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An Investigation on Modeling and Simulation of Chilled Ammonia Process using VOF method

*Master of Science Thesis in the Master Degree Program, Innovative and
Sustainable Chemical Engineering*

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Göteborg, Sweden, 2011

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Abstract

There is a widespread interest in introducing and developing new processes for post-combustion capture of CO₂ nowadays. Chilled ammonia process is one of the most promising processes for this purpose. Computational fluid dynamics (CFD) is used to model and simulate the multiphase flow and also to predict the dynamics of the system in presence of chemical reactions. Volume of fluid is the first choice to model such a system. The kinetic mechanism of the process is quite complicated; it is characterized and introduced to the model using user defined functions. The best approach to model mass transfer through interface of gas-liquid system is investigated.

Key words: CO₂ capture, Chilled Ammonia Process, CFD, kinetic mechanism, volume of fluid

ACKNOWLEDGMENT

I would like to express my deep appreciation to my Supervisor, Professor Bengt Andersson for providing me with such a nice subject and also for inspiring and supporting me during the period I was working on my thesis. I have always enjoyed our scientific discussions.

I am sincerely thankful to Dr. Ronnie Andersson because of his great ideas that helped a lot to overcome challenges of this project.

I would like to thank my friends supporting me with memorable moments.

I dedicate this thesis to my dearest family, without their great support it was impossible to complete this thesis successfully.

April, 2011

Mohammad Khalilitehrani

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1 Introduction

The amount of carbon dioxide emissions is very significant, specifically in industrialized countries nowadays. Therefore, decreasing carbon dioxide emissions have attracted more attention than past by researchers. Several methods have been suggested in order to separate carbon dioxide from flue gas instead of releasing it to atmosphere(Darde2010).

Among above mentioned processes, post treatments have attracted more considerations due to the possibility of implementing on existing plants (Darde2010). Many processes for post capture of CO₂ have been presented by now including absorption using solvents or solid sorbents, pressure and temperature swing adsorption, cryogenic distillation, etc (Mathias2010).

CO₂ capture using aqueous amine solutions are of the most promising processes. In these processes usually the flue gas is contacted with amine solution in an absorber column countercurrently and carbon dioxide reacts with the solvent selectively. Cleaned gas leave the column from top and solvent which is rich by CO₂ is sent to a desorber where it is regenerated at higher temperature and is sent back again to the absorber. The major obstacles with current solvents mostly aqueous ethanolamine (MEA) is degradation and corrosion issues and also relatively high heat required for regeneration in the desorber (Derks2009).

The use of chilled ammonia to capture carbon dioxide was first presented and patented by Eli Gal in 2006. A purpose of this process is to absorb carbon dioxide in low temperature as indicated in the patent in a range from 0-20 C. This process absorbs CO₂ with much lower energy consumption. Moreover, degradation can be prevented using ammonia instead of aqueous amines (Darde2010).

1.1 Chilled Ammonia Process (CAP)

Chilled ammonia process contains a number of steps, first the flue gas is cooled down using direct contact coolers. Temperature should be between 0-10 after this step. The cooled gas is sent to the absorber in which it is contacted countercurrently with chilled ammonia containing a low concentration of CO₂ (CO₂-lean stream). The mass fraction of ammonia in the solvent is normally up to 28wt% and temperature is typically in the range between 0-10. This relatively cold operating condition prevents ammonia evaporation. According to these conditions 90% of the CO₂ from flue gas can be captured. The clean gas leaves the absorber column by its top while the rich stream leaves the bottom of the absorber. The rich-stream is pressurized and sent to a heat exchanger where its temperature increases, before entering the stripper. The pressure and temperature of the stripper are 2-136 atm and 100-150 C, respectively. Under these conditions CO₂ evaporates from the solution and then the solution leaves the top of the stripper. The energy demand should be considered, this energy demand significantly depends on the composition of the CO₂-rich stream entering the stripper. Captured CO₂ should be kept at high pressure. Therefore, there is energy demand for maintaining compressed streams (Darde2010).

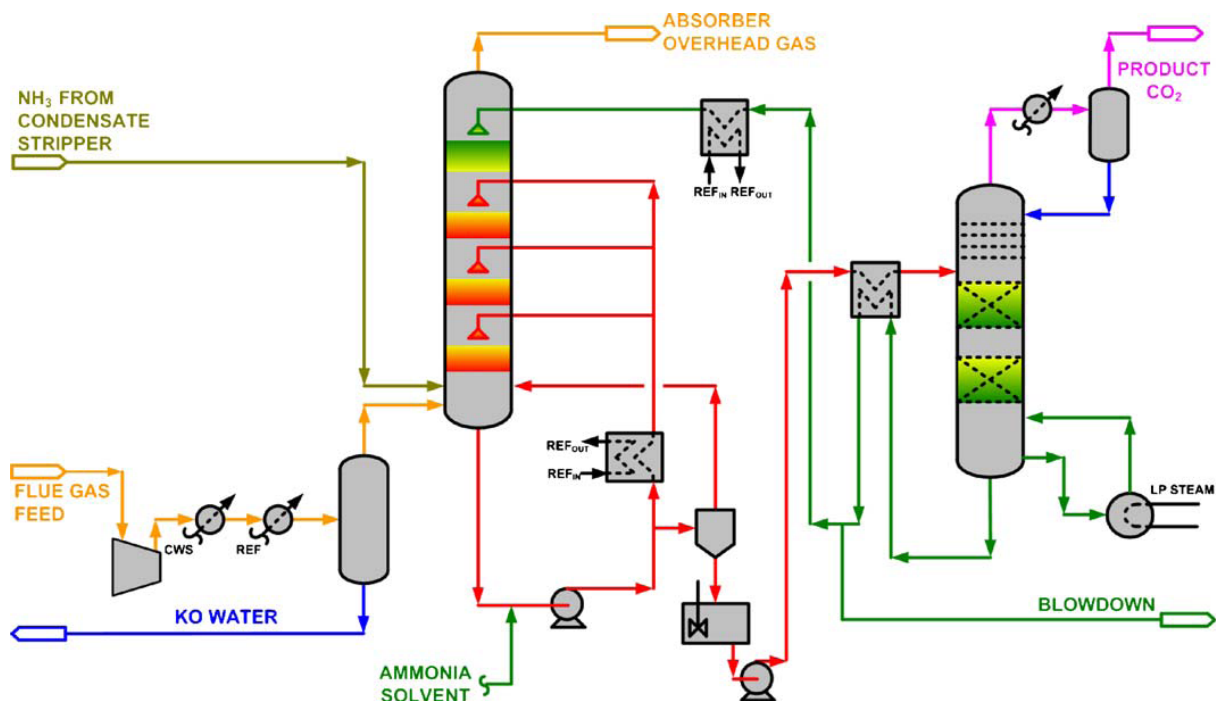
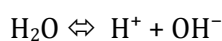
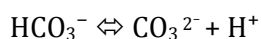
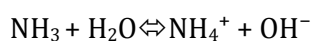


Fig1. Flow sheet of the chilled ammonia process (Mathias2010)

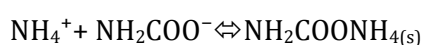
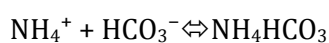
This so-called chilled ammonia process has attracted lots of interests as a post-combustion technology based on a new solvent (Derks2009).

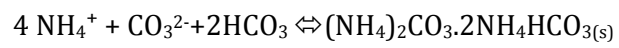
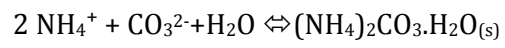
In order to assess different aspects of this process, detailed knowledge on kinetics on one side and the flow on the other side is required. Although, many researches are available in literature about thermodynamic equilibrium of NH₃-CO₂-H₂O system (Derks2009); published references on the kinetics of this system is rare. Actually, interests seem to be more lied on the definition of macroscopic potential of ammonia based solvents such as its cyclic capacity and removal efficiency than the impact of reaction kinetics on the process performance (Bai1997). Kinetic mechanism of this process is quite complicated and includes several reactions and equilibria which are presented below (Mathias2010):

Liquid phase equilibria:

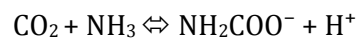


Reversible liquid-solid reactions:





The reaction of carbamate formation also occurs:



2 Aim

This study is a preliminary investigation on an extensive project which involves modeling and simulation of the process of CO₂ capture in chilled ammonia. The aim of the project is to find the best approach to assess different phenomena occurring in this process. Initially, the process is assumed in the simplest geometry and based on available data from literature. More details will be taken into account gradually in time.

This thesis is considered as an appropriate starting point for further investigations on this issue.

3 Numerical Simulation

The physical aspects of all fluid flows can be defined by three principles: Conservation of mass, momentum and energy. These set of equation are solvable for a limited number of flows analytically. More than a century ago the idea of numerical solution of the partial differential equations was established, but could not be used easily before the arrival of modern computers. Numerical simulations improved gradually by increasing capacity and calculation speed of computers and finally led to new method of computational fluid dynamics.

