td>567</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>122</td>
<td>−7</td>
<td>30</td>
<td>−46</td>
<td>68</td>
<td>667</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>43</td>
<td>123</td>
<td>−7</td>
<td>31</td>
<td>−41</td>
<td>71</td>
<td>533</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>147</td>
<td>−1</td>
<td>30</td>
<td>−40</td>
<td>64</td>
<td>833</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>144</td>
<td>−2</td>
<td>34</td>
<td>−38</td>
<td>74</td>
<td>833</td>
<td>0.4</td>
</tr>
<tr>
<td>6</td>
<td>58</td>
<td>121</td>
<td>14</td>
<td>30</td>
<td>−30</td>
<td>74</td>
<td>1000</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>58</td>
<td>138</td>
<td>−10</td>
<td>29</td>
<td>−39</td>
<td>59</td>
<td>1067</td>
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<td>8</td>
<td>59</td>
<td>136</td>
<td>−6</td>
<td>30</td>
<td>−36</td>
<td>55</td>
<td>833</td>
<td>1.3</td>
</tr>
</tbody>
</table>
2.6 Results and discussion

2.6.2 CO\textsubscript{2} feed concentration

The feed concentration of CO\textsubscript{2} in CH\textsubscript{4} or N\textsubscript{2} and the residence time (time period between the J-T expansion and the particle separator for the growth of CO\textsubscript{2} rich droplets) are important factors, which can affect the size of condensed CO\textsubscript{2} rich droplets. In our experiments, the residence time is provided by a circular section tube (“induction pipe”) which is installed between the Joule-Thomson (J-T) valve and the rotational particle separator (fig. 2.3). The residence time can be altered by varying the length and/or the diameter of induction pipe under the same volume flow rate conditions. Keeping the residence time (ca. 0.2 s) constant, the droplet size measurements have been done at different feed concentrations of CO\textsubscript{2} in methane (CH\textsubscript{4}) or nitrogen (N\textsubscript{2}).

Fig. 2.7 shows the comparison of droplet sizes after the 0.2 s residence (growth) time for different feed concentrations of CO\textsubscript{2} in CH\textsubscript{4}. When the feed concentration of CO\textsubscript{2} in CH\textsubscript{4} is increased from 21 mole % to 60 mole %, then the median diameter D\textsubscript{50} of the volume distribution is increased from 7 \(\mu\)m to 20 \(\mu\)m (fig. 2.7a and 2.7c). At the upper end of volume distribution, D\textsubscript{90} is also shifted from 16 to 90 \(\mu\)m (fig. 2.7a and 2.7c). This means that the CO\textsubscript{2} rich condensed droplets are shifted towards the larger sizes when the feed concentration of CO\textsubscript{2} is increased from 21 mole % to 60 mole %. The larger sizes can be due to the increased amount of condensed CO\textsubscript{2} rich liquid present in the gas phase after the J-T expansion. The number of nuclei formed is same during the all measurements (see table 2.1). Thus, the droplets attain a larger size. The number of sampled chords is the same as the number of droplets or nuclei (assuming no agglomeration) formed as explained above (section 2.4). The number of droplets formed does not vary with the feed composition of CO\textsubscript{2} in methane. This is because the number of nuclei formed is strongly dependent upon the initial supersaturation rather than on the feed composition [35]. There is almost no change in droplet size as the CO\textsubscript{2} feed is increased from 21 mole % to 55 mole % (fig. 2.7b). The change appears to occur between 55 and 60 mole %. We show below in section 2.6.4 that there is a change in the amount of condensed CO\textsubscript{2} rich liquid (liquid volume fraction) between 55 mole % and 60 mole %. Rather than affecting number of droplets the size is affected.

Fig. 2.8 shows measured condensed CO\textsubscript{2} rich droplet sizes for different feed concentrations of CO\textsubscript{2} in nitrogen (N\textsubscript{2}). The residence (growth) time is 0.2 s for all the measurements. The corresponding frequency volume distribution for the condensed CO\textsubscript{2} rich droplets in N\textsubscript{2} is shown in fig. 2.9. In case of flue gas (CO\textsubscript{2}/N\textsubscript{2} feed gas mixture), the droplet
size does not change significantly with increase in feed CO$_2$ concentration from 32 mole % to 59 mole %. The median diameter $D_{50}$ of the volume distribution is ca. 8 $\mu$m for all tested CO$_2$ feed concentrations (see fig. 2.8). $D_{90}$ remains around 20 $\mu$m (see fig. 2.8). The number of nuclei (droplets) is also not much affected (see table 2.2).

The important difference between contaminated natural gas (CO$_2$/CH$_4$) and flue gas (CO$_2$/N$_2$) is that in case of flue gas the droplets remain smaller even for higher CO$_2$ feed concentration (60 mole %). The reason can be the difference in the condensed liquid amounts between both cases. It is shown in section 2.6.4 that condensed liquid amount (calculated using theoretical flash) in the gas phase after the J-T expansion is 1 vol. % for 60 mole % CO$_2$ feed in CH$_4$. It is 3 vol. % for nearly the same feed of CO$_2$ in N$_2$. There is no significant change in number of droplets in both cases (see table 2.1 and table 2.2). Therefore, the droplet size becomes bigger in case of contaminated natural gas at higher CO$_2$ feed of 60 mole %. However, this increase in droplet size is partially explained on the basis of condensed liquid amount. A factor 3 increase in condensed liquid amount should bring factor 1.5 increase in the droplet size for the same number density of droplets. However, the observed increase in droplet size is larger than 1.5 in both cases. The volume median diameter $D_{50}$ increases from 9 $\mu$m (60 mole % CO$_2$ in N$_2$) to 20 $\mu$m (60 mole % CO$_2$ in CH$_4$). Similarly, $D_{90}$ shifts from 20 $\mu$m to 90 $\mu$m in both cases for same CO$_2$ feed concentration (60 mole %).

The exceptionally large droplet sizes in case of 60 mole % CO$_2$ feed concentration in CH$_4$ can be linked to another process – namely, film formation on the inner wall of the induction piping. Subsequent shearing off of droplets by the gas could result in larger droplets. Another cause of film formation could be adsorption of small droplets flowing very close to the wall. Wall condensation can happen if the surface temperature is lower than the dew point temperature of the flowing gas. This only happens if there is external cooling whereas in our experiment the cooling source is the expanded gas itself so that the gas should always be cooler than the walls. Thus, wall condensation does not explain the exceptionally big shift of CO$_2$ droplets towards larger sizes for the case of 60 mole % CO$_2$ feed in CH$_4$. To be sure of this large increase for this particular measurement, its reproducibility should be checked. However, the measurement has not been repeated because of the unexpected shut-down of the condensed separation unit in Shell Amsterdam.

Furthermore, under realistic full scale conditions the surface to volume ratio will be much smaller than in our experimental pilot unit case so wall condensation would have a
2.6 Results and discussion

much smaller role. The flows associated with real scale CRS units will be much higher (e.g. 100 kg/s corresponding to 250 MMscfd gas field or a 500 MW coal power plant) than the pilot scale CRS test unit in Amsterdam (max. 0.02 kg/s). This leads to very low surface to volume ratio in the real scale units compared to the pilot scale test unit in Amsterdam. For example, at a flow of 100 kg/s, then in order to maintain the 0.2 s induction time, a pipe of 10 m length and 200 mm diameter will be required. There will be less wall effects even at very high liquid volume load separation conditions (up to 5 vol. %). We expect that majority of condensed CO$_2$ droplets will remain smaller similar to the range which we measured with up to 80 % - 90 % of the droplets less than 20 µm. Our measured CO$_2$ droplet sizes were thus representative of the droplet sizes expected in full scale CRS units.

Another important point to note in both cases, (fig. 2.7 and 2.8) is that the lower ends of the volume distributions remain unaffected with changes in process and feed concentration conditions. i.e. $D_{10}$ remains around 2-3 µm irrespective of the change in feed concentrations of CO$_2$ in CH$_4$. Thus in order to capture 90 % of the condensed liquid CO$_2$ all the droplets down to 2 µm need to be separated.

![Figure 2.7](image_url)

**Figure 2.7:** Cumulative volume distribution based on the diameters of CO$_2$ rich droplets for different CO$_2$ feed concentrations of (a) 21 mole %, (b) 55 mole % and (c) 60 mole % respectively in methane. The corresponding process conditions during the measurements are tabulated in table 2.1.
Figure 2.8: Cumulative volume distribution based on the diameters of CO\textsubscript{2} rich droplets in nitrogen for different CO\textsubscript{2} feed concentrations. The corresponding process conditions during the measurements are tabulated in table 2.2.

Figure 2.9: Frequency volume distribution based on the diameters of CO\textsubscript{2} rich droplets in nitrogen for different CO\textsubscript{2} feed concentrations. The corresponding process conditions during the measurements are tabulated in table 2.2.
2.6 Results and discussion

2.6.3 Separability

In the mechanical separation process under discussion here, CO\textsubscript{2} contaminant condenses out of natural gas or flue gas. Ideally, these condensed CO\textsubscript{2} rich liquid droplets need to be separated completely out of the CH\textsubscript{4} or N\textsubscript{2} rich gas stream to attain 100 % efficient separation.

For the feed concentration of 21 mole % CO\textsubscript{2}, \textit{D}_{90} of the volume distribution lies at 15 \textmu m (shown in fig. 2.7a). Thus more than 90 % of the total condensed liquid volume is due to droplets smaller than 20 \textmu m, which is the standard cyclone cut off at the high flow rates of real gas fields (typically 100 kg/s) [4]. So, if a cyclone would be applied for the separation of condensed liquid CO\textsubscript{2}, more than 90 % of the total condensed liquid volume would remain un-separated from the CH\textsubscript{4} rich gas stream. Cyclones can thus only be applied for separation if all the droplets below 20 \textmu m have more time to grow to this cut off size. This would require long residence times for the growth which is mainly governed by relatively slow coagulation. The growth from the current volume median size \textit{D}_{50} of 6 \textmu m to 20 \textmu m by coagulation takes a few seconds [35]. For example at a typical flow of 100 kg/s (corresponding to 250 MMscfd in industrial gas units), this would require hundreds of meter of cooled and pressurized piping. Even after the growth of the volume median diameter \textit{D}_{50} to the cut off range of cyclones, half of the total condensed liquid volume would still remain un-separated.

We have shown that increasing the CO\textsubscript{2} concentration in the feed shifts the diameters of the CO\textsubscript{2} rich droplets toward larger sizes in case of CH\textsubscript{4} (section 2.6.2). Despite of the higher feed concentrations (for example 60 mole % CO\textsubscript{2}), nearly 50 % of condensed liquid volume load is below the cut off range (20 \textmu m) of cyclones. This would mean that 50 % of the condensed liquid would still remain un-separated. In the case of flue gas, nearly 90 % of the liquid volume consists of the droplets with diameter less than 20 \textmu m. CO\textsubscript{2} condensed droplet in N\textsubscript{2} remain smaller irrespective of the amount of CO\textsubscript{2} in the feed.

We have also shown that the lower tail of the distribution remains unaffected despite the increase of concentration of CO\textsubscript{2} in feed (section 2.6.2). Nearly 10-15 % of the condensed volume is thus contributed by droplets smaller than 2-3 \textmu m independent of CO\textsubscript{2} concentration in feed. If these droplets would not be separated, they will be carried over to the gaseous product stream and thus the desired gas purity will not be achieved. Thus, the particle separator needs to be designed to separate all the droplets down to ca. 0.5 \textmu m to collect the bulk of CO\textsubscript{2} rich liquid.
2.6.4 Liquid fraction

In addition to providing details of the droplet distribution, the optical reflectance measurement also yields the liquid fraction i.e.

\[ F_{\text{liq}} = \frac{V_{\text{liq}}}{V_{\text{liq}} + V_{\text{vap}}} \]  \hspace{1cm} (2.16)

We obtain this experimentally by (1) converting the measured number of droplets to a total volume to obtain the numerator in eq. 2.16 (2) deriving the denominator from a consideration of the total flow (gas + liquid) sampled in a measurement period- the sample volume is determined by parameters which are defined from the high intensity region of the focused laser from which back reflected/scattered signal is collected.

The number distribution of droplet diameters is obtained (section 2.4 above). The volume distribution of droplets of diameter \( D_j \) can be obtained by weighting each fraction of the number distribution by the corresponding droplet volume. Because each signal corresponds to a droplet, then the total volume of droplets sampled in time \( \tau \) is the sum of all the droplet volumes corresponding to the numerator in eq. 2.16.

The volume flow (\( Q_{\text{vol}} \)) per unit area through the laser beam focus then gives a volume sampled \( V_{\text{tot}} \) of

\[ V_{\text{tot}} = \frac{A_{\text{foc}} \tau Q_{\text{rel}}}{A_f} \]  \hspace{1cm} (2.17)

Where, \( A_f \) is the cross sectional area of the flow tube and \( \tau \) is the sampling time. The area sampled of the focused beam \( A_{\text{foc}} \) is determined by the region of the focus height (corresponding to the depth of field eq. 2.4) and the width corresponding to the focal spot size (eq. 2.3) as shown in fig. 2.1b.

\[ A_{\text{foc}} = DOF \times D_{\text{foc}} \]  \hspace{1cm} (2.18)

Combination of eq. 2.18 and eq. 2.17 yields the total volume sampled for the denominator in eq. 2.16. Combining with the known total liquid volume we can obtain the experimental liquid volume fraction.

In this experimental evaluation of the liquid fraction, we only use signal from the most intense region of the focused laser beam. The definition of depth of field (DOF) in eq. 2.4 is based on geometric optics which corresponds to roughly the full length between half maximum intensity points along the axis of the focused beam (refer fig. 2.1a and 2.1b). Along this axis thus, the intensity varies by 50%. However since we wish to only use signal from the most intense portion of the beam, we use a shorter depth of field corresponding to
only a 5 % decrease from the maximum intensity. This depth of field is about 25 % of the geometric one [23].

Condensed liquid volume fractions $F_{\text{liq}}$ after the J-T expansion are also predicted using equation of state flash calculations at the operating pressures, temperatures and feed concentrations of CO$_2$. Fig. 2.10 shows a comparison between the experimentally measured liquid fractions and the predicted values for different feed concentrations of CO$_2$ in CH$_4$. The latter is shown for different depths of field (DOF) in case of CO$_2$ in CH$_4$. We use the standard geometric depth of field definition (eq. 2.4). In a physical model this corresponds to the full width of the half maximum intensity measured along the laser axis. However, signal extinction and subsequent thresholding mean that only signal intensities much closer to the maximum are effectively detected. We can estimate this by fitting our experimental results for different depth of field. The points (c) in fig. 2.10 show that using eq. 2.4 underestimates the liquid fraction obtained from the thermodynamic flash calculations.

By using the modified depth of field (25 % of geometric one), a best match is obtained between the experimental liquid fractions and the flash calculated ones (The solid line is a reference line which represents an ideal case of one to one agreement between experimentally obtained liquid fractions and the ones calculated using flash.) *This of course implicitly includes the modified depth of field discussed above as an effective fitting factor.* (Note that the relative increase in liquid fraction with CO$_2$ feed is itself independent of depth of field.) The liquid volume fractions increase from 0.8 % to 3 % when the amount of CO$_2$ in feed is increased from 21 mole % to 60 mole %. However, as in the case of droplet sizes (section 2.6.2 above), almost all the increase is due to the last 5 % increase of CO$_2$ in the feed.

Fig. 2.11 shows a comparison between experimental liquid fractions and flash calculated ones for different feed concentrations of CO$_2$ in N$_2$. Experimentally obtained values are shown only for the modified depth of field (25 % of the geometric one). A best match between the two is obtained for the modified depth of field (0.25 DOF) like in the case of CO$_2$/CH$_4$ mixtures. There is an increase in liquid volume fraction from ca. 0.2 % to ca. 1 %, when the feed CO$_2$ concentration is increased from 32 mole % to 59 mole %.
CO$_2$ Droplets Condensed from Natural Gas or Flue Gas

**Figure 2.10**: Comparison of the measured liquid volume fractions with the liquid volume fractions predicted using equation of state flash calculations for different CO$_2$ feed concentrations in CH$_4$. The corresponding CO$_2$ feed concentrations in CH$_4$ are 21 mole %, 55 mole % and 60 mole % respectively.

**Figure 2.11**: Comparison of the measured liquid volume fractions with the liquid volume fractions predicted using equation of state flash calculations for different CO$_2$ feed concentrations in N$_2$. 
2.7 Conclusions

1. An optical reflectance method was applied to measure condensing CO\textsubscript{2} rich droplets from natural gas at semi-cryogenic temperatures and high pressures. The method yields the chord lengths rather than actual diameters. These chord lengths need to be converted to the corresponding diameters to obtain the real size of the droplets.

2. The size range of condensed CO\textsubscript{2} rich droplets in methane lies between 2 and 100 µm for growth (residence) time of 0.2 seconds. 50-80 % condensed volume is due to the droplets between 1 and 20 µm. For 100 % efficient separation, a particle separator needs to separate all the droplets down to 0.5 µm in the distribution in the distribution.

