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Kinetic study of carbon dioxide absorption by aqueous solutions of 2(methyl)-aminoethanol in stirred tank reactor

Experimental and Numerical Study of Absorption Process and Mass Transfer Phenomena

Master of Science Thesis

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Abstract

The absorption of carbon dioxide by aqueous solutions of amines is a widespread industrial method of separating CO_2 from mixture of gases. However, there are still improvements needed in different aspects of this process such as finding more efficient solvents. To evaluate the absorption properties of different solvents various experimental techniques exist. One of these methods is using a stirred tank reactor with a flat gas-liquid interface, as the absorption contact region, to measure the kinetics of the ongoing reactions and absorption rate of the liquid solvent. In the present study, the mentioned device is used to determine the absorption rate of methylaminoethanol as the solvent. The accuracy of this methodology is later investigated by using CFD simulations.

Keywords: CO_2*, Amine, Stirred tank reactor, CFD*

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1. Introduction

Gas separation technology is not a new concept in industry. In fact, it has been used in different ways especially to separate acidic compounds from gas streams. Regarding one of the greatest concerns of our century, the high level of green house gases (GHG) in the atmosphere, it has brought even more attention than before. By increasing use of fossil fuels day by day, even higher amounts of GHG is expected. Therefore, finding practical cost effective solutions to control and decrease these gases is essential. Carbon dioxide is one important acidic compound which involves in many separation processes; therefore, finding convenient separation methods for this gas has a high priority.

Absorption of CO2 by using an alkanolamine solution is used vastly in industry. And in spite of all the improvements that have been made to this method until now, it is still a very costly technique. One of the steps demanding lots of improvements is the absorption process, which can be enhanced by understanding the details of absorption which involve kinetics and mass transfer properties of the absorbent material. In this work absorption of CO_2 to aqueous solution of methyl-aminoethanol, a secondary alkanolamine, is studied experimentally using a stirred tank reactor. The flow behavior of this device is also investigated numerically by means of CFD simulations.

2. Background

The increasing level of Carbon dioxide in the earth atmosphere and its contribution to the global warming is one important topic in scientific research lately. Existing enormous amounts of CO_2 in the atmosphere is believed to contribute to global warming[1]. Therefore, finding convincing methods of capture and storage of carbon dioxide seems indispensable. Figure 1 shows a simple schematic of a process plant featured with carbon dioxide capturing equipments for flue gases. The main cost of carbon dioxide capturing process is involved in the absorption step, therefore, in order to find sophisticated cost effective methods, a thorough understanding of possible carbon dioxide absorption methods, plus, the including phenomenon such as mass transfer and chemical reactions is critical.

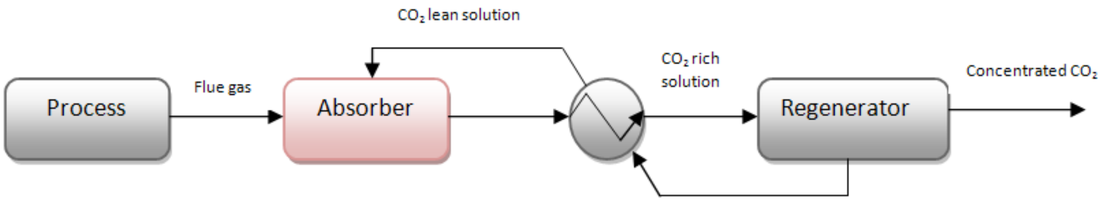

Figure 1 Carbon dioxide capturing steps

Carbon dioxide usually exists as a mixture of gases; therefore, it should be separated in order to be used or stored. It has different sources usually as a by-product of many commercial processes. The main carbon dioxide producing processes are (1) ammonia and hydrogen

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[1] Contributing to almost 60 percent of global warming effects

plants, (2) flue gases from the combustion of fossil fuels,(3) lime kiln operation, (4) sodium phosphate manufacture, (5) industrial fermentation, and (6) natural gas wells [1]. Carbon dioxide is used in food and beverage production, chemical manufacturing, oil and gas recovery and many other processes. Beside its industrial usage, storage of carbon dioxide is also considered lately. However, separation includes the main operational cost of capturing regardless of its subsequent steps. Therefore, many researches focus on this part.