3.1 Computational Fluid Dynamic

CFD is a numerical approach to the governing equations of flow to obtain a numerical definition of the flow field, simply put; it replaces the partial differential equation governing the flow with a system of algebraic equations. The predicted flow can approximately describe the flow field behavior.

General condition of the system like boundaries, physical facts that describe the flow should be found, also the nature of the fluid (compressible/Newtonian) and the flow (Laminar/Turbulent) should be known. Otherwise it is not expected that a correct mathematical model be obtained. After these steps several methods can be used in order to approximate the differential equations to a set of algebraic equations.

This technique is very promising and is applicable in many different areas both industrial and non-industrial. Some of these areas are Chemical process engineering, aerodynamic of aircraft and vehicles, biomedical engineering, etc. A simulation can be a substitution for pilot plants in many applications (Wilhemsson 2004).

3.2 Finite element method

This method is based on a numerical approach to approximate partial differential equations to ordinary differential equations and then solve those equations by standard numerical techniques such as Euler method, bisection method, etc.

In this method the domain is divided into discrete elements. Then differential equations are integrated over the domain and solution is approximated by piecewise functions within the element and equations are solved as a set of non-linear algebraic equations. This method has a high ability to solve the equations for complex geometries (Andersson2010).

3.3 General governing equations

Governing equations in fluid dynamics are based on Conservation of Mass, Momentum and Energy. In this study an Isothermal condition was assumed. Therefore, energy equation will not be solved. Below Continuity and momentum equations which are based on Mass and Momentum conservation laws are described.

3.3.1 Continuity equation

Based on the theory of mass conservation:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho u$$

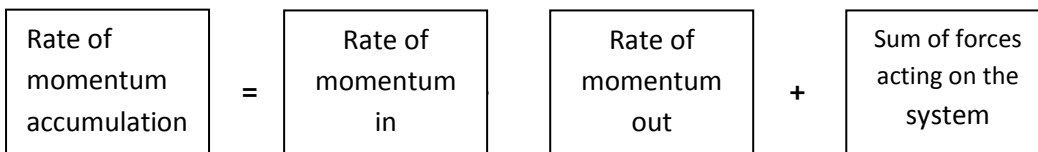
Where ρ is the density and u is the velocity vector. For an incompressible fluid this equation is simplified to (Andersson 2010):

$$\nabla \cdot u = 0$$

3.3.2 Equation of motion (Momentum equation)

Based on Newton's second law the rate of change of momentum of a fluid particle equals the sum of the forces on the particle (Andersson2010).

Two types of forces are known for a fluid particle **Surface forces** like viscous forces and pressure forces and **body forces** like gravity and electromagnetic forces (Andersson,2010).



$$\rho \frac{Du}{Dt} = -\nabla p + \mu \nabla^2 u + F$$

3.4 Multiphase systems

There are two different approaches to multiphase systems. Euler-Lagrange and Euler-Euler. Euler-Euler approach assumes phases as interpenetrating continua. It considers a value of volume fraction for each phase. The sum of these values should be equal to one each cell. There are three different models under Euler-Euler: Volume of Fluid, Mixture model and Eulerian model.

In the current study Volume of Fluid is used which is described in next section.

3.5 Volume of Fluid (VOF)

VOF is an Eulerian approach that tracks the position of interface using volume fraction value. This method is normally used to track the interface in systems with more stratified interfaces. Like open surface falling films, channel flows or systems with large bubbles, droplets, particles or generally immiscible fluids with clearly defined interface. This method is not applicable for the systems in which length scale of interface is much smaller than that of computational domain like very small bubbles or droplets in another fluid. It should be mentioned that interface is not a straight line and it has always a finite curvature. Hence, surface tension forces are important. This method includes two different tasks, the interface reconstruction and the volume fraction re-estimation (Gao2003).

VOF resolves the flow field by solving Navier-Stokes equations and then updates the position of the interface by updating the field of volume fraction. An advantage of this method is that there is no limitation for the position of interface; correspondingly, it is widely used to track the interface of fluids (Gao2003).

This model is based on this idea that phases are not interpenetrating. For any phase, a volume fraction value is added to the cell information, it is clear that the sum of these values should be equal to 1 (Andersson2010).

$$\sum \alpha_i = 1$$

Cell properties are determined as below:

$$\varphi = \sum \alpha_k \varphi_k$$

Where α_k is the volume fraction of phase k and φ_k is a specific property of phase k like density or viscosity.

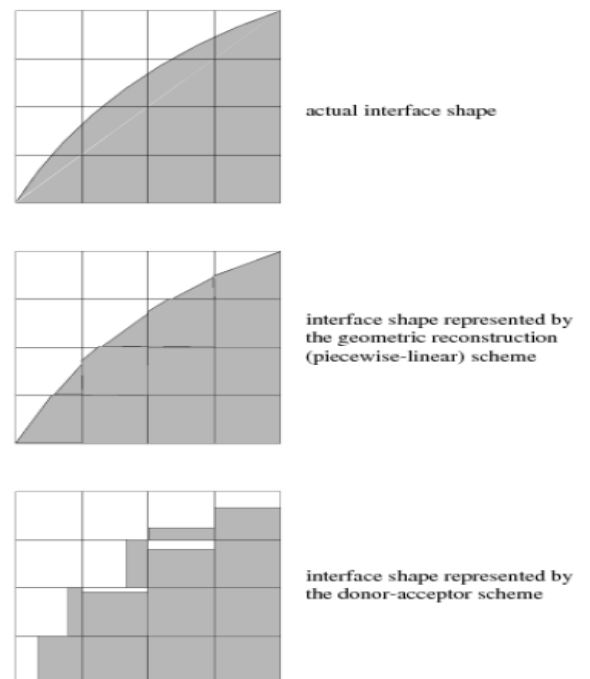
To track the interface, continuity equation for volume fraction of each phase should be solved. This equation is as below:

$$\frac{1}{\rho_q} \left[\frac{d}{dt} (\alpha_q \rho_q) + \nabla \cdot (\alpha_q \rho_q \vec{v}_q) \right] = \delta_{\alpha_q} + \sum (\dot{m}_{pq} - \dot{m}_{qp})$$

In equation above, \dot{m}_{qp} is the mass transfer from phase q to p and vice versa (Ansys.Inc 2010).

To solve this equation, different schemes are available under VOF model. Figure shows the ability of these schemes to track the location of interface

Geometric reconstruction scheme as it can be seen, assumes that interface between two fluids has a linear slope in each cell and solves this slope using a piecewise linear approach. It is the most accurate scheme and is applicable for both structured and unstructured mesh (Ansys.Inc 2010).



4 Theoretical Background

4.1 Flow consideration

For liquid films falling down vertical flat surfaces, laminar flow is assumed for Reynolds numbers less than 2000 from formula below:

$$Re = \frac{4\Gamma}{\mu}$$

Where Γ is liquid mass flow rate per unit width of surface and μ is viscosity. Reynolds number should be defined in order to determine the appropriate model (Laminar or Turbulent)

In this study 1mm thickness was assumed for liquid film which corresponds to Reynolds around 200 which will be assumed as Laminar flow (H.Perry 1997).

4.1.1 Effect of surface traction

The drag force caused by surrounding fluid influences the outer surface of the falling liquid film. Depending on the direction of this force, film thickness would be different which cause natural waves on the outer layer of liquid film (H.Perry 1997).

4.1.2 Ripples

Depending on the film Reynolds number, flows are categorized into three different regimes. These regimes are:

1-Smooth laminar flow, $Re < 20$

2-Flow with surface waves in transition region, $20 < Re < 4000$

3-Fully turbulent flow, $Re > 4000$

The second flow regime can be divided into three sub-regimes: capillary wavy-laminar, inertial wavy-laminar and inertial-wavy-turbulent flow, respectively correspond to $20 < Re < 200$, $200 < Re < 1000$ and $1000 < Re < 4000$. By increasing Re , first capillary waves are incepted on the surface and for higher Reynolds, Roll waves are mostly observed. These two regimes are shown in figure2 (Patnaik 1996):

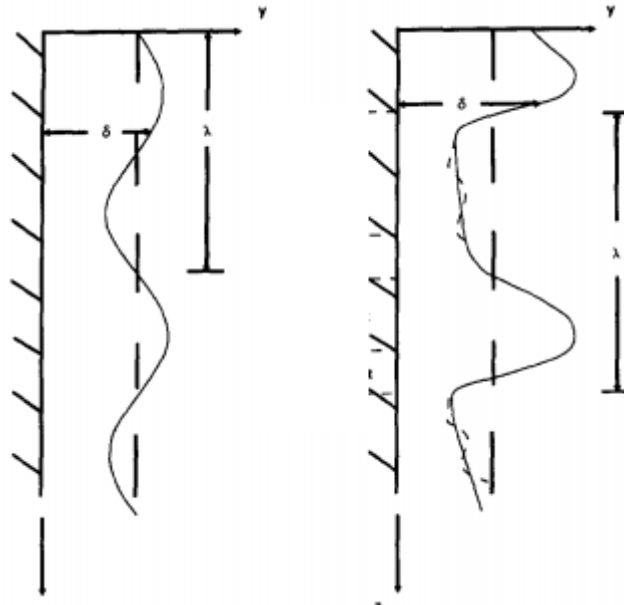


Fig2: Left: capillary waves, Right: Roll waves (Patnaik 1996)

Capillary waves are more like smooth repetitive oscillations (they are also called sinusoidal waves), but roll waves are more like rolling down over a film substrate (Patnaik 1996).