3. The size of CO\textsubscript{2} droplets in methane is insensitive to feed CO\textsubscript{2} at low concentrations but shows more variation at higher concentration levels. Of course, the pressure and temperature after expansion- in combination with feed CO\textsubscript{2} concentration- determines the amount of liquid formed which in turn has a direct impact on the droplet size.

4. Post combustion CO\textsubscript{2} capture from power plants is the other potential application for the mechanical separation method discussed here. The major differences from natural gas are that the CO\textsubscript{2} concentrations are lower and the more volatile component is less soluble in liquid CO\textsubscript{2}. The size of CO\textsubscript{2} rich droplets in nitrogen remains unaffected with change in the feed concentration of CO\textsubscript{2}. Droplets less than 20 µm comprise approx. 90 % of the condensed liquid volume.

5. The measured droplet sizes are independent of the scale of the unit. They depend upon the feed CO\textsubscript{2} concentration, pressure and temperature after the expansion and the residence time. In the real gas field units the residence time would be the same although high flows (ca. 100 kg/s) require longer pipe lines. For the residence time of the present measurements (0.2 s), this residence time is equivalent to ca. 10 m of pressurized insulated 200 mm diameter pipe. This size of piping is a lot shorter than the hundreds of meters of piping, if cyclones were to be used for separation. For optimization residence time could be shortened further to have compact units. The effect of this on the droplets still needs to be assessed.

6. The optical reflectance method can be used for the relative measure of liquid fractions but for the absolute values, the exact sampling volume should be known.

7. The present measurements of CO\textsubscript{2} enriched droplets are done in methane (CH\textsubscript{4}) only. In reality, higher hydrocarbons like ethane, propane etc. (C\textsubscript{2}+) are also present in natural gas. The presence of higher hydrocarbons on the size of condensed CO\textsubscript{2} enriched droplets will also be of interest in future and will probably lead to larger droplets.
Appendix 2A

Average chord length in mono disperse system

Consider a spherical droplet of radius R, which is scanned by the focused laser beam during the measurement by optical reflectance probe (fig. 2A1 and refer section 2.2). The focus can traverse across the droplet through any point inside the circle of radius R as shown in fig. 2A1. Thus a chord $L_i$ is detected, which will lie between 0 and the diameter $D$ of the droplet.

Now, consider a circle of arbitrary radius $r_i$ inside the circle of radius R. The chance of sampling $P(r \leq r_i)$ within this circle of radius $r_i$ is given by:

$$P(r \leq r_i) = \frac{\pi r_i^2}{\pi R^2} \quad (2A1)$$

The left hand side of the eq. 2A1 can also be described as:

$$P(r \leq r_i) = \int_0^{r_i} p(r)dr \quad (2A2)$$

where, $p(r)$ is the probability density of sampling at any radius $r$.

Now by differentiating eq. 2A2, we get the probability density of sampling at radius $r_i$ as follows:

$$p(r_i) = \frac{2r_i}{R^2} \quad (2A3)$$

and $r_i$ can be any radius between 0 and the radius R of droplet.

There is a unique chord length $L_i$ associated with a specific hit of focus at circle of radius $r_i$. So, the chance of sampling chord length $L_i$ is equal to the chance of hitting focus at radius $r_i$ and can also be written as:

$$p(r_i)dr_i = p(L_i)dL_i \quad (2A4)$$

$$p(L_i) = p(r_i) \frac{dr_i}{dL_i} \quad (2A5)$$

where $p(L_i)$ is the probability density of sampling the chord length $L_i$ during the measurement. From the geometry of a spherical droplet of radius R (see fig. 2A1) any chord length $L_i$ and projected radius $r_i$ are related as follows:

$$r_i^2 + L_i^2 = R^2 \quad (2A6)$$

$$\frac{dr_i}{dL_i} = \frac{L_i}{r_i} \quad (2A7)$$
Appendix 2A Average chord length in monodisperse system

Combining eq. 2A5 and eq. 2A7 we get,

\[ p(L_i) = \frac{2L_i}{D^2} \]  \hspace{1cm} (2A8)

So, the probability density \( p(L_i) \) of sampling any chord length \( L_i \) while scanning a droplet of radius \( R \) is given by eq. 2A8 as stated above. The mean of this chord length \( \bar{L} \) is defined as:

\[ \bar{L} = \int_0^\infty L_i p(L_i) dL_i \]  \hspace{1cm} (2A9)

Putting eq. A28 in eq. 2A9 and solving we get:

\[ D = \frac{3}{2} \bar{L} \]  \hspace{1cm} (2A10)

Therefore, for monodisperse droplets the diameter \( D \) is found to be \( 3/2 \) times the mean \( \bar{L} \) of the measured chord length distribution.
Figure 2A1: A spherical droplet of radius $R$ is passing through the focused laser beam and depicts the measurement of chord length $L_i$ while scanning the droplet.
Chapter 3
Droplet Size Predictions (Part 1)

3.1 Introduction

In the condensed centrifugal separation (CRS) units, CO₂ is condensed out of contaminated natural gas or flue gas in the form of fine droplets. The separator after the condensation step has to be capable of separating these CO₂ rich droplets to obtain the required purity of the gas. A key parameter for the design of the separator is the size of the droplets which have to be captured [14]. Condensed CO₂ rich droplet sizes between 2 and 20 µm are reported for the tested process conditions in chapter 2. There is little literature on the size of condensed CO₂ droplets formed by the cooling of contaminated natural gas or flue gas. A few studies report the condensation of higher hydrocarbons (like propane and nonane) in CH₄ and/or CO₂ but these studies aimed to verify the various nucleation rate (see section 3.2) theories using a pulse expansion method [36-39].

In this work, we theoretically predict the size of CO₂ droplets formed by the expansion cooling of contaminated natural gas or flue gas. Contaminated natural gas is modeled as a binary gas mixture of CO₂ and CH₄. Flue gas is modeled as a CO₂ and N₂ binary gas mixture. The theoretical model is developed to characterize the effect of expansion parameters on the condensed CO₂ droplet size and to compare with our CO₂ droplet number density and size measurements. The process parameters that may affect the droplet size are

1. Feed composition of CO₂ in CH₄ or N₂
2. Pressure and temperature before and after the expander
3. Rate of expansion

There are two ways by which the droplet formation can occur during the expansion cooling:

- Homogeneous nucleation and subsequent growth by diffusion (Homogeneous condensation)
- Heterogeneous condensation on foreign particles.

Homogeneous condensation generally leads to higher number densities and smaller sizes of the droplets and is investigated for the worst case estimates of droplet sizes in this work.
Foreign particles like dust, combustion soot particles, previously frozen water vapor traces etc. may be present in the gas before its entry into the expander [39, 40]. These particles act as kernels for the condensation growth. The resulting heterogeneous condensation may suppress the homogeneous condensation partially or completely depending upon the number concentration of foreign particles present in the gas before cooling and the rate of expansion cooling (see chapter 5).

This chapter is organized as follows: A homogeneous nucleation model is described in section 3.2. Section 3.3 describes the cluster growth model. The formulation of a numerical model to predict the size distribution of condensed $\text{CO}_2$ droplets in continuous expansion cooling is given in section 3.4. Results are discussed in Section 3.5.

3.2 Homogeneous nucleation model

Droplet formation by homogeneous condensation can be described into two sequential events:

1. Formation of clusters in the bulk of the gas (Homogeneous nucleation)
2. Growth of these clusters to microscopic size droplets

3.2.1 Cluster formation

A cluster means a number of molecules of gas stuck together. For the description of cluster formation, the classical nucleation theory (CNT) is used. It is assumed that a spherical cluster containing $n_{\text{mole}}$ moles of the component $i$ of the gas liberate energy $G_{\text{form}}$ when formed. The energy released is given by the difference in chemical potential $\mu_{\text{gas}}^i - \mu_{\text{liq}}^i$ of the gas phase and the newly formed liquid (cluster) phase at the pressure of the gas [41]:

\[
G_{\text{form}} = n_{\text{mole}}^i \left( \mu_{\text{gas}}^i - \mu_{\text{liq}}^i \right)
\]  

(3.1)

To create a surface of the cluster, surface tension $\sigma$ Joules per square meter of the surface is required and for a cluster of diameter $d$ the energy $G_{\text{req}}$ is:

\[
G_{\text{req}} = \pi d^2 \sigma
\]

(3.2)

It is assumed that $\text{CO}_2$ and $\text{CH}_4$ or $\text{N}_2$ mixtures behave as an ideal gas mixture and only $\text{CO}_2$ molecules from the gas mixture are participating in the cluster formation (influence of carrier gas $\text{CH}_4$ or $\text{N}_2$ is discussed later in section 3.4). Then, the right side of eq. 3.1 at constant temperature $T$ of the gas is calculated as:
3.2 Homogenous nucleation model

\[ \mu_{gas}^{CO_2} - \mu_{liq}^{CO_2} = \int_{p_i}^p \nu^* dp \]  

(3.3)

where, \( p \) is partial vapor pressure of \( CO_2 \) in the gas mixture and \( p_s^{CO_2} \) is the corresponding saturation vapor pressure of \( CO_2 \). In eq. 3.3, it is assumed that chemical potential of liquid phase (cluster) is approximately equal to the chemical potential of saturated \( CO_2 \) in the gas. Assuming an ideal gas law for the dependency of partial molar volume \( \nu^* \) of \( CO_2 \) in the gas on pressure \( p \) and temperature \( T \), eq. 3.1 can be written as:

\[ G_{form} = n_{mol}^{CO_2} R_u T \ln \left( \frac{p}{p_s^{CO_2}} \right) \]  

(3.4)

where, \( R_u \) is the universal gas constant and \( T \) is temperature of the gas. It is assumed that the cluster has the same density \( \rho_{liq} \) (mol m\(^{-3}\)) as the bulk liquid phase. Energy released given by eq. 3.4 becomes,

\[ G_{form} = \frac{\pi}{6} d^3 \rho_{liq} R_u T \ln \left( \frac{p}{p_s^{CO_2}} \right) \]  

(3.5)

where, \( M^{CO_2} \) is molecular weight of \( CO_2 \). Thus, the net free energy \( \Delta G \) change of the system containing a cluster of size \( d \) is obtained by difference of eq. 3.5 and eq. 3.2 as

\[ \Delta G = G_{req} - G_{form} \]  

(3.6)

\[ \Delta G = \frac{\pi}{6} d^3 \sigma - \frac{\pi}{6} d^3 \rho_{liq} R_u T \ln \left( \frac{p}{p_s^{CO_2}} \right) \]  

(3.7)

The net free energy change given by eq. 3.7 depends upon the size of cluster \( d \) for fixed values of other parameters in the equation. Fig. 3.1 schematically shows a typical variation of net free energy \( \Delta G \) of the system with varying cluster size \( d \). \( \Delta G \) exhibits a maximum at a specific cluster size \( d_{crit} \) called the critical cluster.

Clusters of various sizes (dimers, trimers and so on) continuously form and disintegrate in the gas phase because of continuous statistical fluctuations of gas molecules [42]. If the critical cluster gains a molecule by fluctuations in the gas phase, it lies on the right side of the maximum where the rate of change of \( \Delta G \) with diameter \( d \) is negative. This means that \( \Delta G \) decreases with increase in diameter \( d \). So, further growth of the critical cluster after gaining a molecule is favorable. However, loss of one molecule from the critical cluster favors its collapse because it lies in the region where \( \Delta G \) decreases with decrease in the diameter \( d \). Therefore, the clusters only after the critical size \( d_{crit} \) have the possibility to grow further and called ‘supercritical’ clusters. Moreover, at the maximum of
\( \Delta G \) the energy released \( G_{\text{form}} \) because of the formation of cluster of size \( d_{\text{crit}} \) becomes equal to the energy required \( G_{\text{req}} \). Therefore, the formation of the cluster is only feasible after attaining \( d_{\text{crit}} \) from the energy balance point of view. The minimum ‘supercritical’ cluster size is approximated as the size of critical cluster \( d_{\text{crit}} \). \( d_{\text{crit}} \) is calculated where rate of change of \( \Delta G \) with respect to \( d \) becomes zero and is given as:

\[
d_{\text{crit}} = \frac{4\sigma m_{\text{CO}_2}}{kT \rho_{\text{liq}} M_{\text{CO}_2} \ln \left( \frac{p}{p_s} \right)}
\]

(3.8)

\( \Delta G_{\text{crit}} \) is the corresponding critical energy barrier:

\[
\Delta G_{\text{crit}} = \frac{16\pi \sigma^4}{3k^2T^2 (\ln S)^2} \left( \frac{m_{\text{CO}_2}}{\rho_{\text{liq}} M_{\text{CO}_2}} \right)^2
\]

(3.9)

**Figure 3.1:** Schematic showing a change in the net free energy change \( \Delta G \) of the system with the formation of clusters of size \( d \)
3.2 Homogenous nucleation model

3.2.2 Supersaturation

The ratio \( \frac{p}{p^*_{\text{CO}_2}} \) is often referred to as supersaturation \( S \). \( S \) is the driving force for the cluster formation. Supersaturation \( S \) physically means the excess number of molecules of \( \text{CO}_2 \) present in the gas and given as:

\[
S = \frac{p}{p^*_{\text{CO}_2}} = \frac{yP}{p^*_{\text{CO}_2}} 
\tag{3.10}
\]

3.2.3 Rate of cluster formation

In the Classical Nucleation theory, the relation between the number density of \( \text{CO}_2 \) clusters to the number density of \( \text{CO}_2 \) molecules in the gas phase is given by a classical Arrhenius form \([43]\) as:

\[
N = n^{\text{CO}_2} \exp \left( -\frac{\Delta G_{\text{crit}}}{kT} \right) \tag{3.11}
\]

where, \( N \) is the number density of \( \text{CO}_2 \) clusters and \( n^{\text{CO}_2} \) is the number density of \( \text{CO}_2 \) molecules (monomers) in the gas phase. \( \Delta G_{\text{crit}} \) is given by eq. 3.9. The higher the energy barrier \( \Delta G_{\text{crit}} \), the more difficult is the critical cluster formation. Eq. 3.11 is multiplied by a pre-factor \( K \) to get the rate of cluster formation. \( K \) accounts for the ‘effective’ impingement rate of \( \text{CO}_2 \) molecules on the critical clusters derived from the kinetic theory of gases \([35]\) as:

\[
K = \frac{2n^{\text{CO}_2}}{\pi} \left( \frac{kT}{m} \right)^{\frac{1}{2}} \left( \frac{\sigma m}{kT \rho_{\text{liq}}} \right)^{\frac{1}{2}} \tag{3.12}
\]

\( K \) is the ‘effective’ collision frequency of molecules to the clusters and has the dimensions of inverse of time \((\text{s}^{-1})\). Combining eq. 3.11 and eq. 3.12 gives the steady state flux of clusters passing the critical energy barrier as:

\[
\frac{dN}{dt} = n^{\text{CO}_2} K \exp \left( -\frac{\Delta G_{\text{crit}}}{kT} \right) \tag{3.13}
\]

Using eq. 3.10 for \( \Delta G_{\text{crit}} \), eq. 3.13 can be written as:

\[
\frac{dN}{dt} = n^{\text{CO}_2} K \exp \left[ -\frac{16\pi \sigma^3}{3k^3T^3 \ln S} \left( \frac{m}{\rho_{\text{liq}}} \right)^2 \right] \tag{3.14}
\]

In eq. 3.14, \( \frac{dN}{dt} \) is rate of formation of supercritical clusters \((\text{m}^{-3} \text{ s}^{-1})\), \( k \) \((\text{J K}^{-1})\) is a Boltzmann constant and \( A \) is the Avagadro’s number \((\text{mol}^{-1})\).
Eq. 3.14 gives the rate of formation of supercritical clusters. The nucleation rate of CO$_2$ is obtained for different supersaturations $S$ and the surface tension are shown in fig. 3.2. The rate of cluster formation is very sensitive to the supersaturation $S$ and surface tension $\sigma$. For example, $10^{20}$ m$^{-3}$ clusters are formed in 1 second at $S = 1.4$ and $\sigma = 15$ mN m$^{-1}$. By decreasing the supersaturation to 1.3, the rate of formation of clusters becomes 1 cluster m$^{-3}$ s$^{-1}$. If the surface tension is lowered from 15 to 5 mN m$^{-1}$, the rate of formation of clusters increases from 0 to $10^{20}$ m$^{-3}$ s$^{-1}$ at same $S = 1.05$. Calculations also suggest that a critical value of supersaturation (at which $dN/dt = 1$ m$^{-3}$ s$^{-1}$) must be reached to have a substantial rate of stable cluster formation. Below the critical supersaturation the rate of cluster formation is negligible and after that it becomes very high even with a slight change in $S$.

Fig. 3.3 shows the CO$_2$ critical cluster sizes for different values of surface tension calculated using eq. 3.8. Typical CO$_2$ cluster size lies between 2 and 20 nano-meters. CO$_2$ cluster size is relatively less sensitive to the surface tension than the rate of cluster formation. For example, lowering the surface tension by factor 3 changes the cluster size 15 nm to 5 nm at $S = 1.1$. The sensitivity of $S$ to surface tension becomes even less at high supersaturation. For the range of supersaturation, cluster size typically lies between 20 nm ($\sim$ 500 molecules) and 2 nm ($\sim$ 1/2 molecule).