2.1 Gas purification processes

The gas purification processes can be categorized to several categories in general:[2, 3]

- ***Absorption into a liquid*** which refers to transfer of a soluble component from a gas phase to a liquid phase. This process is one of the most important operations of gas liquid mass transfer. Reaction of gaseous species with liquids and with suspended solid particles in liquids is considered as a special case of absorption. In case of CO_2 Amine absorption, Ammonium absorption and dual-alkali absorption processes could be mentioned. The most sophisticated method is absorption with alkanolamines[2] which has been industrialized for over 60 years now; however, there is still need for improvement.
- ***Adsorption*** is defined as the selective concentration of one or more components of a gas (adsorbate) at the surface of a microporous solid (adsorbent). If the adsorbate reacts chemically with the solid adsorbent, it is called chemisorption. In case of $CO_{2,}$ molecular sieve adsorbent, molecular basket adsorbent, adsorption by activated carbon and lithium based adsorbents can be mentioned.
- ***Membrane permeation*** which is a new technology for gas purification and involves separation of gases by polymeric membranes. The gaseous component penetrates to the other side of the membrane considering the selectivity of the membrane to the certain component. Examples of membranes for CO_2 separation are polymeric, inorganic, Carbon, Alumina and Silica membranes. Although membrane separation processes are advantageous over conventional separation techniques, a realistic membrane providing high flux, high selectivity and stability has not been conceived yet.
- ***Chemical conversion*** includes catalytic and noncatalytic gas phase reactions and the reaction of gas phase with solids.

Selecting between the purification processes requires adequate knowledge of the impurity, process system and cost evaluations. The most common gas separation processes in industry are the removal of CO_2 and H_2S from gas streams. Table1 shows different methods used for removal of these gases:

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[2] Especially monoethanolamine

Table 1 Guidelines for Selection of H_2S and CO_2 Removal Processes[2]

Type of process	H_2S	CO_2	Plant Size	Partial Pressure
Absorption in Alkaline Solution	A	A	H	L
Physical Absorption	A	A	H	H
Absorption/Oxidation	A	-	H	L
Dry Sorption/Reaction	A	-	L	L
Membrane Permeation	A	A	L	H
Adsorption	A	A	L	L
Methanation	-	A	L	L
Notes: A= Applicable, H=High, L=Low				

Absorption in reactive solutions and absorption in physical solvents are both used for treating high volumes of gas streams of CO_2 and H_2S. However, from the economical point of view it is more advantageous to use physical solvents when the partial pressure of acid gas is high (above 200 psia) because the physical solubility of a solvent increases with pressure while a solution's capacity for reacting with CO_2 is almost pressure independent.

The membrane permeation technique is an appropriate method for removal of carbon dioxide from high pressure gases. But as mentioned before it does not seem attractive for large plant sizes. There is also the option of using hybrid methods which are combinations of above techniques to improve the economical aspects. More information concerning different carbon dioxide removal techniques are summarized in the work of *H.Yang et al.*[3]

Ethanolamine absorption process

Among all the mentioned methods absorption of CO_2 with ethanolamines (mostly MEA[3]) in an absorption column is now the most extensive method of carbon dioxide capture in industry with high flow rate streams. Various factors affect the choice of optimal solvent mainly depending on the operating pressure and temperature, regeneration energy consumption, CO_2 recovery, degradation of the solvent due to irreversible reactions and corrosion to the equipment caused by the solvent in plant. On the other hand, amine solution strength, CO_2 loading, and lean amine loading are also considered. Amines are weak bases with aqueous solutions which depending on the amount and type of amine available in the solution, their pH varies between 10-12. Absorption reaction of CO_2 by amines leads to two mechanisms which involve bicarbonate and carbamate formation. The problem of this method is the high operational absorption and desorption costs which are mainly caused by solvent degradation and high temperature demand to recover the solvent.

From the mass transfer point of view this process is categorized as an absorption process with several simultaneous reversible reactions which make it difficult to analyze. The gaseous carbon dioxide diffuses and reacts with liquid amine and water solution which is already

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[3] Monoethanolamine

involving reactions between water and amine inside. Therefore, investigation of such system needs a good understanding of the convective and diffusive mass transport as well as the ongoing reactions.

Methylaminoethanol

The amine used in this work is a secondary amine named methylaminoethanol or MAE. According to the study of *Kumazawae et.al* MAE has good absorption and regeneration characteristics such as high absorption rate and capacity, low corrosion even at a high amine concentration and approximately 20% less regeneration energy as compared with MEA in pilot plant scale [4]. The reaction mechanism of CO_2 with this amine is not in a clear agreement in all literature. In many literatures MAE is referred as a sterically hindered amine while it has been also presented as a conventional amine elsewhere. According to definition of sterically hindered amine MAE is not a hindered amine since it does not have a tertiary or secondary carbon attached, and the ethanol or methyl groups are mildly bulky. However, comparing MAE with a conventional amine like MEA shows that MAE is more hindered than MEA. So in such a comparison, the hindrance effect can make some differences.