In this study based on the Reynolds number, flow is in the capillary wavy-laminar regime. In this regime, surface tension forces are so important in formation of waves. These capillary waves are formed as ripples on the surface with small amplitude and high frequency (Patnaik 1996).

4.2 Mass transfer

Mass transfer through interface depends on transport properties such as diffusivity. It should be considered that when there is parallel flow, mass transfer will be dependent on a combination of properties and conditions. For a stagnant media without velocity gradient, diffusivity may be enough to express the process based on Fick's first law.

$$J = -D\nabla\phi$$

In equation above J is the diffusion flux; D is diffusivity constant and $\nabla\phi$ is the concentration gradient.

Interphase mass transfer is a basic phenomenon for most of the separation processes. When mass is transferred from one phase to another across the interface, the resistance in each phase causes a concentration gradient (H.Perry 1997).

4.2.1 Two-film Theory

This theory assumes an ideal system with two stagnant immiscible fluids and considers mass transport resistances only in two stagnant films neighboring the interface. Therefore, mass transfer will be a stationary diffusive transport through stagnant film layer, shown in figure 3:

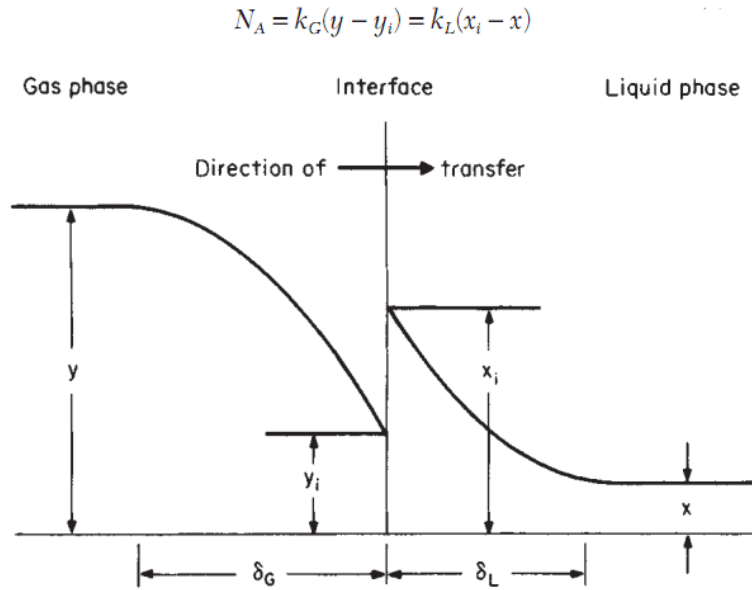


Fig3.mass transfer through interface (Ansys.Inc 2010)

It is assumed that on the interface, there is equilibrium between concentrations of transferring materials in interconnected phases. Based on Henry's law at a constant temperature, the amount of a given gas dissolving in a given volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with the liquid. This equilibrium is expressed by Henry's constant which is a ratio between concentrations in phases specifying the equilibrium state.

$$He = \frac{P_i^g}{C_i^L}$$

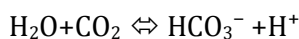
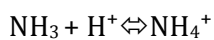
In equation above P_i^g and C_i^L are partial pressure and concentration of transferring material at the interface and in gas phase and liquid phase respectively.

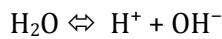
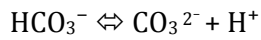
The value of He for CO₂ in 25°C is $2937 \frac{Pa}{(\frac{mol}{m^3})}$ which is used to define the mass transfer flux through the interface in this study (Plambech 1995).

4.3 Kinetics

Kinetics of the reactions and equilibria in CAP process is surveyed in several literatures (Derks 2009). As mentioned before, the kinetic mechanism of this process consists of different multiphase equilibria and reactions. Liquid-solid reactions were neglected, since these reactions are not considerable at the top of absorber column which is studied in this project. Moreover, it causes a 3 phase system which is more difficult to assess.

Liquid phase equilibria:





The reaction of carbamate formation also occurs:



The rate of carbamate formation is the rate determining step of the process. Reaction rate for this step has been studied in several researches. But the results show big differences in predicted values for reaction rate constant. Table 1 shows a comparison of the rate constants from different sources:

Temperature[K]	Puxty et al.(2009)	Pinsent et al. (1956)	Derks & Versteeg(2009)
278	574	107	300
283	915	155	700
293	2217	313	1400

Table1: Reaction Rate constant for carbamate formation ($\text{Lmol}^{-1}\text{s}^{-1}$) from different sources

Note: In this study temperature was chosen at 293 K and the value of 1400 based on Derks and Versteeg was used to determine the rate of carbamate formation (Derks2009).

From the dimension of rate constants, it is found that carbamate formation could be assumed pseudo-first order reaction, since the concentration of NH_3 in the process is high. Based on Derks and Versteeg, the major disadvantage of applying high concentrations of ammonia, is its volatility, which needs post treatments like washing sections to decrease ammonia slip from top of the absorber (Derks2009).

From numerical simulation point of view, direct reactions are very straight forward to be assessed, but equilibria cause stiff ODE systems with highly unstable solutions. The reason is that the rate, by which species approach to equilibrium is very large and the process may be assumed pure instantaneous. Therefore, the value of K_f is extremely large which cause a highly stiff system of ODEs [$y' = k y, k \gg 1$] and is unlikely to be thoroughly handled by Fluent solver (Alfredsson 2010).

5 Methodology

This system is classified as a stratified flow with large and continuous interface. Consequently, VOF model is an appropriate multiphase model for such a system.

5.1 Single-phase case

As the First step, a simplified single-phase system was assumed consists of a liquid falling film with constant diffusive flux from a boundary assumed gas-side to test the possibility of assessing reactions and equilibria using mass source terms

Assuming t is diffusion time and D is diffusion coefficient for CO_2 in solvent, the diffusion length will be \sqrt{Dt} in which the diffusion time is dependent on the falling velocity. It is clear that all reactions occur in the area between liquid-gas interface and \sqrt{Dt} inside the liquid film, where CO_2 and NH_3 co-exist. Source terms for reactions were developed in this step which worked very well. Although the solution was relatively unstable, it was controlled by low under-relaxation factors. Next step was to introduce the countercurrent gas flow. A new geometry should be defined in a way to be able to track the ripples on the interface and the mass transfer through it.

5.2 Multiphase case

5.2.1 Geometry

In the new geometry there is no frozen line as the interface; the interface is completely flexible to be able to track the changes in shape of film's outer surface which is expected because of ripples and it is clear that freezing the interface cause an over-defined settings which does not let the interface to be assessed in VOF model. The only parts which are frozen in this geometry are walls, inlet and outlet boundaries. Moreover the bottom line of the system which is liquid outlet and gas inlet is not split since the liquid outlet boundary is changing because of ripples.

5.2.2 Meshing

In meshing section a structured quadrilateral mesh was chosen without any inflation or initial refinement. It was refined later in Fluent by mesh adaption in parts which required finer mesh.

The most critical region in the system is the region near to the interface, because of important phenomena occurring in this region. The ripples should be tracked, mass transfer through interface should be assessed and as discussed before, because of very short diffusion length, main reactions occur in this region. Accordingly, very fine mesh is required in this region in order to predict all happenings precisely. Diffusion length determines the region should be refined inside the liquid phase. It should also be considered that in VOF model, interface line is approximated with a transition region for volume fraction, clearly coarse mesh make this assumption very rough. Final mesh after these refinements is shown:

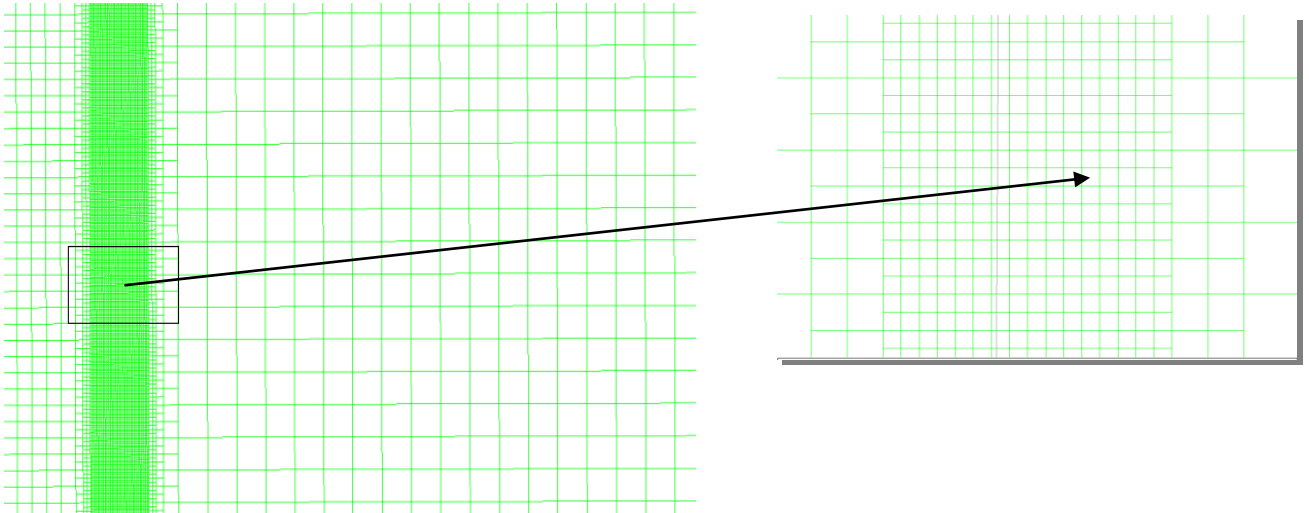


Fig4. Mesh

Cell dimensions are around 40 μm near the interface. Considering the diffusion length estimated in appendix2, the cell dimension should be decreased to at least 20 times smaller than this value to be able to track the gradient of CO_2 concentration. This will increase the computational time drastically.

5.2.3 Boundary conditions

For gas outlet and the bottom line of the system which is liquid film outlet shared with gas inlet, pressure boundaries were chosen. Liquid inlet, on the other hand, was set as velocity inlet on which a developed profile was transferred to avoid unphysical plug flow as inlet boundary.

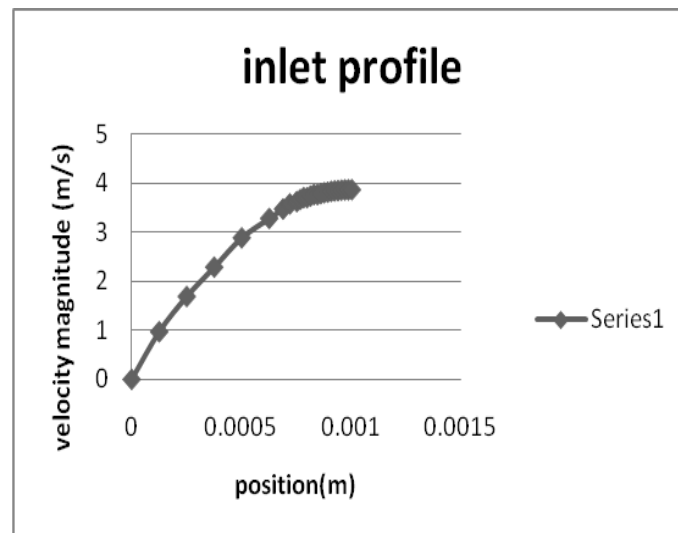


Fig5. velocity profile for liquid inlet

5.2.4 Flow considerations

As mentioned, Reynolds number for a falling film with 1mm thickness is around 200. Comparing to the criteria described in previous section. Flow could be considered as laminar. Therefore, laminar model is valid for such a system.

Additionally, to track ripples on the outer surface, surface tension was introduced in phase interaction panel and mesh was refined in an area around interface to reach more smooth waves. Geometric reconstruction scheme is the best scheme to solve volume fraction in this case by which, excellent profile for volume fraction is obtained. Figure 8 shows these waves incepted on film surface.

For further information around simulation of wavy falling film, interested reader is referred to an article by Gao et al. entitled “wavy falling film flow using VOF method” (Gao 2003).

5.3 UDF

User defined functions are powerful tools in order to rearrange equations solved in FLUENT. UDFs are written in C++ or FORTRAN and easily can be entered to the main solver as source terms, initial values, profiles and even extra transport equations.

A major part of this project was using user defined functions in order to assess different phenomena occurring in the system including Mass transfer through interface, reactions and equilibria.

5.3.1 UDFs for multiphase systems

As described, in euler-euler approach to multiphase systems, a volume fraction value is given to computational cells for each phase. It should be added that although properties are defined for cells containing multiple phases based on volume fractions, each phase has its own set of variables and properties. Therefore, a multi-domain architecture stores the phases in different overlaid sub-domains. These domains can exchange momentum, mass and energy with each other. Pointers are useful tools in multiphase UDFs, by which it is possible to access information, correspond to a specific phase, zone or domain.

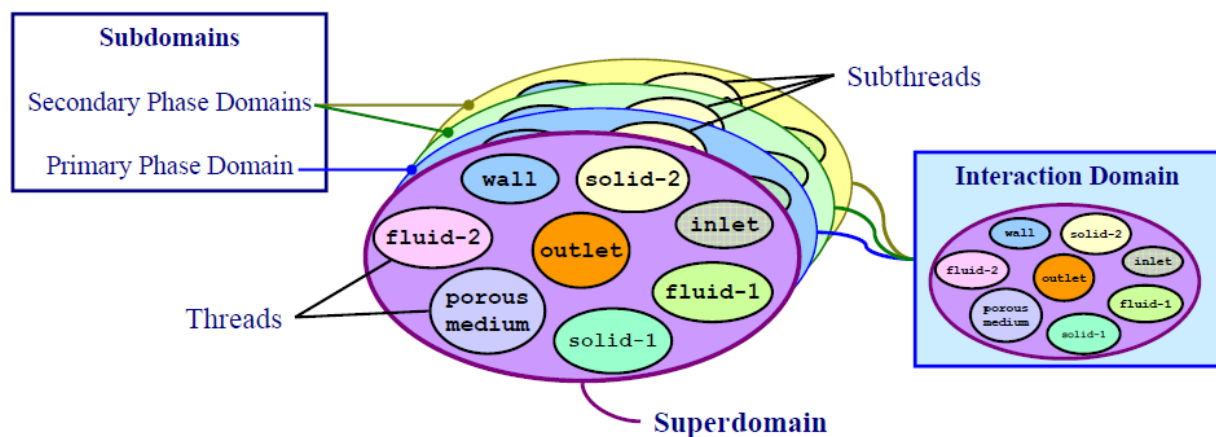


Fig6. Data structures in fluent (Ansys.Inc 2008)

There are also several macros specified for multiphase systems like DEFINE_MASS_TRANSFER, DEFINE_HET_RXN_RATE, etc which avoid complicated codes to define different phenomena for multiphase systems.

5.3.2 Reactions

Reactions and equilibria were determined as mass source terms. The value of reaction rate should be estimated based on specific kinetics available in literature and its value can be

introduced to FLUENT as mass source terms for all species present in the reaction (Reactants and Products). For example, for a reaction like $a + b \rightarrow c + d$, the source term is defined as:

$$\text{Source} = K_f [a][b]$$

It is clear that this source term should be used as negative source terms for reactants and positive for products.

To define equilibrium in a numerical point of view it should be considered that equilibrium consists of a forward and a backward reaction which their rate constants are related by equilibrium constant.

$$K_{eq} = \frac{K_f}{K_b}$$

Consequently, it is possible to determine the source term corresponds to equilibrium like $a + b \leftrightarrow c + d$ as below:

$$\text{Source} = K_f [a][b] - \frac{K_f}{K_{eq}} [c][d]$$

Note: As mentioned before, the value of K_f is very large which make a highly stiff system of ODEs. To handle such a system, one way is to couple more powerful softwares with FLUENT solver, like stiff ODE suite or MATLAB ODE15. Hence, it is possible to choose timesteps much larger than the timescale of the stiff ODE system (Alfredsson 2010).

A simpler but less accurate approach is to assume the rates of approach to equilibrium, orders of magnitude larger than reaction rates. But it needs to set timesteps very small (smaller than timescale of reactions).

This approach causes some problems numerically; looking at the reaction and equilibrium's mechanisms it is realized that these source terms are strongly dependent on each other which make it so difficult to solve the equations explicitly. Therefore, very small under-relaxation factors are needed. Instabilities due to stiff reaction mechanism are hard to control and it can cause unexpected divergences.

To overcome this obstacle several techniques were applied. Inlet composition was set to a composition in equilibrium which avoids very large source terms. The concentration values were defined based on proposed equilibrium compositions for different CO₂ loading in an article by Darde et al. entitled "chilled ammonia process" (Darde2010).