![Figure 3.2: Variation of nucleation rate dN/dt of CO$_2$ with supersaturation S for different values of surface tension $\sigma$](image)

Figure 3.2: Variation of nucleation rate dN/dt of CO$_2$ with supersaturation S for different values of surface tension $\sigma$
3.2 Homogenous nucleation model

**Figure 3.3:** Size of CO$_2$ critical cluster $d_{\text{crit}}$ with supersaturation $S$ for different values of surface tension $\sigma$

3.3 Cluster growth model

After stable clusters are formed by homogeneous nucleation, they can grow either by coagulation among themselves or by diffusion of the gas molecules to the surface of these cluster. In CRS units, cooling of the gas is achieved by expanding the gas in an expander. The time scales of expansion (typically 1 ms) are much faster than the coagulation time scales (on the order of few seconds) [44]. We are not expecting appreciable coagulation effects in case cooling of the gas is achieved by expansion. Moreover, coagulation of clusters leads to decrease in the number density of clusters and neglecting it will give us the upper limit of the number density of droplets formed. Coagulation may have influence in slow processes for example when cooling of the gas is done with chillers [45].

The particle Knudsen number determines whether the statistical mechanics or the continuum mechanics formulation of fluid dynamics for growth of the cluster is used [35]. Here, Kn is defined as the ratio of the mean free path length $\lambda_{\text{molecule}}$ (average distance traveled by the molecules of gas before having a collision) and the physical length scale (size of cluster $d_{\text{cluster}}$). That means $\text{Kn} = \frac{\lambda_{\text{molecule}}}{d_{\text{cluster}}}$. For $\text{Kn} \ll 1$, a continuum approach is valid and the gas can be treated as a continuous fluid. The mean free path $\lambda_{\text{molecule}}$ decreases with the increase in the pressure. CRS units are operated under high...
pressure conditions (30-100 bars). \( Kn \) is calculated for the range of process conditions of CRS units are less than 1 and listed in table 3.1.

A continuum diffusion growth model is used for the growth of cluster. Fig 3.4 schematically shows the flux \( J^i \) (mol s\(^{-1}\)) of the condensable components in the gas towards the cluster. The cause of this molar flux is the difference in the number of CO\(_2\) molecules at the surface of cluster and the bulk of the gas phase. This difference gives rise to the concentration gradient which drives the diffusion according to Fick’s law of diffusion [46]:

\[
J^i = 2\pi D_{coeff}^i (p_i^f - p_i^s)
\]

(3.15)

\( D_{coeff} \) is the diffusion coefficient of component \( i \) in the gas and calculated using the Chapman-Enskog theory [45, 46]. An energy flux \( E^i \) (J s\(^{-1}\)) is released because of the latent heat of condensation and given as:

\[
E^i = J^i \Delta H^i
\]

(3.16)

Where, \( \Delta H^i \) is latent heat of vaporization (J mol\(^{-1}\)) of component \( i \) of the mixture.

Knowing the molar flux (given by eq. 3.15), the growth rate of the cluster is obtained from the mass balance as:

\[
\frac{d}{dt} \left( \frac{\pi d^3 \rho_{pq}}{6} \right) = \sum_i J^i
\]

(3.17)

The left hand side of the equation is the cluster growth and right hand side of equation is the total diffusive flux.

Table 3.1: Knudsen number of CO\(_2\)/CH\(_4\) or CO\(_2\)/N\(_2\) mixtures for different values of supersaturation \( S \), pressure \( P \) and temperature \( T \)

<table>
<thead>
<tr>
<th>Pressure (bars)</th>
<th>Temperature (°C)</th>
<th>Critical cluster diameter (10(^{-9}) m)</th>
<th>Knudsen number (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10</td>
<td>20</td>
<td>5, 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.05, 0.2, 0.5</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>20</td>
<td>5, 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.05, 0.2, 0.4</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>20</td>
<td>5, 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03, 0.1, 0.3</td>
</tr>
</tbody>
</table>
3.4 Carrier gas

In CRS units, CO$_2$ is condensed and then separated out of the contaminated natural gas or flue gas to purify methane CH$_4$ or nitrogen N$_2$. Therefore, we treat CH$_4$ or N$_2$ as a *carrier gas* for CO$_2$. *Carrier gas* usually refers to the *inert* gas component which does not participate in the condensation. In our case, some amount of carrier gas always dissolves in the liquid phase because of the intermolecular interactions associated with the binary gas mixtures. The extent of CH$_4$ or N$_2$ dissolved in liquid phase depends upon the position in the phase envelope of CO$_2$/CH$_4$ or CO$_2$/N$_2$ mixture. CO$_2$ concentration in the liquid phase for the range of process conditions are listed in table 3.2 and table 3.3. For the typical separation conditions of CRS units, the maximum entrainment of carrier gas CH$_4$ or N$_2$ in liquid phase is 0.15 (see table 3.2 and 3.3). This means that the flux of carrier gas molecules towards the cluster can be maximum 15 % of the total diffusive flux. Neglecting the flux of carrier gas molecules will make the rate of depletion of molecules from the gas phase or the rate of growth of a cluster slower. It is shown in chapter 4 that the number density of clusters formed is directly proportional to the rate of growth of a cluster. Moreover, the flux of carrier gas molecules is only small percentage of the total diffusive flux. We consider only the flux of CO$_2$ molecules for the rate of growth of cluster to get the worst case for the

![Schematic showing the growth of CO$_2$ clusters by diffusion of molecules of the gas phase towards the cluster.](image)

**Figure 3.4:** Schematic showing the growth of CO$_2$ clusters by diffusion of molecules of the gas phase towards the cluster. $i$ denotes a component of the gas mixture.
number density of clusters formed. Thus the size of droplets is underestimated for the same liquid amounts.

Inclusion of carrier gas molecules in the liquid CO\textsubscript{2} phase may begin already from the start of formation of critical clusters. Classical nucleation model described above for the calculation of rate of formation of clusters does not take the entrainment of CH\textsubscript{4} or N\textsubscript{2} molecules in the CO\textsubscript{2} cluster during its formation into account. The entrainment of CH\textsubscript{4} or N\textsubscript{2} molecules modifies the \( \Delta G_{\text{crit}} \) (given by eq. 3.9) in two ways:

1. Changing the saturation vapor pressure of CO\textsubscript{2} and thus the supersaturation S.
2. Changing the surface tension of liquid CO\textsubscript{2}

The energy barrier \( \Delta G_{\text{crit}} \) depends mainly upon surface tension \( \sigma \) and supersaturation S (see eq. 3.9). The entrainment of carrier gas molecules (CH\textsubscript{4} or N\textsubscript{2}) in the liquid (CO\textsubscript{2} cluster) phase lowers the saturation vapor pressure of CO\textsubscript{2} \( P_{s,\text{actual}}^{\text{CO}_2} \) compared to the saturation vapor pressure \( P_{s}^{\text{CO}_2} \) of pure CO\textsubscript{2}. Supersaturation S in eq. 3.14 is then replaced by the effective supersaturation \( S_{\text{eff}} \) given as [47]:

\[
S_{\text{eff}} = \frac{p}{P_{s,\text{actual}}^{\text{CO}_2}} = \frac{yP}{P_{s,\text{actual}}^{\text{CO}_2}}
\]  

(3.18)

\( S_{\text{eff}} \) is always less than or equal to S for given \( y^{\text{CO}_2} \), \( P \) and \( T \). Using eq. 3.10 for S, we overestimate the rate of change of S during the expansion cooling. In chapter 4, it will be shown that the number density of clusters formed during the expansion is directly proportional to the rate of change of supersaturation. In our model, we use the S given by eq. 3.10 to get the worst case estimate of the number density of condensed droplets. Thus, we will underestimate the size of condensed droplets for the same condensed liquid amounts.

In addition to the supersaturation S, surface tension \( \sigma \) of pure liquid CO\textsubscript{2} can also change because of the adsorption or entrainment of CH\textsubscript{4} or N\textsubscript{2} molecules in CO\textsubscript{2} clusters. It is difficult to measure or predict the surface tension at the length scale of cluster. We use surface tension of pure liquid CO\textsubscript{2} as basis for our calculations. National Institute of Standards and Technology (NIST) data base is used for the values of surface tension of pure CO\textsubscript{2}.

To summarize, it is assumed that the carrier gas stays inert and does not participate in the rate of formation of clusters and in the rate of growth of clusters. With this assumption, we are calculating the worst case estimates of number density of condensed CO\textsubscript{2} droplets. It
3.5 Model Formulation (Numerical)

is also assumed that bulk liquid CO$_2$ surface tension is true representative of the surface
tension of clusters.

Table 3.2: Molar fraction of CO$_2$ in the liquid phase for the typical separation conditions in CRS
units for CO$_2$/CH$_4$ gas mixture.

<table>
<thead>
<tr>
<th>Pressure (bars)</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed CO$_2$ (mole %)</td>
<td>Temperature $-56$ °C</td>
</tr>
<tr>
<td>20</td>
<td>No liquid</td>
</tr>
<tr>
<td>50</td>
<td>0.86</td>
</tr>
<tr>
<td>80</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 3.3: Molar fraction of CO$_2$ in the liquid phase for the typical separation conditions in CRS
units for CO$_2$/N$_2$ gas mixture.

<table>
<thead>
<tr>
<th>Pressure (bars)</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed CO$_2$ (mole %)</td>
<td>Temperature $-56$ °C</td>
</tr>
<tr>
<td>20</td>
<td>No liquid</td>
</tr>
<tr>
<td>50</td>
<td>0.96</td>
</tr>
<tr>
<td>80</td>
<td>0.96</td>
</tr>
</tbody>
</table>

3.5 Model formulation (Numerical)

A numerical model is formulated to predict the number distribution $f(d)$ of condensed
CO$_2$ droplets formed by the expansion cooling of CO$_2$/CH$_4$ or CO$_2$/N$_2$ mixtures. Known
input expansion parameters are

1. Pressure and temperature before the expander $P_{in}$ and $T_{in}$
2. Pressure after the expander $P_{out}$
3. Feed concentration $y_f^{CO_2}$
4. Expansion rate $\dot{\rho}$
Parameters 1 to 3 listed above are directly measurable physical quantities. We discuss now the rate of expansion.

\[ P_d \propto P dl \]  

(3.19)

Thus, the unknown pressure variation along the expander is approximated as:

\[ P = P_{in} \exp\left( -\frac{al}{L_{exp}} \right) \]  

(3.20)

where \( a = \ln \left( \frac{P_{out}}{P_{in}} \right) \) and at \( l = 0, P = P_{in} \) and \( l = L_{exp}, P = P_{out} \). Pressure variation along the expander is translated to time \( t \) co-ordinate along the direction of flow as:

\[ l \sim v_{avg} t \]  

(3.21)

\[ P = P_{in} \exp\left( -\frac{av_{avg} t}{L} \right) \]  

(3.22)

\[ P = P_{in} \exp\left( -\frac{at}{t_{exp}} \right) \]  

(3.23)

where, \( t_{exp} \) can be approximated as:

\[ t_{exp} = \frac{V_{exp}}{Q_{rot} \Delta P} \]  

(3.24)
where $Q_{\text{vol}}$ is the average volume flow rate ($m^3 s^{-1}$) through the expander and is coupled to the pressure drop across the expander. $V_{\text{exp}}$ is volume of the expander ($m^3$) used for expansion and \( \dot{P} \) is the average expansion rate which characterizes the time scale of expansion and is given as

$$
\dot{P} = \frac{1}{t_{\text{exp}}} \ln \left( \frac{P_{\text{out}}}{P_{\text{in}}} \right) = \frac{1}{P_{\text{in}} t_{\text{exp}}} \frac{P_{\text{out}} - P_{\text{in}}}{P_{\text{in}}}
$$

(3.25)

Now, for a given pressure variation along the expander (given by eq. 3.23) and the input expansion parameters, we describe a procedure to solve for the number distribution $f(d)$ of the droplets formed at the end of expansion in next section.

### 3.5.1 Solution procedure

**Step 1:**
Expansion along the length of expander is divided into $n$ number of small time intervals $\Delta t$ and thus constituting $n+1$ discrete time steps $t_j$. $j$ varies from 0 to $n+1$. $\Delta t$ is a time interval between the two consecutive time steps $t_j$ and $t_{j+1}$. Steady state conditions are assumed during each time interval $\Delta t$. $t_j = 0$ designates the inlet conditions before the expander. Pressure $P$, Temperature $T$ and feed CO$_2$ concentration $y^{CO_2}$ is known at the inlet conditions.

**Step 2:**
Supersaturation $S(t_j)$ at time step $t_j$ is calculated using eq. 3.10 for known $P(t_j)$, $T(t_j)$ and $y^{CO_2}(t_j)$. It is assumed that expansion starts from the dew point line of the feed gas mixture. This means that $S = 1$ at the start of expansion (at $t_j = 0$). We skip the pressure variation till the dew point line in our computations. This is because no clusters can be formed for $S < 1$.

**Step 3:**
After crossing the dew-point line, $S$ starts increasing. Knowing supersaturation $S(t_j)$, the number density of clusters $N(t_j)$ is obtained by discretizing eq. 3.14 as:

$$
N(t_j) = \left( \frac{dN}{dt} \right)_{t=t_j} \Delta t
$$

(3.26)

The diameter $d(t_j)$ of these clusters is calculated from eq. 3.8 as

$$
d(t_j) = \frac{4\sigma m}{kT(t_j) \rho_{\text{liq}} \ln(S(t_j))}
$$

(3.27)
The diameter \( d \) (\( t_j \)) the clusters having number density \( N \) (\( t_j \)) grows for the time interval \( \Delta t \). Clusters also formed during the same duration \( \Delta t \). So, they can grow effectively for half of the time interval \( \Delta t = t_{j+1} - t_j \). \( d (t_{j+1}) \) is calculated by discretizing eq. 3.17 as:

\[
d^2(t_{j+1}) - d^2(t_j) = 8\rho D_{\text{CO}_2} \left(1 - \frac{1}{S(t_j)}\right)
\]

Supersaturation \( S (t_{j+1}) \) decreases because of the loss of \( \text{CO}_2 \) from the gas phase to the surface of clusters. Pressure \( P (t_{j+1}) \) and temperature \( T (t_{j+1}) \) also changes because of the continuous expansion. New clusters having number density \( N (t_{j+1}) \) and diameter \( d \) (\( t_{j+1} \)) form at the time step \( t_{j+1} \). To distinguish between the number density of clusters formed at time step \( t_j \) and \( t_{j+1} \), we introduce a subscript \( k \) to the number density \( N \) of the clusters. Subscript \( k \) denotes the clusters of diameter \( d \) with number density \( N \) formed at each discrete time step \( t_j \). The numbers of clusters \( N_k \) of diameter \( d_k \) (\( t_j \)) grow in time \( t \) during the expansion. All \( N_k \) clusters are tracked in size \( d \) till the end of expansion as shown in fig. 3.6.

### Figure 3.6:
A tracking scheme of the size \( d \) of the clusters having number density \( N_k \). Diagonal shows \( N_k \) clusters of size \( d_k \) originated at each discrete time step \( t_j \) of the expansion.

### Step 4:
Condensed liquid mole fraction \( f_{\text{liq}} \) between the two consecutive time steps \( t_{j+1} \) and \( t_j \) is calculated as:
3.5 Model Formulation (Numerical)

\[ f_{liq} = \frac{\sum_{k=1}^{k=1} m_k(t_j)N_k}{\rho(t_j)} \]  \hspace{1cm} (3.29)

and

\[ m_k(t_j) = \frac{\pi}{6} \left\{ d_k^3(t_j) + d_k^3(t_{j+1}) \right\} \rho_{liq} \] \hspace{1cm} (3.30)

\( Q_f \) is the feed flow rate (mol s\(^{-1}\)).