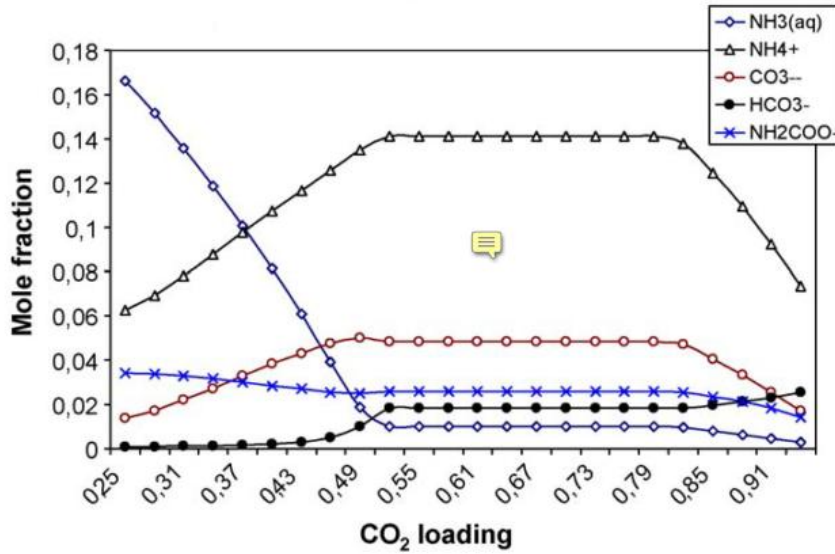


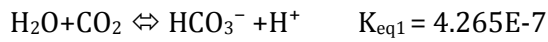
Figure7.equilibrium composition of the liquid phase for 28%wt% in 8°C as a function of CO2 loading (Darde2010)

Note: these values have been obtained for 8°C, for 20°C the composition will be slightly different which are shown in table2

species	Mole fraction
NH_3	0.138
CO_2	9.844e-7
CO_3^{2-}	2.2e-4
HCO_3^-	1.2838e-3
NH_4^+	7.8e-2
H^+	7.54e-12

Table2: The composition of liquid inlet

Another important source of instability is the presence of H^+ in all equilibria, which causes very stiff formulation for concentration of H^+ . To avoid such a problem, several algebraic formulations for estimation of $[H^+]$ were examined. First, a logical constant value was chosen as the concentration of H^+ ; then some arrangements based on the concentrations of other species were tested and finally an algebraic averaging on estimated values for $[H^+]$ from equilibrium constants using some logical weighting factors was defined to estimate $[H^+]$, which gives both reasonable results and more stable solution. This new formulation is shown:



$$H_1 = C_{\text{NH}_4} / (C_{\text{NH}_3} * k_{\text{eq}2})$$

$$H_2 = k_{\text{eq}1} * C_{\text{CO}_2} / C_{\text{HCO}_3}$$

$$H_3 = k_{\text{eq}3} * C_{\text{HCO}_3} / C_{\text{CO}_3}$$

$$C_{\text{H}} = (C_{\text{NH}_3} * H_1 + C_{\text{CO}_2} * H_2 + C_{\text{HCO}_3} * H_3) / (C_{\text{NH}_3} + C_{\text{HCO}_3} + C_{\text{CO}_2})$$

This kind of formulation for $[\text{H}^+]$, makes the solution more stable, but it should be considered that it is not the most accurate algebraic formulation for $[\text{H}^+]$, it may be improved for further investigations.

5.3.3 Mass transfer

Mass transfer through interface is another important part of Chilled ammonia process to be assessed by UDFs, which was defined by a macro specified for this purpose entitled "DEFINE_MASS_TRANSFER". To define this phenomenon, mass transfer rate should be calculated inside the cells which are present in interface region (as discussed before in VOF model interface is tracked as a transition region).

To model this phenomenon, mass transfer coefficient should be estimated. Another parameter to be defined is the effective interfacial area per unit volume (a_i). It is assumed that ripples on the outer surface do not have a considerable influence on mass transfer. Without any ripples on the surface, interface will be a straight line. Based on Two film theory, mass transfer rate could be written as:

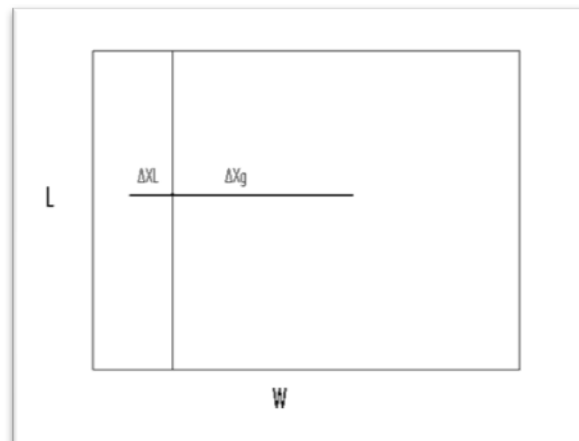
$$K_L a_i (C_i - C_{\text{bulk}})$$

Where K_L is mass transfer coefficient, a_i is effective interfacial area and C_i and C_{bulk} are interfacial and bulk concentrations of transferring component respectively. Figure below and following Calculations show the procedure to estimate different mass transfer parameters.

$$K_L = \frac{D_L}{\Delta X_L}$$

$$\Delta X_L = \alpha_L \cdot \frac{W}{2}$$

$$\Delta X_g = \alpha_g \cdot \frac{W}{2}$$



Where α_i is the volume fraction of Phase i, ΔX_i is the thickness of the film in each phase regarding two film theory and D_L is diffusivity of transferring material in liquid phase.

In a cell, the effective interfacial area per unit volume will be equal to $\frac{L}{LW}$ or $\frac{1}{W}$.

Therefore, the rate of mass transfer can be written as:
$$\frac{2 \cdot D_L \cdot (C_i - C_{bulk})}{\alpha_L \cdot W^2}$$

To estimate the cell dimension, a loop was determined around all nodes of each cell to find the maximum difference between X-coordinates of all pairs of nodes. This maximum value is considered as cell dimension in X axis.

This kind of formulation for mass transfer through interface causes a mesh dependent solution and it seems that assuming a center of mass for each phase is not a valid assumption based on VOF model formulations. Correspondingly, VOF model does not seem an appropriate model for mass transfer through interface, since concentration gradient will not be estimated accurately, without assuming center of mass for each phase within cells inside interface region.

In order to gain a mesh independent formulation for mass transfer, it was tried to obtain a formulation in which the net flux of CO₂ from gas phase to liquid phase be unchanged by mesh adaption. Assuming a constant value for effective interfacial area (a_i) it is possible to rearrange the formulation in a way that net flux of CO₂ remains constant. Below this new formulation for mass transfer is described:

A simple multiphase system with only two cells is assumed. In such a system and using the same approach as above, the source term corresponds to mass transfer rate is estimated as below:

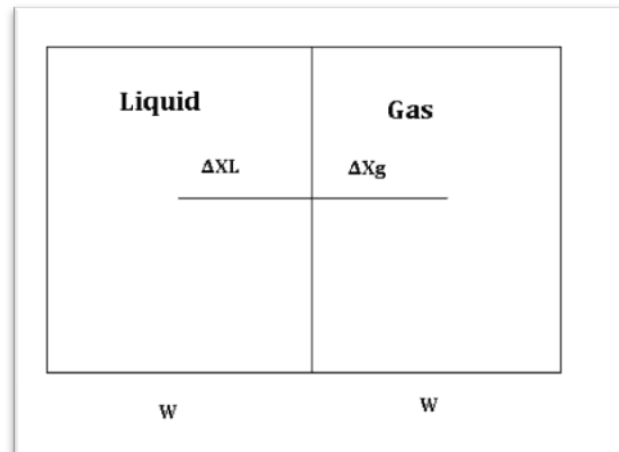
In this system:

$$\Delta X_L = \frac{W}{2}$$

And the source term will be:

$$\frac{2 \cdot D_L \cdot (C_i - C_{bulk}) \cdot a_i}{W}$$

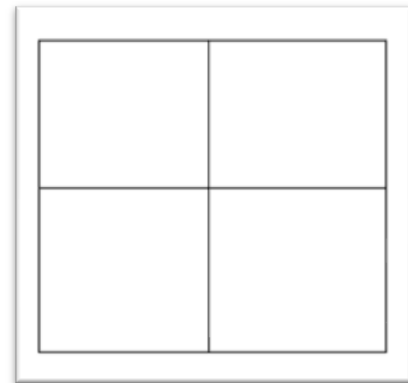
In equation above (a_i) is the effective interfacial area.



For $0 < \alpha < 1$, the volume of the secondary phase which is basis to estimate the amount of mass transferred through interface, is smaller with a factor of α . Therefore, applying this source term which is obtained from the simple system above, the amount of mass will be $1/\alpha$ times smaller. Hence, it would be more logical to have a formulation which is not dependent on α .

It may be concluded that this formulation is also mesh dependent, because source term is function of cell dimensions. But, it should be noted that in this formulation by refining the mesh the net flux remains constant. This fact can be approved analytically below:

Considering the refined cell presented here, looking at the formulation above, mass transfer rate for each refined cell will be greater by a factor 2, on the other hand, the volume of each cell is 4 times smaller. Accordingly, half amount of mass is transferred within each cell comparing to the original cell before refinement. Regarding that in new mesh structure, instead of each cell there will be two cells neighboring the interface; the amount of mass transferring through the interface in the whole system remains unchanged. It can be concluded that the net flux of CO₂ in the whole system will remain constant through mesh adaption. It should be pointed out that the concentration of CO₂ in cells in this interface region and the reaction rate will increase by the same factor which is a drawback of this formulation, but considering the volume of liquid phase in the cells in aforesaid region, the Net amount of CO₂ transferring through interface and reacting inside the liquid phase remain independent of cell dimensions.