**Step 5:**

Amount of CO\(_2\) vapor at time step \( t_{j+1} \) is reduced by the amount of the condensed liquid (calculated above in step 4) as:

\[ Q_f y^{CO_2}(t_{j+1}) = Q_f y^{CO_2}(t_j) - Q_f f_{liq} \] \hspace{1cm} (3.31)

**Step 6:**

Temperature \( T \) at time step \( t_{j+1} \) is obtained by combining the energy equation, the momentum equation and the equation of state of gas. Energy equation for the gas mixture is given as:

\[ dh + M_{avg} v dv = dq \] \hspace{1cm} (3.32)

Here, \( h \) is specific enthalpy of the gas mixture (J mol\(^{-1}\)), \( v \) is velocity of the flow (m s\(^{-1}\)), \( M_{avg} \) is the mean molar mass of the gas mixture and \( dq \) is heat generated because of the condensation (J mol\(^{-1}\)). \( dq \) is given as:

\[ dq = dy \Delta H \] \hspace{1cm} (3.33)

where, \( \Delta H \) is the latent heat of vaporization of condensing CO\(_2\) at temperature \( T \) (\( t_j \)) (J mole\(^{-1}\)). Momentum equation for the mixture is given as:

\[ dP = M_{avg} \rho du \] \hspace{1cm} (3.34)

Combining with eq. 3.34, eq. 3.32 can be written as:

\[ dh = \frac{dP}{\rho} + dq \] \hspace{1cm} (3.35)

Assuming that the gas mixture behaves perfectly, eq. 3.35 can be written as:

\[ c_p dT = \frac{dP}{\rho} + dq \] \hspace{1cm} (3.36)

Where, \( c_p \) is specific heat of the gas mixture as:
\[ c_p = \sum_i y_i c_{pi} \]  

(3.37)

Combining the equation of state, which relates pressure \( P \) and temperature \( T \) of the gas mixture with the molar density \( \rho \) as:

\[ \rho = \frac{1}{Z R_g T} \]  

(3.38)

In eq. 3.38, \( Z \) is the compressibility factor quantifying the real gas effects of gas mixture. We choose \( Z = 1 \) in our computations. Combining eq. 3.38 with eq. 3.36 we get,

\[ \frac{c_p}{R_g} \frac{dT}{T} = \frac{dP}{P} + \frac{dq}{R_g T} \]  

(3.39)

For \( dq = 0 \), eq. 3.39 can be solved for temperature at every discrete time step \( t_{j+1} \) in expansion as:

\[ \frac{T(t_{j+1})}{T(t_j)} = \left( \frac{P(t_{j+1})}{P(t_j)} \right)^{\frac{\gamma - 1}{\gamma}} \]  

(3.40)

Eq. 3.39 can also be written in the analytical form for temperature \( T \) at any time \( t \) during the expansion as:

\[ T = T_{in} \exp \left( -\frac{\gamma - 1}{\gamma} P t \right) \]  

(3.41)

Temperature \( T \) at start of expansion (at \( t_j = 0 \)) is known. \( \gamma \) is usually termed as adiabatic index of expansion for the expanding gas mixture. Temperature \( T(t_{j+1}) \) given by eq. 3.40 can be corrected for the heat release because of the condensation as:

\[ T_{corr}(t_{j+1}) = T(t_{j+1}) + \left( f_{liq} \frac{\Delta H}{y(t_j) - f_{liq} c_p} \right) \]  

(3.42)

Heat release because of the condensation increases the temperature of the gas phase surrounding the clusters. The corresponding supersaturation \( S \) at time step \( t_{j+1} \) will decrease at same partial pressure of \( \text{CO}_2 \). This is because of the increase in saturation vapor pressure of \( \text{CO}_2 \) with increase in temperature of the gas (see eq. 3.10). The rate of cluster formation varies inversely with \( S \). Net effect will be to reduce the total number density of clusters formed during the expansion. We neglect this temperature correction of the isentropically expanding gas (given by eq. 3.42) to calculate the worst case for the number density of clusters formed.
3.6 Results and discussion

Starting from \( t_j = 0 \) (inlet of the expander), above mentioned steps 1 till 6 are repeated till the end of expansion \( (t = t_{\text{exp}}) \). Finally at the end of expansion a number distribution \( f(d) \) of condensed droplets is obtained.

3.6 Results and discussion

In this section, we discuss a typical result for droplet size distribution calculated using the model described above for the known process conditions. The size distribution is calculated for the typical process conditions of CRS units. The feed composition of \( \text{CO}_2 \) in \( \text{CH}_4 \) is 50 mole %. The pressure \( P_{\text{in}} \) and temperature \( T_{\text{in}} \) before the expander is 100 bars and 287 K. The average expansion rate is \( 1000 \text{ s}^{-1} \), which is typical in the case of expansion turbines [45]. Fig. 3.7 shows a calculated variation of supersaturation \( S \) for the specified process parameters. \( S \) increases because of the decrease in temperature and pressure of the gas during the expansion. The point \( a \) represents the start of expansion in fig. 3.7. The corresponding number density of clusters \( N_k \) formed at each time step \( t_j \) during the expansion is shown in fig. 3.8. The supersaturation \( S \) rises till 1.02 before nucleation starts (point \( b \) in fig. 3.7 and 3.8). As soon as the clusters appear, \( \text{CO}_2 \) molecules from the gas phase starts diffusing to the surface of cluster. The depletion of \( \text{CO}_2 \) molecules from the gas phase decreases the supersaturation \( S \) (refer eq. 3.10). But at \( b \), the number density of clusters \( N_k \) is not sufficiently high. Thus the rate of depletion is small and consequently supersaturation keeps on rising and cluster formation continues as shown fig. 3.7 from \( b \) to \( c \). At \( c \), the number density of clusters sharply rises to ca. \( 10^{15} \text{ m}^{-3} \). This sharp rise in number density of clusters increases the rate of depletion of \( \text{CO}_2 \) from the gas. At \( c \) the rate of decrease in supersaturation (because depletion of \( \text{CO}_2 \) from the gas) becomes equal to the rate of its increase (because of expansion). After \( c \), the supersaturation \( S \) decreases very swiftly till \( e \). The rate of cluster formation also quenches because of this sharp decrease in supersaturation. The number density of clusters becomes \( 10^3 \text{ m}^{-3} \) at \( d \) as shown in fig. 3.8.

After formation the diameter of the clusters grows in time by diffusion of \( \text{CO}_2 \) molecules to their surface (see fig. 3.9). The diameter growth rate is faster in the beginning and becomes slower later. This is because of the decrease in driving force for diffusion (as concentration of \( \text{CO}_2 \) in vapor phase starts approaching its equilibrium concentration as indicated by \( e \) in the fig. 3.9). After \( e \) the droplet diameter grows to the equilibrium size corresponding to the thermodynamic phase equilibrium conditions till the end of expansion.
A size distribution of droplets at the end of expansion is shown in fig. 3.10. For the specified process parameters, the model predicts the number of condensed CO₂ droplets on the order of $10^{15}\text{ m}^{-3}$. The average droplet size is ca. 2.3 µm.

**Figure 3.7:** Calculated variation of supersaturation $S$ during the expansion

**Figure 3.8:** Calculated number density of clusters $N_k$ formed during the expansion. $\Delta t = 0.5 \times 10^{-6}$ s between two consequent time steps ($t_{j+1} - t_j$) is used for these calculations.
3.6 Results and discussion

**Figure 3.9:** Growth of diameter $d_k$ of the clusters having $N_k = 10^{15}$ m$^{-3}$ in time during the expansion cooling. Corresponding decrease of vapor fraction of CO$_2$ in the gas phase is also shown.

**Figure 3.10:** Predicted size distribution of condensed CO$_2$ droplets in CH$_4$ after the expander.
Figure 3.11: Number densities $N_k$ of clusters formed during the expansion calculated for different average expansion rates in an expander. Time of expansion $t_{\text{exp}}$ is divided into 2000 discrete time steps for these calculations.

Simulations have been performed for the following range of process conditions:

- Average rate of expansion ($10^0$-$10^5$ $s^{-1}$)
- CO$_2$ feed composition (20-80 mole %)
- Pressure before the expansion (15-100 bar)
- Pressure after the expansion (6-60 bar)
- Temperature before the expansion ($\approx$30-200°C)

The following general conclusions can be drawn:

1. The predicted droplet size distribution is mono-disperse in nature under CRS process conditions.

2. Nucleation (formation of CO$_2$ clusters) is a much faster process than the expansion. Number densities of the clusters formed during the expansion for different expansion rates is shown in fig. 3.11. The width of nucleation pulse (time during which clusters form) does not vary much by varying expansion rates in the range $10^1$-$10^5$ $s^{-1}$. The period during cluster formation occurs is very small as compared to the time of expansion ($\approx$ 5% of the total expansion time).

3. The rate of expansion and the rate of depletion of CO$_2$ from the gas results in a maximum in supersaturation $S$ in time. Different rate of expansions changes the peak values of $S$ and hence the number density of the clusters formed during the expansion. For the same condensed volume fractions, the size of droplets gets affected.
3.6 Results and discussion

4. Most of the clusters are formed near the peak of the supersaturation S because of the strong dependency of rate of formation of clusters on supersaturation S.

5. Before the peak of supersaturation, the depletion of CO$_2$ from the gas phase is almost negligible. Most of the depletion of CO$_2$ from the gas phase occurs after the peak of the supersaturation. CO$_2$ vapor fraction decreases significantly only after the peak of supersaturation.
Chapter 4
Droplet Size Predictions (Part 2)

4.1 Introduction

The numerical model of chapter 3 predicts an almost monodisperse droplet size distribution for the CRS process conditions. Furthermore, the time during which clusters are formed is very short compared to the time of expansion for the CRS process conditions. In this chapter an analytical model is proposed for design purposes that predicts the average number density and the mean size of condensed CO\(_2\) droplets. The main assumption in this analytical model is that the clusters grow by diffusion of CO\(_2\) molecules from the gas only after a ‘maximum’ supersaturation is reached. This allows for a division of the cluster formation into two time regions (see next section for details):

1. Accumulation time region (cluster formation)
2. Growth time region (growth of the clusters by diffusion to form microscopic droplets)

The formulation of an analytical model is given in section 4.2-4.4. Results are discussed in section 4.5.

4.2 Formulation

4.2.1 Accumulation region \((t \leq t_c)\)

CO\(_2\) is condensed out of the CO\(_2/\)CH\(_4\) or CO\(_2/\)N\(_2\) gas mixture by expansion cooling in CRS units. The pressure and temperature of the gas decreases during the expansion. Fig. 4.1a shows a liquid-vapor saturation line for pure CO\(_2\). CH\(_4\) or N\(_2\) is assumed to act as a non-condensable gas. The solid line on the top of the saturation line schematically shows a decrease in the partial pressure of CO\(_2\) during the expansion. As the expansion proceeds, first the saturation line is crossed at \(a\). After crossing the saturation line, CO\(_2\) from the gas phase should condense (cluster formation and subsequent growth) immediately and the partial pressure of CO\(_2\) should stay along the saturation line until the end of expansion.
Figure 4.1: (a) Schematic shows a decrease in the partial pressure of CO$_2$ during the expansion of CO$_2$/CH$_4$ or CO$_2$/N$_2$ gas mixture. CH$_4$ or N$_2$ is assumed to act as a non-condensable gas (b) Corresponding variation is supersaturation $S$ (c) Corresponding variation in rate of formation of clusters $dN/dt$ and the diameter $d$ of the clusters.
4.2 Formulation

The condensation usually get delayed because the gas needs to reach ‘critical supersaturation’ to begin the formation of clusters (refer chapter 3). So, the partial pressure keeps on reducing further along the path \( a \) to \( c \). The gas phase then contains more \( \text{CO}_2 \) than at the corresponding saturation conditions and is called supersaturated. The corresponding increase in supersaturation \( S \) is shown in fig. 4.1b. This supersaturation is the driving force for the formation of clusters in the gas. The reduction in partial \( \text{CO}_2 \) pressure and increase in \( S \) continues from \( c \) to \( g \) till the end of expansion in case no condensation happens.

We consider a time region, named as *accumulation region* from \( t = t_a \) to time \( t = t_c \) as shown in fig. 4.1c. In this time region only formation of stable clusters occurs. The growth of these clusters is governed by the diffusion of the molecules of \( \text{CO}_2 \) towards their surface (refer chapter 3). It is assumed that that the clusters do not grow in this region. This means that no loss of \( \text{CO}_2 \) from the gas by diffusion occurs. Clusters themselves do not contribute much to the decrease in the vapor fraction of \( \text{CO}_2 \) because of their very small sizes (typical size of cluster is on the order of nano-meters for \( \text{CO}_2 \)).

First, we formulate for the number density of clusters \( N_c \) formed in the accumulation time region between \( t = t_a \) and \( t = t_c \). As per CNT, the rate of formation of clusters strongly depends on logarithm of supersaturation \( S \). To calculate the number density of clusters \( N_c \), the equation for the change of supersaturation \( S \) in the accumulation time region is required and is derived in the next section.

**Supersaturation \( S (t \leq t_c) \)**

Supersaturation \( S \), as described in chapter 3, is given as:

\[
S = \frac{y^{\text{CO}_2} P}{p_{s}^{\text{CO}_2}} 
\quad \text{(refer eq. 3.10)}
\]

Taking the logarithm on both sides of eq. 3.10, we get:

\[
\ln S = \ln y^{\text{CO}_2} + \ln \frac{P}{p_{s}^{\text{CO}_2}(T)}
\quad \text{(4.2)}
\]

Differentiating eq. 4.2 with respect to time \( t \) gives,

\[
\frac{d}{dt} \ln S = \frac{d}{dt} \ln y^{\text{CO}_2} + \frac{d}{dt} \ln \frac{P}{p_{s}^{\text{CO}_2}(T)}
\quad \text{(4.3)}
\]

Eq. 4.3 gives the rate of change of logarithm of supersaturation \( S \) with time \( t \). This rate of change depends upon

1. the rate of change in vapor fraction \( y^{\text{CO}_2} \) of \( \text{CO}_2 \) in the gas phase
   (first term on the right hand side of eq. 4.3).
2. the rate of change of pressure $P$ of the gas relative to the saturation vapor pressure $p_s$ of CO$_2$ (second term on the right hand side of eq. 4.3).

When no condensation happens then the vapor fraction $y_{CO_2}$ of CO$_2$ in the gas phase is constant. The first term on the right side of eq. 4.3 becomes zero. Then, eq. 4.3 can be written as:

$$\frac{d}{dt} \ln S = \frac{d}{dt} \ln P = \frac{d}{d \ln P_s(T)} \ln p_s(T) \frac{d}{dt} \ln T$$  \hspace{1cm} (4.4)

Eq. 4.4 gives the rate of change of logarithm of S in time $t \leq t_c$.

The first term on the right side of eq. 4.4 is the rate of change of pressure $P$ of the gas during the expansion. The pressure variation along the expander (section 3.5) can be expressed as:

$$P = P_m \exp(-Pt)$$ \hspace{1cm} (refer eq. 3.23)

Taking logarithm and differentiating with time of eq. 3.23, we get

$$\frac{d}{dt} \ln P = -\dot{P}$$  \hspace{1cm} (4.5)

In the second term on right side of eq. 4.4, temperature $T$ variation in time is calculated by assuming the isentropic gas expansion (refer chapter 3) as:

$$T = T_m \exp \left( -\frac{\gamma - 1}{\gamma} \dot{P} t \right)$$ \hspace{1cm} (refer eq. 3.41)

Taking logarithm and differentiating with time $t$ of eq. 3.41, we get:

$$\frac{d}{dt} \ln T = -\frac{\gamma - 1}{\gamma} \dot{P}$$  \hspace{1cm} (4.6)

The change of saturation vapor pressure $p_s$ of CO$_2$ with temperature $T$ in the second term on the right hand side of eq. 4.4 can be approximated using the Clausius-Clapereydon equation [48]:

$$\frac{d \ln p_s(T)}{d \ln T} \approx \frac{\Delta H}{R_u T}$$ \hspace{1cm} (4.7)

where, $\Delta H$ is the molar enthalpy of vaporization of CO$_2$ (J mol$^{-1}$) and $R_u$ is a universal gas constant (J mol$^{-1}$K$^{-1}$).

Using eq. 4.5, 4.6 and 4.7 with eq. 4.4 we get:

$$\frac{d}{dt} \ln S = \dot{P} \left( \frac{\gamma - 1}{\gamma} \frac{\Delta H}{R_u T} - 1 \right) = \dot{P} \beta$$ \hspace{1cm} (4.8)
4.2 Formulation

Eq. 4.8 gives us the rate of change of supersaturation $S$ in the time region $t_a \leq t \leq t_c$. $S = 1$ at $t = t_a$. The rate of change of logarithm of $S$ depends upon the product of average expansion rate and the parameter $\beta$. $\beta$ is positive and approximately 1 for the range of process conditions of CRS units. This means that when no condensational growth of clusters is happening, the rate of change of $S$ is positive and is proportional to the average rate of expansion. In other words, $S$ increases in the accumulation time region. The faster expansion leads to the faster rise in $S$.

Eq. 4.8 is solved to get the supersaturation $S$ at any time $t$ in the accumulation time region as:

$$\ln S = P \beta(t - t_a) \quad (4.9)$$

$S = 1$ at $t = t_a$ and $S = S_c$ at $t = t_c$.

After knowing the supersaturation $S_c$ (at $t = t_c$) using eq. 4.9, we now calculate for the number density of clusters $N_c$ (at $t = t_c$) in the following section.