Another challenge is that when it is assumed that the interface is a group of cells instead of a line, it will be difficult to assess physical phenomena such as mass transfer in such an unphysical domain. To overcome this limitation with VOF model, it was attempted to limit mass transfer source term to less number of cells. Setting a smaller range of α value in which mass transfer is happening may make the formulation more reasonable.(closer to a line)

5.4 Steady solution

As the final step steady solution was considered. According to previous discussions on instabilities, under-relaxation factors should be chosen very small which make the solution highly time consuming. In order to control instabilities, first a transient solution was performed for a time around 0.5 ms to obtain a better initial point for the steady solution. This solution will be highly time consuming regarding very small under-relaxation factors. Unfortunately, because of limited time, results from this step are not ready to present.

5.5 Judging convergence

In this study because of very small under-relaxation factors used to stabilize the solutions, residual values are very rough criteria to check convergence with. It is also impossible to judge convergence by monitoring variables within the simulation because very small under-relaxation factors cause very small change in each iteration. In order to judge convergence, the criteria were mass imbalance in each cell over the whole system. For steady solution the maximum value of mass imbalance was around 0.2% which is reasonable.

6 Results & Discussions

As discussed before, mass transfer and reactions mostly happen inside the interface region. Taking the waves on the outer layer of falling film into account will make the solution much more unstable. Moreover, having waves on the surface, there will be no steady point for the solution. It should be noted that assuming a straight line as the interface is not physically valid and continuity equation will not converge accurately. But, because of low Reynolds number and smooth sinusoidal waves on the surface, it can be inferred that waves do not affect mass transfer considerably.

Based on aforesaid reasons, the investigation was divided into two parts: flow investigation and CO₂ capture mechanism including mass transfer and kinetics. These two parts should be merged together later, in order to assess different aspects of the process more precisely.

6.1 Flow

To model the flow, a simple case was considered without mass transfer and reactions. To have a better assessment of flow behavior, Geo reconstruction scheme with very small timesteps was applied to track the interface. As mentioned, Reynolds number for such a flow is around 200. This value of Re corresponds to capillary wavy-laminar regime which was described in section 4.1.2. Figure 8 shows Capillary waves which were expected to be formed on the outer surface of the flow.

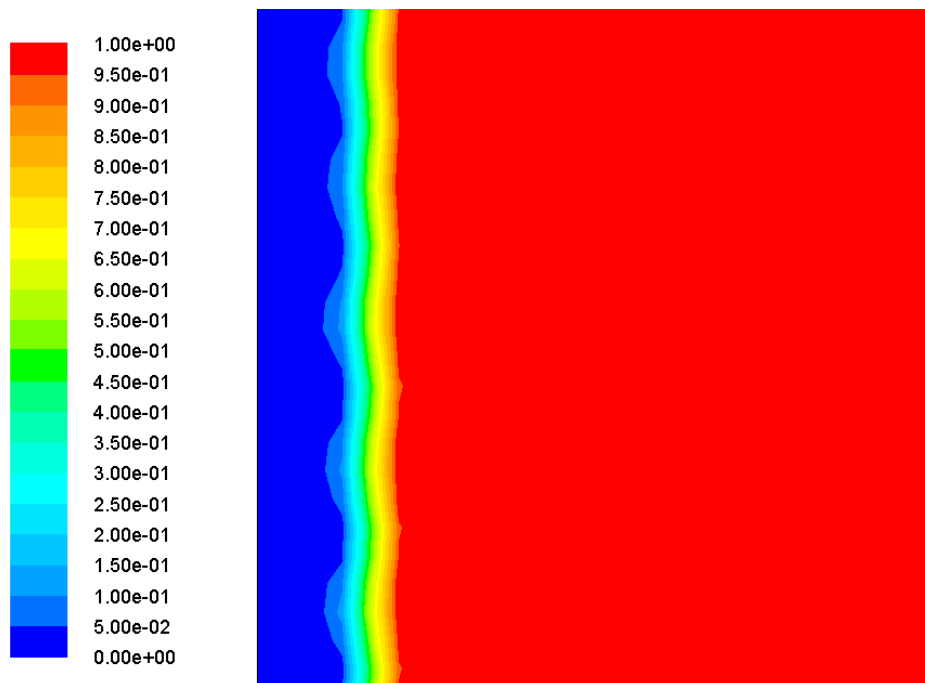


Fig8. Formation of waves on the surface

6.2 CO₂ Capture mechanism

As discussed before, VOF model assumes a region in which volume fractions of phases are gradually changed in a number of cells. This assumption is not physically valid, since interface is a 2D object which is treated as a 3D object providing an unphysical domain in which solving transport phenomena such as mass transfer through interface causes conceptual contrasts.

It should be noted that VOF is an appropriate model to predict the flow behavior for this class of multiphase flows but according to aforesaid reasons, it cannot be a proper model to define processes like the current process including mass transfer and reactions inside the interface region.

In order to have a better approximation of mass transfer inside the interface region, α value was limited to a smaller range, to obtain narrower interface. Consequently, mass transfer occurs in a thinner region resembling interface closer to a line, which is more desirable. This fact could be observed in figure 9. It is only required to find appropriate values for mass transfer parameters to fit the results on experimental data.

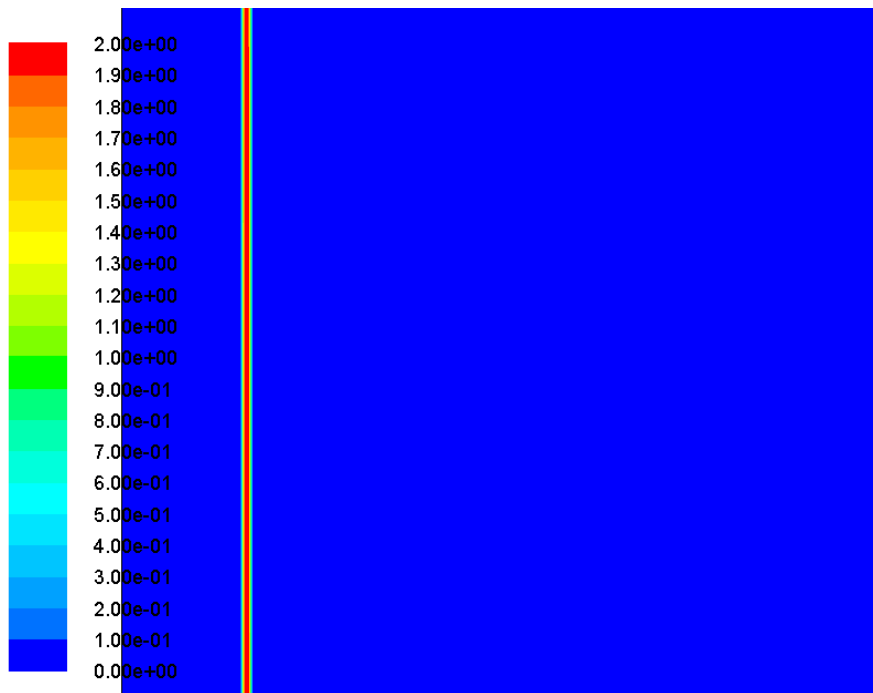


Figure9. Contour of mass transfer rate

Results from steady solution were not reasonable. It may need a longer simulation time because of very small under-relaxation factors. As mentioned before, considering the waves that should be naturally formed on the outer surface there is no possible steady solution. (Convergence issues)

To be able to compare results from single phase and multiphase cases, in case of single phase the constant concentration on gas-side boundary (an slip wall with constant concentration of CO₂ assumed gas-side boundary of liquid falling film), was defined based on the equilibrium concentration on the interface estimated by Henry's constant and partial pressure of CO₂ in gas phase as discussed in section 4.2.1. The value of 3.5e-4 was estimated as mass fraction of CO₂ on mentioned boundary.

In case of multiphase, because of several problems with steady solution discussed above a transient solution was performed instead of steady solution. The results corresponding to the transient solution have been obtained after 1ms (1000 timesteps).

For further investigation as discussed later the solution should be performed with higher mesh resolution and higher number of timesteps.

Results from these two different cases are presented below:

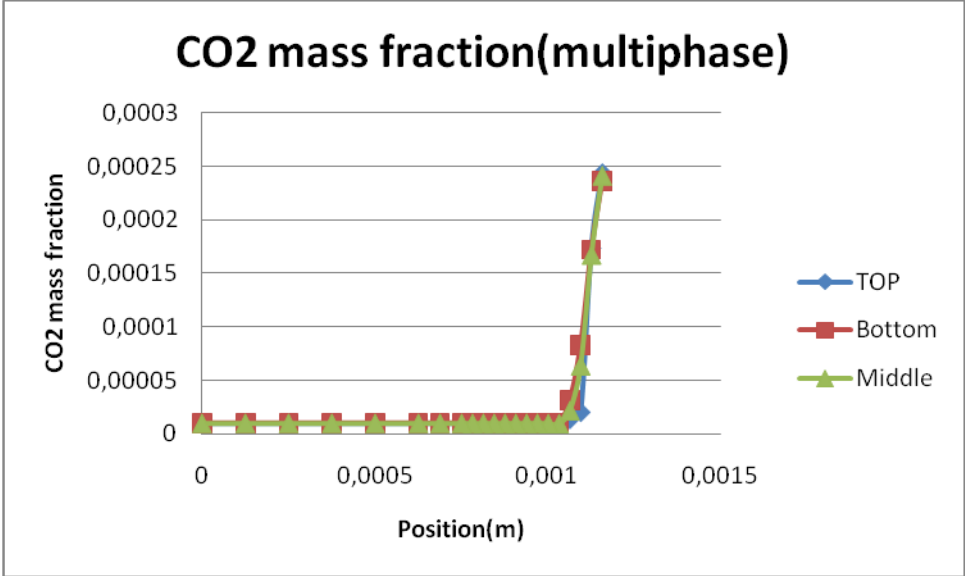


Fig10. Plot of mass fraction of CO₂(multiphase case)

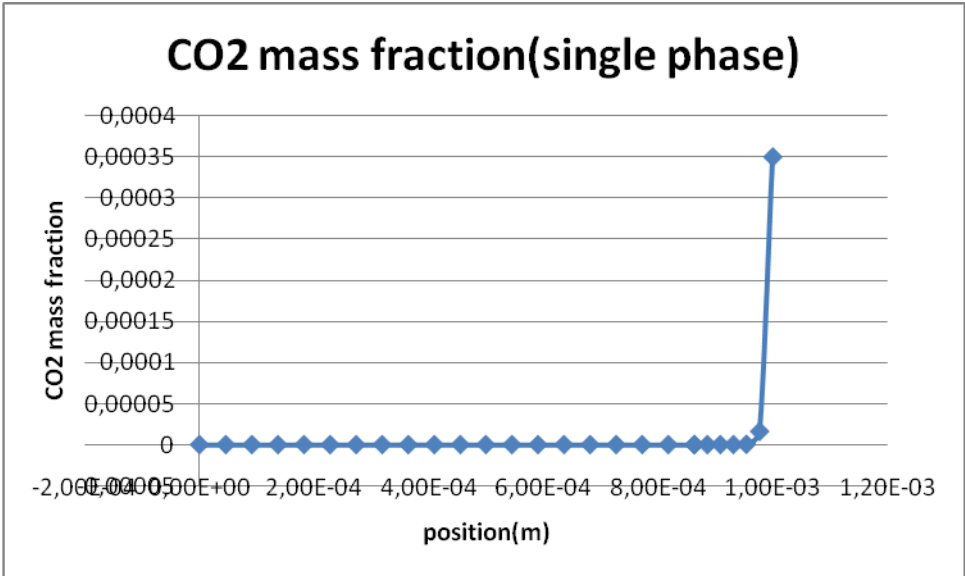


Fig11. plot of mass fraction of CO₂(single phase)

Looking at the results for multiphase system (Figure 10) and considering that the thickness of liquid film is 1mm, it is clear that CO₂ can be only observed in cells which mass is directly transferred from gas to liquid phase (cells inside the interface region). To be more specific, diffusion of CO₂ in liquid phase is not observable. Results from single phase case (Figure11) also prove this issue. In the case of single phase, it can be seen that the value of CO₂ mass fraction is immediately dropped in the first cell from the value 0.00035 to 0.000016. To find the reason,

diffusion length should be considered. Based on the calculations in Appendix2, the diffusion length is $7.7\mu\text{m}$. This value shows that the resolution is not high enough to track the concentration gradient inside the liquid phase and this observation that CO_2 will not diffuse from cell to cell inside the liquid phase seem logical in this case. Therefore, mesh should be refined several times near the interface as mentioned in section 5.2.2.

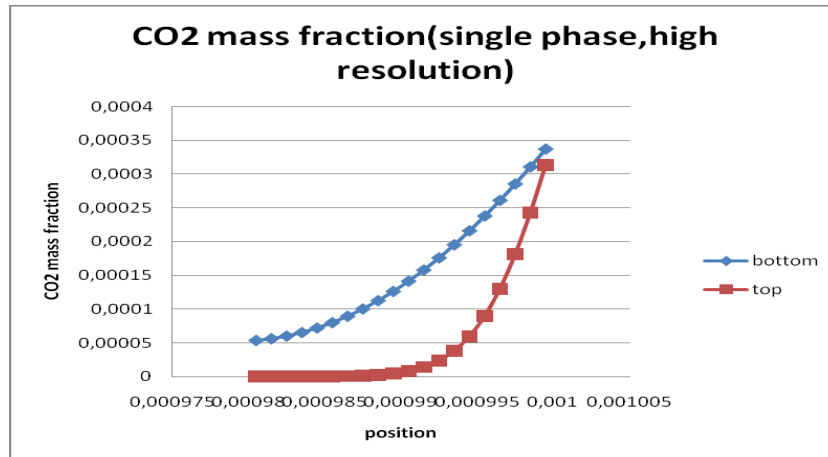


Fig12. Gradient of CO_2 concentration in liquid phase (single phase, high resolution)

To look at the gradient of CO_2 inside the liquid phase, high mesh resolution was applied using inflation near the gas-side boundary of falling film with $1\mu\text{m}$ thickness of each layer. Results from top and the bottom of the system show that CO_2 diffuses more at the bottom because of longer residence time.

It is possible to apply the same method for multiphase system and obtain smooth concentration gradient for CO_2 . This will increase the computational time drastically. Considering that residence time is around 25ms which means 25000 timesteps (timestep = 10^{-6}s) and also the number of iterations per timestep, also the number of cells after those refinement, It can be inferred that the solution needs a very long time to obtain reasonable results. Consequently, this step was skipped due to the lack of time. It may be investigated as the next step of this project in further investigations.

To show that UDFs work properly, figure13 and 14 show the rate of carbamate formation and PH inside the liquid phase, respectively. It can be observed that results look reasonable.

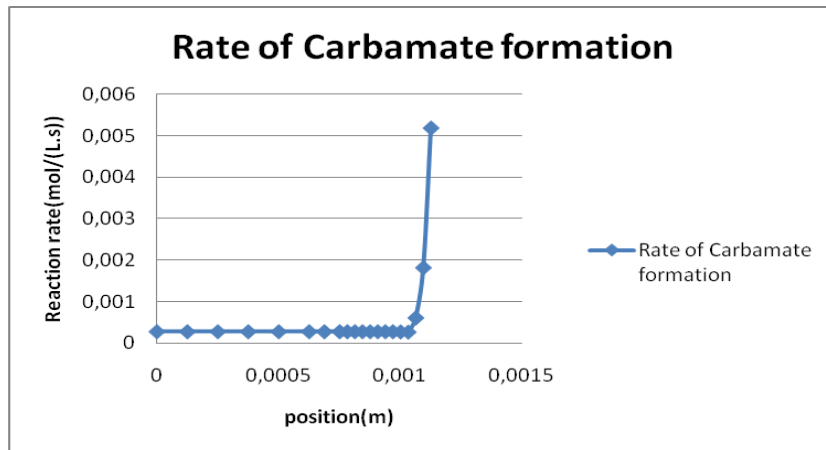


Fig13. Plot of reaction rate

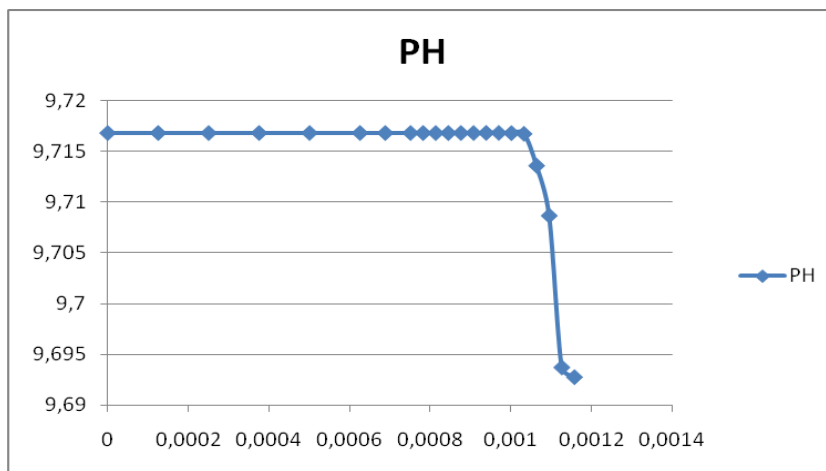


Fig14. PH

6.3 Grid Dependency check

Since the formulation of mass transfer is dependent on cell dimensions, the solution is not absolutely grid independent. As mentioned, it was attempted to make the net flux of CO₂ independent of cell dimensions in a logical way. Unfortunately steady solution for very fine mesh had convergence issues. The comparison was done between two different meshes in same transient solutions and the net flux was obtained by an integral on mass transfer rate over the whole system. Results show 15% difference. This difference is because of different gradients for α value in different mesh structures.