**Number of clusters $N$ ($t \leq t_c$)**

As described before, the rate of formation of clusters is given according to the classical nucleation model as:

$$\frac{dN}{dt} = n^\text{co}_2 K \exp \left( - \frac{16\pi\sigma^3}{3kT^2} \left( \frac{m}{\rho_{\text{liq}}} \right)^2 \right) \quad \text{(refer eq. 3.14)}$$

In eq. 3.14, we introduce a dimensionless surface energy $\theta$. $\theta$ is the measure of energy required to form a cluster of specific size normalized by the thermal energy of the molecules in the gas as:

$$\theta = \frac{\sigma a}{kT} = (36\pi)^{1/3} \frac{\sigma}{kT} \left( \frac{m}{\rho_{\text{liq}}} \right)^{2/3} \quad (4.10)$$

$\theta$ depends upon the surface tension $\sigma$, temperature $T$, mass of a molecule $m$ and the bulk liquid density. We use the surface tension of pure CO$_2$ for the values of $\theta$ in our calculations. The change in $\theta$ during the expansion because of the decrease in temperature is neglected. Using eq. 4.10 in eq. 3.14 we get:

$$\frac{dN}{dt} = n^\text{co}_2 K \exp \left( - \frac{4\theta^3}{27(\ln S)^2} \right) \quad (4.11)$$

Eq. 4.11 gives the rate of formation of clusters which mainly depends upon the square of logarithm of supersaturation and dimensionless surface energy $\theta$. We derive above for the
supersaturation $S$ at any time $t$ in the accumulation region given by eq. 4.9. Using eq. 4.9 for supersaturation $S$ in eq. 4.11, the number density of the clusters $N_c$ formed in time $t_c$ can be calculated. For time $t \leq t_a$, $S \leq 1$ and the rate of formation of clusters is zero.

**Solution procedure for $N_c (t = t_c)$**

We now solve for $N_c$ using eq. 4.11 and eq. 4.9. During the expansion, the number density of CO$_2$ molecules $n^{CO_2}$ and the collision frequency $K$ are also a function of time because of the decreasing pressure and temperature. As found from the numerical calculations that the most of the clusters $N$ are formed near the maximum of supersaturation $S$ (refer chapter 3). This is because of the strong dependency of the rate of formation of clusters on supersaturation $S$ (eq. 4.11). As an example, changing $S$ from 1.05 to 1.06 increases the rate of CO$_2$ cluster formation from 1 to $10^{20}$ m$^{-3}$s$^{-1}$ (refer fig. 3.2 in chapter 3). The rate of formation of clusters and also the number density of clusters sharply reduces for time $t < t_c$. It is assumed that the number density of CO$_2$ molecules $n^{CO_2}$ and the collision frequency $K$ is constant in eq. 4.11 and their values are fixed at time $t_c$.

Now to simplify, eq. 4.11 is transformed into new variables $\eta$ and $u$. $\eta$ is defined as:

$$\eta = \frac{N \beta}{n^{CO_2} K_c a}$$  \hspace{1cm} (4.12)

and

$$u = \frac{\ln(S)}{a}$$  \hspace{1cm} (4.13)

where $a$ is:

$$a = \left(\frac{4 \theta}{27}\right)^{1/2}$$  \hspace{1cm} (4.14)

Using eq. 4.12-4.14, eq. 4.11 for the rate of formation of clusters is transformed into new variables $\eta$ and $u$ and written as:

$$\frac{d\eta}{du} = \exp\left(-u^{-2}\right)$$  \hspace{1cm} (4.15)

Eq. 4.15 is solved analytically for $\eta$ in terms of $u$ as:

$$\eta = u \exp\left(-\frac{1}{u^2}\right) - \sqrt{\pi} \text{erfc}\left(\frac{1}{u}\right)$$  \hspace{1cm} (4.16)
4.2 Formulation

In eq. 4.16 gives the values of $\eta$ in terms of $u$. $u$ depends on supersaturation $S$ and dimensionless surface energy $\theta$.

At time $t = t_c$, $u = u_c = \frac{\ln(S_c)}{a}$ and $\eta = \eta_c$ as:

$$\eta_c = u_c \exp \left( -\frac{1}{u_c^2} \right) - \sqrt{\pi} \text{erfc} \left( \frac{1}{u_c} \right)$$  \hspace{1cm} (4.17)

where,

$$\eta_c = \frac{N_c \cdot P \beta}{n_{CO_2}^c K_a}$$  \hspace{1cm} (4.18)

Eq. 4.17 gives the number density of clusters $N_c$ formed in the accumulation time region.

4.2.2 Growth region ($t \geq t_c$)

After the formation of $N_c$ clusters in time $t_c$, we consider a growth time region for time $t \geq t_c$. In this region, the growth of the clusters takes place by diffusion of CO$_2$ molecules from the gas phase towards the clusters. As a result, the decrease in partial pressure of CO$_2$ is enhanced as shown in fig. 4.1a from $c$ till $e$. Supersaturation $S$ also decreases as shown in fig. 4.1b. As described above, $S$ changes during the expansion cooling is because of (a) change in the pressure of the gas relative to the saturation vapor pressure of CO$_2$ (second term of eq. 4.3) (b) change in the CO$_2$ vapor fraction from the gas (first term of eq. 4.3). CO$_2$ vapor fraction in the gas decreases because of the growth of clusters. Therefore, the first term contributes to the decrease in $S$.

In addition to the growth of $N_c$ clusters, the cluster formation also occurs in the growth region. We assume that the number density of the clusters $N_d$ formed in the growth time region is same as the number density of clusters $N_c$ formed in the accumulation time region. Only a small portion of the growth region contributes to the formation of clusters because of the high sensitivity of rate of cluster formation to the supersaturation (refer eq. 4.11). Cluster formation in the growth time region is considered only for $t_c \leq t \leq t_d$ ($t_d$ is calculated later). Furthermore, it is assumed that a single class of $2N_c$ clusters grows from time $t \geq t_c$. The decrease in supersaturation $S$ is calculated because of the depletion of mainly CO$_2$ from the gas on $2N_c$ clusters. From the calculated decrease of supersaturation in the growth region, the number of clusters $N_d$ is obtained (the area under the curve shown by a dotted line from $c$ to $d$ in fig. 4.1c).
We first derive for the decrease in supersaturation $S$ in the portion of the growth time region during which $N_d$ clusters form in the next section.

**Supersaturation $S$ ($t_c \leq t \leq t_d$)**

As described above, the rate of change of supersaturation $S$ is given as:

$$
\frac{d}{dt} \ln S = \frac{d}{dt} \ln y_{CO_2} + \frac{d}{dt} \ln \frac{P}{P_s(T)} \quad (\text{refer eq. 4.3})
$$

In the portion of growth time region from $c$ till $d$, the supersaturation $S$ changes mainly because of the decrease of vapor fraction of CO$_2$ from the gas phase. The effect of second term in eq. 4.3 is to increase the supersaturation $S$ and is negligible. The second term becomes important only in the later phase of the growth when the rate of depletion is decreased because of the proximity to the saturation conditions as shown in fig. 4.1a and 4.1b from $e$-$f$. Then, the rate of depletion slows down because the concentration of CO$_2$ in gas phase starts approaching its equilibrium value. This means that $S$ becomes approx. 1.

The time $t$ in eq. 4.3 is replaced by time $t^* = t - t_c$ for mathematical simplicity. Neglecting the second term in eq. 4.3, it reduces to:

$$
\frac{d}{dt^*} \ln S = \frac{d}{dt^*} \ln \frac{y_{CO_2}}{y_f} \quad (4.19)
$$

The change in the vapor fraction of CO$_2$ is because of the formation of liquid CO$_2$ droplets, the simple mass balance of the amount of CO$_2$ in total feed flow $Q_f$ gives:

$$
y_{CO_2} Q_f = (y_{CO_2} - f_{liq}^{CO_2}) Q_f \quad (4.20)
$$

and $f_{liq}^{CO_2}$ is given as:

$$
f_{liq}^{CO_2} = \frac{\pi}{6} d^3 \rho_{liq} (2N_c) \quad (4.21)
$$

Thus, eq. 4.20 becomes

$$
y_{CO_2} y_f = 1 - \frac{\pi}{6} d^3 \rho_{liq} (2N_c) y_f^{CO_2} \quad (4.22)
$$

Taking the logarithm of eq. 4.22 on both sides gives,

$$
\ln \frac{y_{CO_2}}{y_f} = -\frac{\pi}{6} d^3 \rho_{liq} (2N_c) y_f^{CO_2} \rho \quad (4.23)
$$
4.2 Formulation

where, \( d \) is the diameter of growing cluster, \( \rho \) is the molar gas density, \( \rho_{\text{liq}} \) is the liquid phase density, \( y_{f}^{CO_2} \) is the feed CO\(_2\) molar concentration and \( 2N_c \) are the mean number density of clusters. In eq. 4.23, the diameter \( d \) of the cluster is growing and is a function of time \( t^* \). The rate of growth of diameter \( d \) is not much sensitive to the supersaturation \( S \) as the rate of cluster formation. In the portion of the growth time region (for \( t_c \leq t \leq t_d \)) which contributes to the cluster formation, we assume a linear growth of the square of the diameter of cluster given as (refer eq. 3.28 in chapter 3):

\[
d^2 = 8\rho D_{\text{coeff}} \frac{1}{\rho_{\text{liq}}} y_{f}^{CO_2} \left(1 - \frac{1}{S_c}\right)(t^*)^{3/2}
\]

(4.24)

Using eq. 4.24 in 4.23, we get

\[
\ln \frac{y_{f}^{CO_2}}{y_{f}^{CO_2}} = -\frac{\pi}{6} \frac{\rho_{\text{liq}}}{y_{f}^{CO_2}} \rho \left(8\rho D_{\text{coeff}} \frac{1}{\rho_{\text{liq}}} y_{f}^{CO_2}\right)^{3/2} \left(1 - \frac{1}{S_c}\right)^{3/2} (2N_c)(t^*)^{3/2}
\]

(4.25)

and eq. 4.18 in eq. 4.25 we get

\[
\ln \frac{y_{f}^{CO_2}}{y_{f}^{CO_2}} = -\frac{\pi}{3} \frac{\rho_{\text{liq}}R_e}{k} \left(8\rho D_{\text{coeff}} \frac{1}{\rho_{\text{liq}}} y_{f}^{CO_2}\right)^{3/2} \left(\frac{\eta K a}{\beta P}\right)^{3/2} \left(1 - \frac{1}{S_e}\right)^{3/2} (t^*)^{3/2}
\]

(4.26)

\[
\ln \frac{y_{f}^{CO_2}}{y_{f}^{CO_2}} = -G \left(\frac{\eta K a}{\beta P}\right) \left(1 - \frac{1}{S_e}\right)^{3/2} (t^*)^{3/2}
\]

(4.27)

In eq. 4.27, \( G \) governs the rate of growth of a square of the diameter of a single cluster (see eq. 4.24) and depends mainly on the feed concentration of CO\(_2\) in the gas mixture. \( G \) is given as:

\[
G = \frac{\pi}{3} \frac{\rho_{\text{liq}} R_e}{M k} \left(8\rho D_{\text{coeff}} \frac{1}{\rho_{\text{liq}}} y_{f}^{CO_2}\right)^{3/2}
\]

(4.28)

Differentiating eq. 4.28 with time \( t^* \) gives:

\[
\frac{d}{dt^*} \ln \frac{y_{f}^{CO_2}}{y_{f}^{CO_2}} = -\frac{3}{2} \frac{\eta K a}{\beta P} \left(1 - \frac{1}{S_c}\right)^{3/2} (t^*)^{1/2}
\]

(4.29)

and using eq. 4.29 in eq. 4.19, the rate of change of supersaturation \( S \) in the growth time region is obtained:

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\[ \frac{d}{dt} \ln S = -\frac{3}{2} G \left( \frac{\eta K_c a}{\rho \beta} \right) \left( 1 - \frac{1}{S_c} \right)^{3/2} (t^*)^{3/2} \quad (4.30) \]

At \( t^* = 0 \), \( S = S_c \).

Solving eq. 4.30 we get,

\[ \ln \frac{S}{S_c} \approx -G \left( \frac{\eta K_c a}{\rho \beta} \right) \left( 1 - \frac{1}{S_c} \right)^{3/2} (t^*)^{3/2} \quad (4.31) \]

Eq. 4.31 gives the supersaturation \( S \) at any time \( t \) in the growth time region during which \( N_d \) clusters form.

**Number of clusters \( N \) (\( t_c \leq t \leq t_d \))**

We use eq. 4.31 for the supersaturation \( S \) in eq. 4.11 to obtain the expression for rate of formation of clusters in the growth region:

\[ \frac{dN}{dt} = n_c^{\text{co}} K_c \exp \left\{ - \left( \frac{\ln S}{a} - G \left( \frac{\eta K_c}{\rho \beta} \right) \left( 1 - \frac{1}{S_c} \right)^{3/2} (t^*)^{3/2} \right)^{2} \right\} \]

(4.32)

Eq. 4.32 is used to obtain the number density of clusters \( N_d \) at time \( t_d \) and consequently the supersaturation \( S_c \).

**Solution procedure for \( N_d \) (\( t = t_d \))**

Using the definition of \( \eta \) in eq. 4.32, we get:

\[ \frac{d\eta}{dt^*} = \frac{\rho \beta}{a} \exp \left\{ - \left( u_c - G \left( \frac{\eta K_c}{\rho \beta} \right) \left( 1 - \frac{1}{S_c} \right)^{3/2} (t^*)^{3/2} \right)^{2} \right\} \quad (4.33) \]

In eq. 4.33, \( t^* \) varies from \( t^* = 0 \) or \( t = t_c \) till the time = \( t_d - t_c \). \( t_d^* \) is obtained by making the denominator in the exponent of eq. 4.33 equals to 0 at which \( \frac{d\eta}{dt^*} = 0 \) as:

\[ u_c - G \left( \frac{\eta K_c}{\rho \beta} \right) \left( 1 - \frac{1}{S_c} \right)^{3/2} (t^*)^{3/2} = 0 \quad (4.34) \]

Thus,

\[ t_d^* = u_c^{2/3} \left( \frac{\rho \beta K_c}{G} \right)^{2/3} \eta_c^{2/3} \left( \frac{1}{S_c} \right)^{-1} \quad (4.35) \]
4.2 Formulation

To mathematically simplify the limits of integral, we introduce a dimensionless time variable $\tau$ which varies from 0 to 1 as:

$$\tau = \frac{t^*}{t_d^*} = \frac{t^* G^{2/3} K_c^{2/3} \eta_c^{2/3} \left(1 - \frac{1}{S_c}\right)}{\beta^{2/3} u_c^{2/3} \bar{P}}$$

(4.36)

In terms of this new time variable $\tau$, eq. 4.33 is re-formulated as:

$$\frac{d \eta}{d \tau} = \frac{P \beta}{G^{2/3}} \left(\frac{P \beta}{K}\right)^{2/3} \frac{1}{a \eta_c^{2/3}} \left(1 - \frac{1}{S_c}\right)^{-1} \exp\left(\frac{-1}{u_c^2 \times (1 - \tau^{3/2})^2}\right)$$

(4.37)

where, $\tau$ varies from 0 till 1 and at $\tau = 0$, $\eta = \eta_c$.

Eq. 4.37 can be solved for $\eta_d$ by integrating the left side of eq. from 0 to 1 provided that the supersaturation $S_c$ is known. Supersaturation $S_c$ is determined from the condition that the number density of the clusters $N_d$ (integral of eq. 4.37 from $\tau = 0$ to 1) equal to the number density of clusters $N_c$ (from eq. 4.17). After knowing the supersaturation $S_c$ (at $t = t_c$), $N_c = N_d$ is obtained using eq. 4.17 or eq. 4.37. The average number density of clusters $N_{avg}$ is $2N_c$. 
4.3 Dimensionless process parameters

According to eq. 4.37, the mean number density $N_{\text{avg}} = 2N_c$ of CO$_2$ clusters formed by expansion cooling depends upon the following dimensionless process parameters:

The parameter $A$ is the ratio between the rate of expansion and the diffusion growth rate:

$$A = \frac{\text{Rate of expansion}}{\text{Diffusion growth rate}} = \frac{P \beta}{G^{2/3}} \quad (4.38)$$

The numerator in $A$ is the rate of expansion which brings the gas in a supersaturated state. The denominator in $A$ is proportional to the rate of growth of a cluster (eq. 4.24 and eq. 4.28). It determines the rate of depletion of CO$_2$ from the gas for a fixed number density $N$ of the clusters and consequently quantifies the rate of decrease of supersaturation (eq. 4.31). The supersaturation and also the rate of formation of clusters attain a maximum during the expansion because of these two competitive rates. The relative value of the numerator to the denominator in $A$ determines the maximum of the supersaturation and the number density of clusters formed during the expansion.

The parameter $B$ (eq. 4.39) is the ratio between the rate of expansion and the collision frequency:

$$B = \frac{\text{Rate of expansion}}{\text{Collision frequency}} = \frac{P \beta}{K} \quad (4.39)$$

Collision of the molecules to the surface of the critical clusters formed (refer section 3.2) generates the net flux of the stable clusters. The time scale of the expansion ($1/P \sim 10^{-3} \text{s}$) is usually much smaller than the time scale of having 1 collision with the surface of the critical cluster ($1/K \sim 10^{-10} \text{s}$). $K$ typically lies between $10^9$-$10^{11} \text{ s}^{-1}$ for the range of process conditions of CRS units.