6.4 Discussions

The major drawback with VOF model is that although interface is physically a line or a curve (2D object), it is assumed a region in which phase is gradually changed (3D object). This assumption may have no effect on prediction of the flow, but for actual physical phenomena happening through the interface, this region is an unphysical domain that causes conceptual contradictions in estimating those phenomena from a numerical point of view.

It should be pointed out that assuming interface as a straight line (neglecting waves on the surface) may be far from reality. Since diffusion length inside the liquid phase is very small and the effect of waves on mass transfer could be considerable.

Assuming ripples on the outer surface of the falling film there is no steady solution for this process. Therefore, it should be solved in transient mode at least for couple of seconds and with very small timesteps and under-relaxation factors (more iteration per timestep) which was impossible to be done because of limited time. (Results were presented for a time around 1ms)

There are no experimental data to compare the results with. Hence, there are no criteria to check the validity of assumptions and simplifications. Experimental studies should be performed to validate the results.

7 Conclusions

Results show that modeling and simulating the Chilled ammonia process using Volume of Fluid method, is possible only if the resolution be very high near the interface. Especially, to assess mass transfer, reactions and equilibria.

Generally, reaction systems are not likely to be handled by Fluent solver. To be more specific, these classes of reacting flows cause very stiff ODE systems requiring several assumptions and simplifications to stabilize the solution.

8 Future works

The first evaluation on the current work could be decreasing the cell dimensions to around $1\mu\text{m}$ near the interface to be able to track the gradient of CO_2 concentration inside liquid phase. It should be applied for multiphase case in order to obtain more reasonable results.

The model should be fit with experimental results to obtain more appropriate parameters for mass transfer should be done.

The effect of waves on mass transfer and also other phenomena such as maragoni effect and heat of reactions should be considered.

As mentioned, there is a more accurate way to deal with chemical equilibria which is coupling more powerful ODE solvers, like stiff ODE suite, with Fluent.

Finally, the real geometry of absorber column consisting packing materials with inclined surfaces should be taken into account.

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(Plambech 1995; Patnaik 1996; Bai 1997; H.Perry 1997; Gao 2003; Ansys.Inc 2008; Derks 2009; Alfredsson 2010; Andersson 2010; Ansys.Inc 2010; Mathias 2010)

Appendix 1

Final UDF :

```
#include "udf.h"
# include "math.h"
# include "metric.h"

real M_CO2=0.0440061; // [kg/mol]
real M_NH3=0.01703061; // [kg/mol]
real M_NH4=0.0180134; // [kg/mol]
real M_HCO3=0.06180154; // [kg/mol]
real M_CO3=0.060; // [kg/mol]
real M_H =0.001; // [kg/mol]
real M_NH2COOH=0.061; // [kg/mol]
real keq1=0.0004265;
real keq2=1700000;
real keq3=0.0000000562;
real kH2O=0.00000001;
real k1=10.;
real k2=10.;
real k3=10.;
real kr=1.4; // [m3/mol/s]
// Operating pressure
/*real Pinn=101325.; */
// Variables
real T,P; // Temperature, pressure, total concentration, mass fractions
enum{NH3,CO3,NH4,HCO3,hydrogen,Cdioxide};
DEFINE_MASS_TRANSFER(gas_liq_source, c,t,from_index,from_species_index,
to_index, to_species_index)
{
Thread *gas = THREAD_SUB_THREAD(t,from_index);
Thread *liq = THREAD_SUB_THREAD(t,to_index);
real
PCO2,He,H,grad,Conc_i,alpha,Grad,H1,H2,H3,constant,source,Cb,den,CCO2,CHCO3
2,CH,CNH32,CNH42,CCO32,CHCO3,CNH3,CNH4,CCO3,sourceCO2,sourceNH3,sourceCO3,s
ourceNH2COOH;
real D1=8.8e-11;
double distx=0.;
double distoldx=0.;
double x=0.;
double xi=0.;
int n;
Node * node;
c_node_loop(c,t,n)
{
node = C_NODE(c,t,n);
x = NODE_X(node);
if (n==0.)
{xi=x;}
distx=fabs(x-xi);
if (distx>distoldx)
{distoldx=distx;}
}
C_UDMI(c,t,5)=distoldx;
den= C_R(c,liq);

CNH3=C_YI(c,liq,NH3)*den/M_NH3;
CCO3=C_YI(c,liq,CO3)*den/M_CO3;
```

```

CNH4=C_YI(c,liq,NH4)*den/M_NH4;
CHCO3=C_YI(c,liq,HCO3)*den/M_HCO3;
/*CH=C_YI(c,liq,hydrogen)*den/M_H;*/
CCO2=C_YI(c,liq,Cdioxide)*den/M_CO2;
if (CNH3 > 0. && CHCO3 > 0. && CCO3 > 0.)
{
H1=CNH4/(CNH3*keq2);
H2=keq1*CCO2/CHCO3;
H3=keq3*CHCO3/CCO3;
}
CH=(CNH3*H1+CCO2*H2+CHCO3*H3)/(CNH3+CHCO3+CCO2);
C_UDMI(c,t,4)=CH;
if (CCO2 >=1.e-10)
{
sourceCO2=k1*(CCO2-CH*CHCO3/keq1); // [mole/m3/s]
}
else{sourceCO2=0.;}
if ((CNH3>=1.e-10))
{
sourceNH3=k2*(CNH3*CH-CN4/keq2); // [mole/m3/s]
}
else{sourceNH3=0.;}
sourceCO3=k3*(CHCO3-CH*CCO3/keq3); // [mole/m3/s]
if ((CCO2>=1.e-10)&&(CNH3>=1.e-10))
{
sourceNH2COOH=-kr*CCO2; // [mole/m3/s]
}
else{sourceNH2COOH=0.;}
C_UDMI(c,t,0)=sourceCO2;
C_UDMI(c,t,1)=sourceNH3;
C_UDMI(c,t,2)=sourceCO3;
C_UDMI(c,t,3)=sourceNH2COOH;
PCO2=C_YI(c,gas,1)*(C_P(c,gas)+101325.);
He=2937;
alpha=C_VOF(c,liq);
Conc_i=PCO2/He;
grad=fabs(Conc_i-CCO2);
if (C_VOF(c,liq)>0.09& C_VOF(c,liq)<0.92 && grad> 0. )
{
source =100000*Dl*fabs(Conc_i-CCO2)/(alpha*distoldx);
}
else{source=0.;}
return (source);
}
DEFINE_SOURCE(CO2_rxrate,c,t,dS,eqn)
{
return - C_UDMI(c,t,0)*M_CO2; // [kg/m3/s]
}
DEFINE_SOURCE(NH3_rxrate,c,t,dS,eqn)
{
return -C_UDMI(c,t,1)*M_NH3; // [kg/m3/s]
}
DEFINE_SOURCE(NH4_rxrate,c,t,dS,eqn)
{
return C_UDMI(c,t,1)*M_NH4; // [kg/m3/s]
}
DEFINE_SOURCE(HCO3_rxrate,c,t,dS,eqn)
{
return (C_UDMI(c,t,0)- C_UDMI(c,t,2))*M_HCO3; // [kg/m3/s]
}

```

```

DEFINE_SOURCE(CO3_rxrate,c,t,dS,eqn)
{
return C_UDMI(c,t,2)*M_CO3;           //           [kg/m3/s]
}

/*DEFINE_SOURCE(H_rxrate,c,t,dS,eqn)
{
real source;
source=C_UDMI(c,t,0)+ C_UDMI(c,t,2);
if ((source<=1.e-7)&&(source>= -1.e-7))
{
source=source;           //           [mole/m3/s]
}
else{source=0.;}
return source*M_H;           //           [kg/m3/s]
}*/
DEFINE_SOURCE(CO2_2rxrate,c,t,dS,eqn)
{
return C_UDMI(c,t,3)*M_CO2;           //           [kg/m3/s]
}
DEFINE_SOURCE(NH3_2rxrate,c,t,dS,eqn)
{
return C_UDMI(c,t,3)*M_NH3;           //           [kg/m3/s]
}
DEFINE_SOURCE(NH2COOH_2rxrate,c,t,dS,eqn)
{
return - C_UDMI(c,t,3)*M_NH2COOH;           //           [kg/m3/s]
}

```

Appendix2

Diffusion Length:

$$D_L^{CO_2} = 2 \cdot 10^{-9}$$

$$V_{outer-surface} \approx 4 \text{ m/s}$$

$$L_{column} = 0.1 \text{ m}$$

Therefore,

$$t_{residence} \approx 0.025 \text{ s}$$

$$\text{Diffusion length} = \sqrt{D_L^{CO_2} \cdot t_{residence}} = \sqrt{2 \cdot 10^{-9} \cdot 0.025} = 7.7 \mu\text{m}$$