The parameter $\theta$ quantifies the energy required to form a cluster relative to the thermal energy of the molecules. $\theta$ mainly depends on the temperature of the gas mixture as the surface tension changes inversely with temperature.

$$\theta = \frac{(36\pi)^{1/3}}{kT} \sigma \left( \frac{m}{P_{\text{liq}}} \right)^{2/3} \quad (4.40)$$

Dimensionless number density $N^*$ is the number density of clusters relative to the amount of CO$_2$ molecules in the feed gas.
4.4 Results and discussion

\[ N^* = \frac{\text{number density of clusters}}{\text{number density of } CO_2 \text{ molecules}} = \frac{N}{n^{CO_2}} \] 

(4.41)

To summarize, the dimensionless number density of clusters \( N^* \) is a function of three dimensionless process parameters:

\[ N^* = f(A, B, \theta) \] 

(4.42)

4.4 Results and discussion

4.4.1 Effect of process conditions (Dimensionless form)

In this section the influence of the three dimensionless parameters \( A, B \) and \( \theta \) (eq. 4.38–eq. 4.40) on the dimensionless number density of condensed \( CO_2 \) droplets is investigated.

\( N^* \) vs \( A \)

Fig. 4.2 shows a variation of the dimensionless number density \( N^* \) with the parameter \( A \) keeping \( B \) and \( \theta \) constant. \( N^* \) increases with the increase in parameter \( A \). At increased values of \( A \), expansion becomes relatively fast. Faster expansion leads to fast creation of supersaturation. To compete with the fast rate of increase of supersaturation resulting from the faster expansion rate, the loss of \( CO_2 \) from the gas to the clusters increases and the number density of clusters becomes larger.

\( N^* \) vs \( \theta \)

Now, we calculate how the dimensionless number density is changing with the dimensionless surface energy. In fig. 4.2 variation of \( N^* \) with \( A \) is shown for different values of \( \theta \). For the same \( A \), \( N^* \) decreases with the increase in \( \theta \). This is because higher dimensionless surface energies results in the higher critical energy barriers of the cluster formation at the same supersaturation of the gas. Less molecules are able to form clusters and the number of clusters formed relative to the number of \( CO_2 \) gas molecules is reduced. Calculations show that changing the dimensionless surface energy from 1 to 4.5 will result in a factor 100 decrease in the dimensionless number density of clusters (shown later in section 4.4.2). Thus, higher dimensionless surface energies result in the production of a smaller number of bigger droplets.
N* vs B

Changing $B$ for same $A$ and $\theta$ does not have much influence on $N$ as is shown in fig. 4.2. As long as the ratio of expansion rate to diffusion growth rate and the dimensionless surface energy remains same, $B$ does not influence $N^*$. 

![Graph showing variation of dimensionless number density $N^*$ of droplets with dimensionless parameter $A$. $A$ is a ratio of expansion rate $P$ and growth rate $G^{2/3}$. Calculations of $N^*$ are done for different values of dimensionless surface energies $\theta$.](image)

**Figure 4.2:** Variation of dimensionless number density $N^*$ of droplets with dimensionless parameter $A$. $A$ is a ratio of expansion rate $P$ and growth rate $G^{2/3}$. Calculations of $N^*$ are done for different values of dimensionless surface energies $\theta$.

### 4.4.2 Effect of process conditions

In this section, we calculate the number densities and the size of condensed CO$_2$ droplets for the operating range of process conditions of CRS.

**Average expansion rate**

The expansion rate can be varied by changing the design of the expander used for cooling of the gas. Different type of expanders such as valves, turbines, supersonic can have different expansion rates. The average expansion rates for different expansion devices are listed in table 4.1:

<table>
<thead>
<tr>
<th>Type of expander</th>
<th>Average rate of expansion $(s^{-1})$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves or turbines</td>
<td>$10^4$ - $10^7$</td>
<td>44, 49</td>
</tr>
<tr>
<td>Supersonic nozzles</td>
<td>$10^5$-$10^5$</td>
<td>44, 49</td>
</tr>
<tr>
<td>Volume based cloud chambers, piston expansion machines</td>
<td>$10^1$ - $10^2$</td>
<td>44, 49</td>
</tr>
</tbody>
</table>
4.4 Results and discussion

In CRS units, turbines or valves will be employed to achieve the expansion cooling of the gas. Fig. 4.3 shows the variation of the number density of clusters with rates of expansion lying between \(10^0-10^6\) s\(^{-1}\). The number densities are calculated for a typical value of growth rate parameter \(G^{2/3} = 10^{12}\) s\(^{-1}\) which is calculated for 50 % CO\(_2\) feed composition (eq. 4.28) and \(\theta = 1\) which corresponds to the surface tension of 2 mN/m for pure liquid CO\(_2\) (effect of \(\theta\) on \(N\) is discussed later). For the expansion rates of \(10^0\) s\(^{-1}\), the number density is on the order of \(10^{13}\) m\(^{-3}\). By increasing the expansion rate to \(10^6\) s\(^{-1}\), the number density increases up to \(10^{21}\) m\(^{-3}\).

The number densities of clusters are significantly affected by changing the rate of expansion and thus the size of condensed droplets can be influenced for the same condensed liquid amounts.

**Feed concentration CO\(_2\)**

In contaminated natural gas, CO\(_2\) feed compositions typically lie between 20 mole % and 80 mole %. For flue gas cleaning application, CRS becomes beneficial only at higher CO\(_2\) feed concentrations typically more than 50 mole % [50].

Fig. 4.4 shows a variation of the number density with CO\(_2\) with varying feed CO\(_2\) conc. between 20 % and 80 % CO\(_2\). For this range of feed conc. \(G^{2/3}\) is on order of \(10^{10-10^{12}}\) s\(^{-1}\). Calculations are shown for typical expansion rate of \(10^3\) s\(^{-1}\) of turbines and \(\theta = 1\) (effect of \(\theta\) on \(N\) is discussed later). There is no significant change in the number density of droplets with the change in feed concentration of CO\(_2\). This is in accordance with our CO\(_2\) droplet size measurements in methane or nitrogen also (see section 4.5).

**Pressure and temperature before the expander**

Pressure and temperature of the feed gas before the expander can be varied to access the different regions of the phase envelope. In practice, pressure and temperature at the inlet of expander are chosen such that recovery of CO\(_2\) from the feed stream along with the amount of CO\(_2\) in condensed liquid phase is maximized (liquid phase enrichment) after the expansion. Optimal separation pressure and temperature after the expansion (separation conditions) means the maximum possible recovery and the maximum possible enrichment of the condensed liquid phase.

The pressure and temperature before the expander, calculated for the optimal separation conditions, depends on the feed CO\(_2\) concentration in the gas. As an example, for 20 mole % CO\(_2\) feed in CH\(_4\), pressure and temperature before the expander for the optimal
point is 50 bars and $-50 \degree \text{C}$. For 50 mole % CO$_2$ feed in CH$_4$, the pressure and temperature before the expander becomes 70 bars is $-5 \degree \text{C}$ [12]. This means that at higher CO$_2$ feed concentration, the required pressure and temperature of the gas (for the highest recoveries and maximum liquid phase enrichment) before the expander increases. This inlet pressure $P_{\text{in}}$ influences the number density of CO$_2$ molecules, which remains in the order of $10^{27}$ m$^{-3}$ over the pressure range of 50-100 bars. The corresponding inlet temperature has an affect on the surface tension of liquid CO$_2$ and lies in the range between 20 $\degree\text{C}$ and $-50 \degree\text{C}$ for the optimal separation conditions [12]. The inlet temperature corresponds to the minimum possible temperature while staying in the vapor regime at the given inlet pressure (just above the dew point temperature at the inlet pressure for the given feed composition). For this inlet temperature range, $\theta$ lies between 1 and 4.5 (these values correspond to the surface tension of 2 and 15 mN/m for pure liquid CO$_2$. The number densities of droplets with varying expansion rate as shown in fig. 4.3 are calculated for the range of $\theta$ between 1 and 4.5 and at 50 mole % feed CO$_2$ conc. in the gas. The number densities increase for lower surface energies.

Increasing CO$_2$ feed concentration increases the required inlet temperature and inlet pressure before the expander for the optimal separation conditions. This indirectly implies the decrease in dimensionless surface energy and results in a higher number density. The droplet size will become smaller for the same condensed amounts.
4.4 Results and discussion

**Figure 4.3:** Number density of droplets $N$ with varying expansion rate at fixed value of growth rate parameter $G^{2/3} = 10^{12} \text{ s}^{-1}$. Calculations of $N$ are done for different values of dimensionless surface energies.

**Figure 4.4:** Number density of droplets $N$ with varying feed concentration at fixed value of expansion rate of $10^3 \text{ s}^{-1}$. Calculations of $N$ are done for different values of dimensionless surface energies.
Mean diameter of droplets

For the process conditions discussed so far, the number density $N$ lies between $10^{10}$ m$^{-3}$ and $10^{21}$ m$^{-3}$ and most of the condensation growth is completed within the time scale of expansion. Knowing the number density of clusters and assuming no coagulation, the mean droplet size can be calculated for the known condensed liquid volume fraction $F_{\text{liq}}$ as:

$$d_{\text{avg}} = \left( \frac{6 F_{\text{liq}}}{\pi N} \right)^{\frac{1}{3}}$$  \hspace{1cm} (4.41)

The condensed liquid volume fraction is the ratio of volume of the condensed liquid per cubic meter of the gas. $F_{\text{liq}}$ depends on the pressure $P_{\text{out}}$ and temperature $T_{\text{out}}$ at the outlet of the expander.

In a condensed rotational separation, very high condensed volumes up to 5 % are possible [12]. Using eq. 4.41, the average size of droplets can be obtained for the predicted number density of droplets for the given condensed liquid volume fractions. Fig. 4.5 shows a variation of droplet diameter with different expansion rates for the condensed volume fractions of 1 %.

At the typical expansion rates of turbines ($\sim 10^3$ s$^{-1}$), the droplet sizes lie between 0.5 and 10 µm for the range of surface energy between 1 and 4.5. At faster expansion rates of $10^6$ s$^{-1}$, the predicted average droplet size lies between 0.01 and 0.2 µm. For very slow expansions of 1 s$^{-1}$, the average droplet size becomes bigger and lies between 10 µm and 200 µm.

![Figure 4.5: Size of the condensed CO$_2$ droplets with varying expansion rates at fixed value of $G^{2/3} = 10^{12}$ s$^{-1}$](image)

Figure 4.5: Size of the condensed CO$_2$ droplets with varying expansion rates at fixed value of $G^{2/3} = 10^{12}$ s$^{-1}$
4.4 Results and discussion

**Effect of coagulation and concentration of foreign particles**

Cluster-cluster interactions (coagulation) are neglected in the model described above. The upper limit of the number density of droplets formed is constrained by the coagulation process. Coagulation becomes important for a number density of droplets greater than $10^{18} \text{ m}^{-3}$ [35]. For $N < 10^{18} \text{ m}^{-3}$, the time scale of coagulation (to decrease the number density of droplets by factor 10) is in the order of a few seconds [35]. This time is much lower than the time between expansion and separation. Therefore, coagulation has no significant influence on number density and thus the droplet size. However, for $N > 10^{18} \text{ m}^{-3}$ (for the expansion rates faster than $10^5 \text{ s}^{-1}$) coagulation becomes fast and the time scale of coagulation is in same order of residence time between expansion and separation. This means that the upper limit of number density of droplets is constrained by coagulation process and will be always less than $10^{18} \text{ m}^{-3}$. Thus, lower limit of diameter becomes 0.2 µm for condensed volume fractions of 1%. This means that size of condensed droplets will be always more than the 0.2 µm for CRS process conditions.

The lower end of number densities of droplets is constrained by the number concentration of foreign particles (if present) in the gas mixture before the expansion. The number concentration of foreign particles present in flue gases is typically in order of $10^{12} \text{ m}^{-3}$ [35].

This means that the range of number density of droplets always lie between $10^{12}$- $10^{18} \text{ m}^{-3}$ irrespective of the process conditions. The corresponding range of droplet sizes becomes 0.2µm and 20 µm for the condensed volume fractions of 1%.

### 4.4.3 Comparison predictions and measurements

A J-T valve is used for the expansion cooling of CO$_2$/CH$_4$ or CO$_2$/N$_2$ mixtures in the measurements of chapter 2 (see fig. 4.6 and 4.7). To compare with model predictions the average expansion rate of the J-T valve has to be estimated. The dew point line of the feed gas is crossed in the accelerating flow through the conical orifice and most of the clusters form near the dew point line. The average expansion time is

$$t_{valve} \sim \frac{V_{valve}}{Q_{vol}}$$

where, $V_{valve}$ is the volume of the conical region through which flow is accelerating. It is approximated from the geometry of valve and is ca. 130 mm$^3$. $Q_{vol}$ is the volume flow rate and is calculated from the known mass flow rate divided by average density of the flow.
The density of the flow is averaged over the inlet pressure $P_{in}$ and the pressure at the orifice $P_{orifice}$. $P_{orifice}$ is estimated as:

$$P_{orifice} = P_{in} \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}}$$  \hspace{1cm} (4.43)

Using eq. 3.25, the average expansion rates $P$ in J-T valve is obtained. These are in order of $10^2 \, \text{s}^{-1}$ and listed in table 4.2. After calculating the average expansion rate, the pressure and temperature at the intersection of dew point line and the isentropic expansion path are obtained using binary flash calculations. The dimensionless surface energy $\theta_{dew}$ is obtained using eq. 4.40 at temperature $T_{dew}$. Fig. 4.8 shows a comparison between measured number densities and predicted number densities of condensed CO$_2$ droplets in nitrogen. Measured number densities of condensed CO$_2$ droplets are a factor 30 less than the predicted ones and thus the average predicted droplet size is factor 3 smaller than the measured droplet sizes.

Table 4.2: List of the calculated process parameters required for the prediction of average number densities of condensed CO$_2$ droplets in nitrogen. Serial numbers correspond to the measurements listed in table 2.2

<table>
<thead>
<tr>
<th>S.No.</th>
<th>$P_{dew}$ (bara)</th>
<th>$T_{dew}$ (°C)</th>
<th>$\theta_{dew}$ (-)</th>
<th>Expansion rate (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>-41</td>
<td>3.5</td>
<td>352</td>
</tr>
<tr>
<td>2</td>
<td>87</td>
<td>-30</td>
<td>2.7</td>
<td>390</td>
</tr>
<tr>
<td>3</td>
<td>104</td>
<td>-18</td>
<td>1.9</td>
<td>342</td>
</tr>
<tr>
<td>4</td>
<td>116</td>
<td>-16</td>
<td>1.8</td>
<td>259</td>
</tr>
<tr>
<td>5</td>
<td>130</td>
<td>-7</td>
<td>1.3</td>
<td>245</td>
</tr>
<tr>
<td>6</td>
<td>93</td>
<td>-4</td>
<td>1.2</td>
<td>353</td>
</tr>
<tr>
<td>7</td>
<td>137</td>
<td>-11</td>
<td>1.5</td>
<td>190</td>
</tr>
<tr>
<td>8</td>
<td>135</td>
<td>-7</td>
<td>1.3</td>
<td>175</td>
</tr>
</tbody>
</table>
4.4 Results and discussion

Figure 4.6: (a) Drawing of J-T valve used for the expansion cooling of CO$_2$/CH$_4$ and CO$_2$/N$_2$ mixtures in C3-sep. pilot scale test rig at Shell Amsterdam (b) Schematic shows the pressure variation across the valve. All dimensions are in mm.

Figure 4.7: Photograph of J-T valve used for the expansion cooling in condensed separation pilot scale test rig at Shell Amsterdam
Figure 4.8: Comparison of measured and predicted number densities of homogeneously condensed CO$_2$ droplets in nitrogen

4.4.4 Comparison (Numerical vs analytical model)

Fig. 4.9 shows a comparison between the number density predicted by the analytical model and the numerical model for different expansion rates. The predictions agree well with each other for the given process parameters.

Figure 4.9: Comparison of the number density of homogeneously condensed CO$_2$ droplets predicted by the numerical and analytical model at different expansion rates.
4.5 Conclusions

1. A numerical and analytical model is formulated to predict the size of condensing CO$_2$ droplets formed by expansion cooling of CO$_2$/CH$_4$ or CO$_2$/N$_2$ mixtures. The analytical model is well in agreement with the numerical predictions. The analytical model gives a tool for the process engineer to estimate the size of condensed CO$_2$ droplets under varying process conditions.

2. The droplet number density depends mainly upon the rate of expansion and the surface tension of the condensing CO$_2$.

3. From the numerical model we obtain the distribution of droplet sizes formed in the expansion cooling which is quite mono-disperse. However, measurements give a range of droplet sizes showing the poly-disperse distribution of the droplets. The possible reason can be the difference in the expansion rates of the stream lines of the flow through an expander. Two or three dimensional computational models are needed to get more insight.

4. Measured number densities in Amsterdam measurements are a factor 30 less than the predicted average number densities. This over-prediction of the number densities of droplets can be because of the real gas effects such as change in supersaturation S or change in surface tension, which are not incorporated in the present model. However, from a designer perspective, our model gives the worst case (lower band) estimate of the condensed CO$_2$ droplet sizes in methane or nitrogen.

5. Prediction and measurements both suggest smallest droplets down to 1 µm. This means that a separator needs to be designed to collect all the droplets down to 1 µm for an efficient operation.

6. The measured number density of condensed CO$_2$ droplets ($10^{14}$ m$^{-3}$) are only a couple of orders higher than previously observed foreign particles in gases ($10^{11}$-10$^{13}$ m$^{-3}$) as reported in the literature [51-53]. This means that if foreign particles were present in the gas, they might be sufficient to suppress homogeneous condensation. In that case, the condensed CO$_2$ droplet size would be governed by the diffusion growth only for the fixed number concentration of foreign particles in the gas.
Appendix 4A

Dimensionless surface energy of pure liquid CO$_2$

Figure 4A1: Variation of dimensionless surface energy of pure CO$_2$ with temperature
Chapter 5  
Experimental Validation of Droplet Growth Model

5.1 Introduction

The purpose of this chapter is to validate the droplet growth model of the chapter 3. For this, the heterogeneously condensed water droplets formed by the isentropic expansion cooling of humid air in a converging-straight nozzle are measured (section 5.2). The ambient air used in the experiments usually contains foreign particles. Typical number concentrations of foreign particles are between $10^{11}$-$10^{13}$ m$^{-3}$ of gas [51-53]. Furthermore, water-vapor requires high supersaturation to condense homogeneously in comparison to CO$_2$. The combined effect is that homogeneous nucleation is suppressed [35] in the experiments described here. Only heterogeneous condensation is observed in the experiments (section 5.3). The model of chapter 3 can still be used to predict the diffusional growth of the droplets by replacing the time dependent number concentration $N(t)$ of eq. 3.26 by the number concentration of foreign particles $N_{\text{foreign}}$.

This chapter is organized as follows: Section 5.2 describes the experimental set up. Section 5.3 shows the results followed by discussion in section 5.4. Conclusions are given in Section 5.5.

5.2 Experimental

5.2.1 Description test rig

A schematic of the experimental set up is shown in fig. 5.1. The measuring equipment used in the experimental set up are listed in table 5.1. An 850 kW boiler (a) is used to produce saturated steam at pressure up to 8 bars controlled by a pressure regulator (b). A pneumatic control valve (c) controls the mass flow of saturated steam (0.005 kg/s-0.095 kg/s). The mass flow rate of the saturated steam is measured using a Coriolus flow meter.

The saturated steam is then injected into the flow of dry air (maximum 0.4 kg/s) which is taken from the compressed air line (maximum pressure 10 bar). The mass flow of dry air
is controlled using the pneumatic control valve (f) and is measured using a thermal mass flow meter. A heat exchanger (h) is installed in the air line to pre-heat the dry air prior to the injection of dry saturated steam into it. After the injection of saturated steam into the pre-heated dry air, the dry saturated steam and dry air flow together through a 1 m long and 110 mm diameter pipe to form a homogeneously mixed water-vapor and air mixture (humid air). This humid air is then fed through the test section (g).

The pre-heating of dry air ensures that the humid air remains free of the condensate droplets before its entry into the test section. Fig. 5.2 shows the feed stream compositions $Y_f$ (kg of water-vapor/kg of air) and the corresponding measured temperatures at the inlet of the test section (g). The solid line in fig. 5.2 is the saturation line for the water-vapor. The region right of the saturation line represents the gas phase containing air and water-vapor only. Here, the partial pressure of water-vapor in the air is less than its saturation vapor pressure at the given temperature. To avoid condensate formation in humid air before its entry into the test section (g), the temperature at the inlet of the test section (g) should not be less than the corresponding saturation line value for the given feed stream composition $Y_f$ (kg of steam/kg of air). As an example, for the feed composition 0.2 kg of steam/kg of air, the temperature at the inlet of test section should be either 72 °C or more than 72 °C. During our experiments, $Y_f$ is varied by controlling the mass flow of saturated steam and the mass flow of dry air independently. The temperature at the inlet is varied such that it lies on or to the right of the saturation line. This is done by adjusting the pre-heating of the dry air for the given feed stream composition $Y_f$.

The test section (g) consists of a converging-straight nozzle made from poly-methyl methacrylate (PMMA) (see fig. 5.2 and fig. 5.3). The nozzle inlet is of diameter 110 mm and the outlet has a rectangular cross section having dimensions 45 × 20 mm. The section of the nozzle having minimum cross-sectional area, the throat, is rectangular and has the same dimensions as the outlet. The static pressure at inlet and at the throat of the nozzle is measured using absolute piezoelectric pressure transducers (0-10 bar, accuracy = 0.25% full scale). The temperature at the inlet of the nozzle and outlet of nozzle is measured using K-type thermocouples.

Prior to the main process of injection of saturated steam in air, a small amount of saturated steam is made to flow through the vent line (d) and (e) for at least 1 hour. This start up process is done to bring the inner walls of the steam line to the same temperature as the main flow of steam. This ensures that the steam remains dry before its injection. The
5.2 Experimental

steam line is also well insulated with glass wool to minimize the heat losses to the surroundings.

Figure 5.1: Schematic of the experimental test set up

Table 5.1: List of the measuring equipments in the experimental set up

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Flow meter air</td>
</tr>
<tr>
<td>2.</td>
<td>Pressure sensor air</td>
</tr>
<tr>
<td>3.</td>
<td>Temperature sensor air</td>
</tr>
<tr>
<td>4.</td>
<td>Flow meter steam</td>
</tr>
<tr>
<td>5.</td>
<td>Pressure sensor steam</td>
</tr>
<tr>
<td>6.</td>
<td>Temperature sensor steam</td>
</tr>
<tr>
<td>7.</td>
<td>Pressure sensor inlet nozzle</td>
</tr>
<tr>
<td>8.</td>
<td>Thermocouple inlet nozzle</td>
</tr>
<tr>
<td>9.</td>
<td>Pressure sensor outlet nozzle</td>
</tr>
<tr>
<td>10.</td>
<td>Thermocouple outlet nozzle</td>
</tr>
</tbody>
</table>
Figure 5.2: Feed compositions $Y_f$ of the humid air and the corresponding temperatures at the inlet $T_{in}$ of the test section. The solid line represents the saturation line for the water-vapor. The inlet temperatures lie on or the left of the saturation line showing the absence of condensate in the humid air before its entry into the test section.

Figure 5.3: Drawing of the test section (All dimensions are in mm)
5.2 Experimental

Fig. 5.4: Photograph of the test section

5.2.2 Droplet characterization

During the nearly isentropic expansion in the test section, the temperature and the pressure of humid air reduce [48]. Also, the saturation pressure of water-vapor reduces because of the decrease in temperature. Water-vapor in the humid air starts to condense on the foreign nuclei and a fog is created. The photograph shown in fig. 5.5 depicts the production of fog during measurements. The amount of condensate formed depends upon the temperature and pressure at the outlet of nozzle. The measurements of condensed water droplet sizes are done right after the outlet of the nozzle. Measurements are done for the range of feed compositions of humid air \((Y_f = 0.05-0.34 \text{ kg of water-vapor/kg of air})\) keeping the air flow constant. Measurements are also done for the range of air flow rates \((m_{\text{air}} = 0.15-0.32 \text{ kg/s})\) keeping the feed composition constant. The process conditions during the measurements are listed in Appendix 5C.

A laser diffraction technique (Malvern Spraytec) is used for the droplet size measurements. A 20 mm diameter laser beam with wavelength 680 nm is passed through the flow of humid air containing water droplets at the outlet of the test section. Water droplets in the air scatter the light and a scattered light intensity pattern is obtained on the detectors placed in the direction perpendicular to the flow. The volume distribution of
droplets $f(d^3)$ is inferred from this measured scattered intensity pattern using Mie theory [54, 55]. In addition to the size of droplets, the laser diffraction method also measures the condensed liquid volume concentration $F_{meas}$ using the Lambert’s Beer law [56]. From the measured liquid volume concentration, the number density of droplets $N_{drops}$ formed is obtained as:

\[
N_i(d) = F_{meas} \frac{f_i(d^3)}{d_i^3} \quad (5.1)
\]

\[
N_{drops} = \sum_i N_i(d) \quad (5.2)
\]
5.3 Results

Fig. 5.6 shows a typical measured volume distribution of the heterogeneously condensed water droplets at the outlet of the test section. Volume median diameter $d_{50}$ is 4 $\mu$m. Lower decile diameter $d_{10}$ of the measured volume distribution is ca. 2 $\mu$m. Most of the condensed water droplets are lying between 1 and 10 $\mu$m. To compare the measurements with the model predictions, the volume mean diameter $d_{(3,0)}$ is obtained from the measured volume distribution as:

$$d_{(3,0)} = \left( \sum_i f_i(d) d_i^3 \right)^{1/3}$$  \hspace{1cm} (5.3)

where, $f(d)$ is the number frequency distribution of the condensed droplets obtained from the measured $f(d^3)$.

Fig. 5.7 shows the experimentally obtained number density of condensed droplets for the tested process conditions during the experiments. For all conditions, the droplet number density is around $10^{12}$ m$^{-3}$ of air. As the droplet number concentration does not change during the heterogeneous condensation, $N_{\text{foreign}} = 10^{12}$ m$^{-3}$ of air is used for the comparison with the model.

Fig. 5.8 and 5.9 give the observed mean volume diameters $d_{(3,0)}$ during the experiments. In fig. 5.8, feed composition of humid air $Y_f$ is varied for a constant air flow rate $m_{\text{air}}$. In fig. 5.8, the air flow is varied at constant feed composition. The air flow rate also has an effect on the average rate of expansion. This is because flow rate is directly coupled to the pressure drop across the expander and also influences the time of expansion for a given volume of expander (see eq. 3.24 and eq. 3.25). Converging-straight nozzle acts as an expansion device in our experiments. Volume of the nozzle used is $8 \times 10^{-4}$ m$^3$. For the range of flow rates in our experiments, the average expansion rate is calculated using eq. 3.24 and eq. 3.25. The average expansion rate is on the order of $10^2$ s$^{-1}$ (see appendix 5C) and does not vary much for the range of flow rates in our experiments.

The predicted droplet sizes based on the model (described in chapter 3 and adapted for the heterogeneous condensation) are shown by the solid line. The predictions are in agreement with the measurements for different feed compositions and constant air flow rate. For a constant feed composition, the predictions suggest a slight increase in the condensed droplet size from 2 to 3 $\mu$m with varying air flow rate between 150 g/s and 320 g/s. At higher flows, pressure drop (pressure ratio) across the nozzle increases.
Consequently, temperature drop and amount of condensed liquid increases. Therefore, the model predicts a slight increase in the droplet size for a fixed foreign particle concentration $N_{\text{foreign}} = 10^{12} \text{ m}^{-3}$ of air. No change in the condensed droplet size is measured with changing air flow rate as predicted. However, measured droplet sizes are quite in range with the predictions (within 25 %) except the two measurements which are en-circled in the figure. This offset can be because of several reasons such as contaminated optics of Spraytec Malvern, change in background noise during the measurements and uncertainty in the amount of foreign particles in the air. Nevertheless, the model seems to be applicable for the design purposes.

**Figure 5.6:** Typical measured volume distribution of heterogeneously condensed water droplets in air at the outlet of test section.
5.3 Results

**Figure 5.7:** Experimentally obtained number density of the condensed water droplets in air at different air flow rates and feed compositions of the humid air.

**Figure 5.8:** Variation of measured volume mean diameter with feed composition at constant air flow. The solid line shows the predicted droplet sizes based upon the model described in section 3.3. This model is adapted for heterogeneous condensation by replacing the time dependent number concentration $N(t)$ with constant $N_{\text{foreign}}$. For the predictions, number concentration of foreign particles $10^{12}$ m$^{-3}$ of air is used.
Figure 5.9: Measured volume mean diameter d (3, 0) with varying air flow rate $m^{\text{air}}$. Feed composition is kept constant for all measurements. The solid line shows the predictions of droplets sizes based on the model described in section 3.3. This model is adapted for heterogeneous condensation by replacing the time dependent number concentration $N (t)$ with constant $N_{\text{foreign}}$. For the predictions, number concentration of foreign particles $10^{12} \text{ m}^{-3}$ of air is used.

5.4 Discussion

In this section, influence of input process parameters,

(a) Expansion rate

(b) Amount of foreign nuclei

to the model, on the heterogeneous condensed droplet size is calculated and discussed. These parameters are not controlled in our experiments.

Fig. 5.10 shows a calculated variation of supersaturation $S$ (based on the model described in section 5.3) during the expansion for three different expansions rates. The number concentration of foreign nuclei is $10^{12} \text{ m}^{-3}$ of air for the calculations. For expansion rates < 1000 s$^{-1}$, S reaches approximately 1 at the end of expansion. The heterogeneously condensed water droplet size after the expansion approaches the corresponding equilibrium size $d_{eq}$. This indicates that the thermodynamic phase equilibrium is nearly established.

For the range of tested flow rates ($m^{\text{air}} = 0.15$-$0.30 \text{ kg/s}$) and feed compositions of humid air ($Y_f = 0.02$-$0.28 \text{ kg of water-vapor/kg of air}$) during our experiments, the expansion time is sufficient to reach the thermodynamic phase equilibrium at the end of test section. The corresponding equilibrium diameter $d_{eq}$ at the end of test section is calculated
5.4 Discussion

(appendix 5A) and listed in appendix 5C. This calculated $d_{eq}$ is nearly same as the observed volume mean diameter during our experiments for all tested process conditions.

For faster expansions ($> 1000 \text{s}^{-1}$), $S$ is much larger than 1 at the end of expansion. This means that the phase equilibrium is not established and the heterogeneous condensation growth of droplets is not over yet. An extra time is required to complete the condensation growth of the droplets and reach the corresponding thermodynamic phase equilibrium conditions. The characteristic time scale for the condensation growth (see appendix 5B) is:

$$t_{growth} \sim \frac{1}{ND_{coeff} d_{max}}$$  \hspace{1cm} (5.4)

where,

$$d_{max} = \left( \frac{6y_f \rho_f}{\pi N \rho_{lag}} \right)^{1/3}$$  \hspace{1cm} (5.5)

![Figure 5.10: Calculated supersaturation profiles for different rate of expansions during the expansion cooling of humid air](image)

As shown in fig. 5.10, the maximum supersaturation does not exceed more than 1.2 for the number concentration of foreign nuclei $N_{\text{foreign}} = 10^{12} \text{m}^{-3}$ of air and expansion rates of $10^2 \text{s}^{-1}$. For water-vapor, the rate of cluster formation obtained using classical nucleation theory is zero for the calculated supersaturations. This indeed implies that homogeneous nucleation is absent during our experiments.
Fig. 5.11 shows the calculated supersaturations based on the model during the expansion for different number concentrations of foreign nuclei $N_{\text{foreign}}$ in the range of $10^{11}$ to $10^{13}$ m$^{-3}$ of air. The rate of expansion is $10^2$ s$^{-1}$ for the calculations. For $N_{\text{foreign}} < 10^{11}$ m$^{-3}$ of air, $S$ remains much higher than 1 at the end of expansion. It means that condensation growth is not yet finished and the induction section is required to complete the condensational growth.

Figure 5.11: Calculated supersaturation profiles for different number concentration of foreign nuclei during the expansion cooling of humid air
5.5 Conclusions

The diffusion growth of water droplets in air during the isentropic expansion in converging-straight nozzle is measured. The growth model of chapter 3 predicts the droplet size to 25% of the measured sizes. This allows for the use of model for the practical design calculations.

In contrast to the experiments described here, typical condensed rotational separation (CRS) units have CO₂ as the main condensing component and operate under high pressure. The rate of condensation growth of the droplets mainly depends on (a) diffusion coefficient (D) of the condensable component in the carrier gas (b) gas density (c) feed concentration (yᵢ) of the condensable component (see section 3.3). The dependence of diffusion coefficient on the pressure can be expressed by Chapman-Enskog theory [58]. As per this theory, the product of density (ρ) and diffusion coefficient (D_{coeff}) in Fick’s law is nearly independent of the pressure. The diffusion coefficient of CO₂ in N₂ or CH₄ is roughly on the same order as of the water-vapor in air at standard atmospheric pressure and temperature conditions (D_{coeff}^{H₂O-N₂} or D_{coeff}^{CO₂-N₂} or D_{coeff}^{CO₂-CH₄} ≈ 10^{-5} m²/s). This justifies the practical applicability of the experiments described here for CRS units.
Appendix 5A

Equilibrium droplet size

Here, we calculate the equilibrium droplet size \( d_{eq} \) which corresponds to the thermodynamic phase equilibrium conditions at the outlet of the test section (refer fig. 5.3 for the test section). The equilibrium droplet size \( d_{eq} \) depends on the amount of condensed liquid at outlet of the test section and the number concentration of foreign particles \( N_{\text{foreign}} \) in the air. We first calculate for the condensed liquid amount which depends on:

(a) Pressure and temperature drop across the test section
(b) Feed concentration of water-vapor in air

Applying energy conservation at the inlet (in) and outlet (out) of the test section we get:

\[
h_{\text{in}} + \frac{1}{2}(v_{\text{in}})^2 M_{\text{avg}} = h_{\text{out}} + \frac{1}{2}(v_{\text{out}})^2 M_{\text{avg}}
\]

(5A1)

where \( h \) denotes the molar enthalpy of the water-vapor and air mixture (J/mol), \( v \) is the flow velocity averaged over the cross-sectional area (A) of the test section and given as:

\[
v = \frac{Q_{\text{vol}}}{A}
\]

(5A2)

\( Q_{\text{vol}} \) is the volume flow rate.

The total enthalpy \( h \) is sum of the individual enthalpies of all components constituting the mixture. Thus, eq. 5A1 is written as:

\[
(1 - y_{\text{in}}^{H_2O})h_{\text{air}} + y_{\text{in}}^{H_2O}h_{\text{in}}^{H_2O} + \frac{1}{2}(v_{\text{in}})^2 M_{\text{avg}} = (1 - y_{\text{in}}^{H_2O})h_{\text{air}} + y_{\text{out}}^{H_2O}h_{\text{out}}^{H_2O} + \frac{1}{2}(v_{\text{out}})^2 M_{\text{avg}}
\]

(5A3)

In eq. 5A3, \( y_{\text{in}}^{H_2O} \) is the mole fraction of water-vapor in air. Superscripts \( H_2O \) and \( \text{air} \) denotes the water-vapor and air respectively. On the right hand side of eq. 5A3, contribution of liquid phase in the total enthalpy (h) compared to other terms of the eq. is small and is neglected. Furthermore, \( h_{\text{out}}^{H_2O} \sim \Delta H_{\text{H}_2O}(T_{\text{out}}) \) and \( h_{\text{in}}^{H_2O} \sim \Delta H_{\text{H}_2O}(T_{\text{in}}) \). \( \Delta H_{\text{H}_2O} \) is the latent heat of vaporization of water-vapor (J mol\(^{-1}\)) and does not vary much over the temperature range in our experiments (2500-2300 kJ/kg for the range of temperatures between 0 -70 °C). Also, \( v_{\text{in}} \ll v_{\text{out}} \) for our experiments. Eq. 5A2 is further simplified into,

\[
y_{\text{out}}^{H_2O}h_{\text{out}}^{H_2O} - y_{\text{in}}^{H_2O}h_{\text{in}}^{H_2O} = (1 - y_{\text{in}}^{H_2O})(h_{\text{in}}^{air} - h_{\text{out}}^{air}) - \frac{1}{2}(v_{\text{out}})^2 M_{\text{avg}}
\]

(5A4)
Appendix 5A Equilibrium droplet size

In eq. 5A4, \( y_{in}^{H_2O} = y_f^{H_2O} \) and \( y_{out}^{H_2O} \) is calculated using eq. 5.4 after obtaining \( Y_{out} \) which is given as [10]:

\[
Y_{out} = \frac{M_{H_2O}^{in}}{M_{air}} \frac{p_f^{H_2O}(T_{out})}{p_{out} - p_s^{H_2O}(T_{out})} \tag{5A5}
\]

Eq. 5A4 in combination with eq. 5A5 is solved for the condensed liquid mole fraction \( f_{liq} \) (moles of water/mole of mixture) and the temperature at the outlet of test section \( T_{out} \):

\[
f_{liq} = y_{in} - y_{out} \tag{5A6}
\]

Further, condensed liquid volume fraction \( F_{cal} \) is calculated as:

\[
F_{cal} \sim \frac{f_{liq} \rho}{\rho_{liq}} \tag{5A7}
\]

After calculating the condensed liquid volume concentration \( F_{cal} \) using eq. 5A7, the equilibrium droplet size \( d_{eq} \) for a given number concentration of foreign nuclei \( N_{foreign} \) is obtained:

\[
d_{eq} = \left( \frac{6}{\pi} \frac{F_{cal}}{N_{foreign}} \right)^{1/3} \tag{5A8}
\]
Appendix 5B

Characteristic time scale of condensation growth

In this appendix, we calculate the characteristic time scale of the condensation growth of the droplets formed by the expansion cooling.

5B.1 Growing droplet diameter \( d(t) \) during the expansion

As described in chapter 3, the rate of condensation growth on the foreign nuclei (or on the cluster) suspended in the gas given as:

\[
\frac{d}{dt} \left( \frac{\pi}{6} d^3 \rho_{liq} \right) = 2\pi \rho_{coeff} d^3 \left( 1 - \frac{1}{S} \right)
\]

(refer eq. 3.17)

A dimensionless diameter \( d^* \) is defined as the ratio of diameter \( d \) of growing droplet to the maximum possible diameter \( d_{\text{max}} \) of the droplet. The maximum possible diameter \( d_{\text{max}} \) is calculated for the case, when all water-vapor present in air is condensed in the form of droplets on the number of foreign nuclei \( N_{\text{foreign}} \) as:

\[
d_{\text{max}} = \left( \frac{6 \gamma_f \rho_f}{\pi N_{\text{foreign}} \rho_{liq}} \right)^{1/3}
\]

(5B1)

We define the dimensionless time \( t^* \) as:

\[
t^* = 2\pi (\rho_{\text{ref}} / \rho_f) N_{\text{foreign}} D_{\text{coeff, ref}} d_{\text{max}} t
\]

(5B2)

\( D_{\text{coeff, ref}} \) is the diffusion coefficient of condensable component (water-vapor) in the carrier gas (air) at standard atmospheric pressure and temperature conditions.

Eq. 5.6 is then transformed into these dimensionless variables \( d^* = \frac{d}{d_{\text{max}}} \) and \( t^* \) as:

\[
\frac{d(d^*)}{dt^*} = (d^*) \frac{\gamma_{H_2O}^f}{\gamma_{H_2O}^f} \left( 1 - \frac{1}{S} \right)
\]

(5B3)

On the right side of eq. 5B3, the ratio \( \gamma_{H_2O}^f / \gamma_{H_2O}^f \) represents the depletion term for the concentration of water-vapor in air. Concentration \( \gamma_{H_2O}^f \) of water-vapor in air is decreasing because of the diffusion of water-vapor molecules on the surface of foreign nuclei and is coupled to \( d^* \) (see eq. 4.20 and eq. 4.22) as:

\[
y^* = 1 - d^3
\]

(5B4)
Appendix 5B Characteristic time scale of condensation growth

Using eq. 5B4 in eq. 5B3 we get,

\[
\frac{d(d^*)}{dt} = (1-d^*)(d^*)\left(1 - \frac{1}{S}\right)
\]  \hspace{1cm} (5B5)

In eq. 5B5, \(S\) is supersaturation and is not independent of \(d^*\) or \(t^*\). We already derived in chapter 4, the rate of change of supersaturation during the expansion cooling depends upon the rate of change of condensable vapor concentration (\(y\)) in the gas and the rate of expansion cooling as:

\[
\frac{d\ln S}{dt} = \frac{d\ln(y)}{dt} + \beta P
\]  \hspace{1cm} (refer eq. 4.3)

We transform eq. 4.4 into \(t^*\) and \(d^*\) and it becomes,

\[
\frac{d(\ln S)}{dt^*} = \frac{d(\ln(1-d^*^3))}{dt^*} - \left(\frac{\beta P}{N_{\text{foreign}}D_{\text{fmax}}D_{\text{max}}}\right) = \frac{d(\ln(1-d^*^3))}{dt^*} - \alpha
\]  \hspace{1cm} (5B6)

In eq. 5B6, \(\alpha\) represents the ratio of characteristic time scales of expansion and diffusional condensation growth. Eq. 5B6 and Eq. 5B5 can be solved simultaneously to obtain the growth of droplet of diameter \(d\) in time \(t\).

The condensation growth of the droplet of diameter \(d\) is completed (given by eq. 5B5 and eq. 5B6), when the thermodynamic phase equilibrium conditions are reached at the end of expansion. In other words, when \(d\) approaches the corresponding equilibrium diameter \(d_{\text{eq}}\). The phase equilibrium conditions are changing because of the change in pressure and temperature of the flowing air/water-vapor mixture during the expansion cooling. This means that \(d_{\text{eq}}\) is actually a function of time \(t\) during the expansion and is calculated in next section.

### 5B.2 Changing equilibrium droplet size \(d_{\text{eq}}(t)\) during the expansion

In appendix 5A, we calculate the equilibrium droplet size corresponding to the phase equilibrium conditions at the outlet of our test section. Here, we calculate the variation of the equilibrium diameter \(d_{\text{eq}}(t)\) during the expansion. We intend to calculate the time scale in which the growing diameter \(d\) (t) of the droplet will approach the equilibrium diameter \(d_{\text{eq}}(t)\) in time.

The difference of equilibrium condensable vapor concentration \(y_{v,\text{eq}}^o\) and the feed concentration \(y_{f,\text{eq}}^o\) can be translated into the equivalent equilibrium diameter \(d_{\text{eq}}\) as:
Experimental Validation of Droplet Growth Model

\[ N_{\text{foreign}} \frac{\pi}{6} d_{eq}^3 \rho_{\text{liq}} = \rho (y_f^{H,O} - y_s^{H,O}) \]  \hspace{1cm} (5B8)

\[ N_{\text{foreign}} \frac{\pi}{6} d_{eq}^3 \rho_{\text{liq}} = \rho y_f^{H,O} \left( 1 - \frac{y_s^{H,O}}{y_f^{H,O}} \right) \]  \hspace{1cm} (5B9)

In eq. 5B9, the ratio \( \frac{y_f^{H,O}}{y_f^{H,O}} \) is changing it time \( t \) because of the change in pressure and temperature conditions during the expansion. The change in this ratio is derived from eq. 4.4 by omitting the first term on the right side of the equation as:

\[ \frac{y_f^{H,O}}{y_f^{H,O}} = \exp(P \beta t) \]  \hspace{1cm} (5B10)

Now, using eq. 5B10 in 5B9 and defining \( d_{eq}/d_{max} \) and \( t^* \) as the dimensionless equilibrium diameter and the dimensionless time, we get

\[ \frac{d_{eq}^3}{d_{max}^3} = 1 - \exp(-\alpha t^*) \]  \hspace{1cm} (5B11)

The two simultaneous differential equations eq. 5B6 and 5B5 are solved to obtain \( d^* \) in time \( t \) for given \( P, N_{\text{foreign}} \) and \( d_{max} \). Eq. 5B11 can also be solved for dimensionless equilibrium diameter \( d_{eq}/d_{max} \) in time \( t \) during the expansion. Fig. 5B1 shows a typical variation of \( d^* \) and \( d_{eq}/d_{max} \) with \( t^* \) for different \( \alpha \). \( d \) approaches the equilibrium diameter \( d_{eq} \) with in the time of expansion as long as \( \alpha < 1 \), (expansion is slower than diffusion). The characteristic time scale for the condensational growth of the droplet is approximated as:

\[ t_{\text{growth}} \sim \frac{1}{N_{\text{foreign}} D_{\text{coeff}} d_{max}^4} \]  \hspace{1cm} (5B12)
Figure 5B1: Variation of dimensionless diameter ($d/d_{\text{max}}$) and dimensionless equilibrium diameter ($d_{\text{eq}}/d_{\text{max}}$) with dimensionless time $t^*$ for two different values of $\alpha$. As long as expansion is faster than the characteristic growth time scale ($\alpha < 1$), $d$ approaches $d_{\text{eq}}$ with in the time of expansion. The thermodynamic phase equilibrium is established at the end of expansion.
Appendix 5C

Process conditions

Table 5C1. List of process conditions during the measurements of heterogeneously condensed water droplets. The last two columns of this table are not direct measurements but calculated for the corresponding process conditions.

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<th>$N_{\text{drops}}$ (m$^3$ of air)</th>
<th>$d$ (3,0) (µm)</th>
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## Appendix 5C Process conditions

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All shaded rows in the table 5C.1 are wrong measurements because of the lens contamination or change in background noise during the droplet size measurement. Typical examples of wrong measurements are depicted during the transmission measurements and as shown below in fig. 5C1

![Figure 5C1: Measured transmission values during the measurement of heterogeneously condensed water droplets in air](image-url)
Chapter 6
Conclusions

The process of condensed rotational separation relies on expansion cooling to preferentially condense one of the components from a gas mixture. As a result a mist of micron sized droplets is formed that are subsequently separated. The expander has to be designed in such a way that the droplet size is above 0.5 µm for the effective mechanical separation. A model is developed and experimentally validated for the prediction of the droplet size after expansion.

Size measurements for CO\textsubscript{2} rich droplets formed by the isenthalpic expansion cooling (using a J-T valve) of CO\textsubscript{2}/CH\textsubscript{4} or CO\textsubscript{2}/N\textsubscript{2} gas mixtures were performed in a pilot scale CRS test unit in Shell Amsterdam. Measurements were done for feed concentrations between 20 mole % and 60 mole % in nitrogen (N\textsubscript{2}) and methane (CH\textsubscript{4}). There will always be some gas volume between the expander and the separator in which droplets grow. The corresponding residence time (induction time) was 0.2 s for the tested process conditions.

An optical reflectance probe was used for the measurements for CO\textsubscript{2} rich droplets. The optical reflectance method yields the chord lengths rather than the actual diameters. These chord lengths need to be converted to the corresponding diameters to obtain the real diameters. This method can be used for the relative measure of liquid fractions but for absolute values, exact sampling volume should be known.

Measured CO\textsubscript{2} rich droplet sizes ranged between 1 and 100 µm for the tested process conditions with typically 50-90% of the droplets in the range 1-20 µm. The measured number densities of the condensed CO\textsubscript{2} droplets were on order of 10\textsuperscript{14} m\textsuperscript{-3} of the gas.

A model is developed based on classical nucleation theory to compare and characterize the influence of process parameters on the condensed CO\textsubscript{2} droplet size. Homogeneous condensation was considered to illustrate the worst case estimate for number densities and droplet sizes. The model predicted a nearly mono-disperse size distribution of condensed CO\textsubscript{2} droplets formed by the continuous expansion cooling of CO\textsubscript{2}/CH\textsubscript{4} or CO\textsubscript{2}/N\textsubscript{2} mixtures.
Expansion was faster than the formation of clusters (droplets) itself for the CRS process conditions. On this basis, a simple analytical model was developed to obtain the mean number density and size of homogeneously condensed droplets under varying process conditions. The process conditions influencing droplet number density were combined into three dimensionless parameters. The calculated droplet number density is mainly affected by the average rate of expansion and the surface tension of condensing liquid. For the typical expansion rates of turbines and valves \((10^2-10^3 \text{ s}^{-1})\) and for the range of surface tension of pure CO\(_2\) between 2 mN/m and 15 mN/m, the calculated number density of homogeneously condensed CO\(_2\) droplets was between \(10^{12}-10^{16} \text{ m}^{-3}\) of the gas. The corresponding condensed CO\(_2\) droplet sizes were between 1 and 10 \(\mu\text{m}\) for 1 % liquid volume load based on the analytical model predictions. For 5 vol. % liquid load, the calculated droplet size will range between 2 \(\mu\text{m}\) and 20 \(\mu\text{m}\).

A continuum diffusion growth model used for the predictions of homogeneously CO\(_2\) droplet sizes was validated experimentally by expanding humid air in a converging straight nozzle. In this case, droplets were formed heterogeneously. Measured water droplet sizes were quite in agreement with the predictions of the model based on the continuum diffusional growth. Our analysis based on condensation of steam droplets in air suggest that induction time can be further shortened further because the condensation growth of the droplets could be completed within the expansion time (~ 1 ms). A shortened induction time will enhance the compactness of the condensed separation unit. However, this effect still needs to be tested for CO\(_2\) droplets.
Bibliography

44. Ehrler F.; Reppe K.H.; Schubler J.; Treffinger P. Wright W. Special cloud chambers for investigations of homogeneously nucleated spontaneous condensation. Experiments in Fluids, 1996, 27, 363

47. Konopka P. Binary condensation on soluble aerosols- on the activation and growth of the stratospheric aerosol from coupled HNO$_3$-H$_2$O uptake. Journal of Aerosol Science, 1997, 28, 1411


50. Theunissen T.; Golombok M.; Brouwers J.J.H.; Bansal G.; Benthum van R. Liquid CO$_2$ droplet extraction from gases. Energy, 36 (5), 2011, 2961


55. Malvern Sparytec manual 2010


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Curriculum Vitae

Gagan Bansal was born in Ludhiana, India on 12 April 1984. He finished his high school in 2001. He obtained his B.Tech. in mechanical engineering from Punjab Technical University, India in 2005. This included two internships in manufacturing optimization at GS Radiators and metal cutting shaper mechanism improvement at GS Auto Int. Ltd.

He then obtained his M.Tech. from Indian Institute of Technology at Kanpur, India with specialty in fluid and thermal sciences. His graduation thesis goal was a study of droplets condensing on the underside of an inclined substrate. This project was funded by Bhabha Atomic Research Centre, India. Parts of his graduation work were published in Nanoscale and Microscale Thermophysical Engineering 2009 (vol. 13, pp 184-201).

After graduation, he started his PhD in the process technology group in mechanical engineering department TU Eindhoven, The Netherlands. His PhD project was funded by Shell International Exploration and Production. The goal was to find the size of condensed CO$_2$ droplets in methane and nitrogen under varying process conditions. Parts of this work were published in Industrial Engineering and Chemistry Research 2011 (vol. 50, pp 3011-3020) and Energy 2011 (vol. 36, pp 2961-2967).