2.2 Objective

In order to evaluate the absorption properties of different solvents the reaction kinetics must be known. In the present work, to study the kinetics of CO_2 absorption by 2(methylamino)-ethanol[4] solutions, the absorption rate of aqueous solutions of MAE in various concentrations and temperatures is measured experimentally using a stirred tank reactor. To evaluate the results and distinguish the influence of convective flow on the experimental results, a numerical study using CFD simulation tools is also done. The experimental part of this project is done at University of Malaya, Kuala Lumpur, and the numerical simulations are carried out at Chalmers University of technology.

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[4] MAE

3. Theory

3.1 Gas-liquid absorption

3.1.1 Mass transfer theory

Absorption of gas to a liquid can occur due to molecular diffusion. However, molecular diffusion is a very slow process naturally. Chemical reactions can enhance the mass transfer and increase the rate of absorption and the absorption capacity in gas-liquid absorbing systems. There are mainly three common theories to explain the mass transfer phenomenon in such systems: Danckwerts's surface renewal theory, Higbie's penetration theory and film model. The simplest model is film theory with the assumption of a stagnant film and steady diffusion, therefore, neglecting any convective movement on the surface; penetration theory is assuming unsteady diffusion with constant exposure time, while, in surface renewal theory the frequency distribution of the liquid element exposure time to the gas phase is taken into account. However, the most complicated model is the film surface renewal which considers the liquid surface stagnant or continuously renewed depending on the degree of turbulence. Two-film theory is the most commonly used among these models; however, since convection has a very important effect in this simulation, the penetration theory has been preferred in this case.

3.1.1.1 Penetration theory

In Higbie's penetration model the gas penetrates the liquid element during a constant time of exposure. This theory describes the mass transport as an unsteady diffusion in contrast with the film theory which assumes the steady diffusion.

According to this theory, penetration depth is calculated by:

$$x_p = \sqrt{\pi D t} \qquad 3.1$$

Where *t* indicates the exposure time of liquid elements to the gas phase. The gas absorption rate is proposed as follows by this theory:

$$N_A = k_L A(C_{iL} - C_L) = 2\sqrt{\frac{D}{\pi t_c}} A(C_{iL} - C_L) \qquad 3.1$$

3.2 Reaction mechanism[6]

The alkanolamines are consisted of at least one hydroxyl group which helps the solubility in water, and an amino group which provides the necessary alkalinity in water to absorb the acidic gases. Reactions of CO_2 and amine produce three forms of chemically combined CO_2: carbamate, bicarbonate and carbonate ions[7]. The reaction mechanism of aqueous amines can be generally described as bicarbonate formation and carbamate formation. The reactions between carbon dioxide and aqueous primary and secondary amine mixtures involve CO_2 hydration reaction:[8]

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \qquad 3.3$$

This is a very slow reaction and can be neglected compare to the reaction below. This reaction can enhance mass transfer even at low concentrations of hydroxyl ion:

$$CO_2 + OH^- \rightleftarrows HCO_3^- \qquad 3.4$$

Bicarbonate can again be deprotonated by a base molecule:

$$HCO_3^- + B \rightleftarrows CO_3^{-2} + BH^+ \qquad 3.5$$

The base molecule is an amine molecule or a hydroxyl ion (OH^-). Bicarbonate formation is a slow reaction, but amine molecules have a catalytic effect on this reaction. It seems that these molecules lower the activation energy required to start the reaction.

The other reaction is the reaction between CO_2 and amine present in the mixture which leads to carbamate formation. The Zwitterion mechanism proposed by *Caplow (1968)* describes carbamate formation in two steps. First step is the formation of the "zwitterion" intermediate:

$$CO_2 + NR_2H \rightleftarrows NR_2H^+COO^- \qquad 3.6$$

Any of the bases present in the mixture can deprotonate the zwitterion to a carbamate ion and a protonated base:

$$NR_2H^+COO^- + B \rightleftarrows NR_2COO^- + BH^+ \qquad 3.7$$

The above reaction typically occurs instantaneously, therefore the previous reaction, zwitterions formation, is more likely to be rate limiting. Accordingly, the overall reaction with amine resulting in carbamate formation is:

$$CO_2 + 2NR_2H \rightleftarrows NR_2COO^- + NR_2H_2^+ \qquad 3.8$$

Different concentrations of carbamate and bicarbonate may exist in an aqueous amine CO_2 solution which is due to the reversibility of the above reactions.

At very high pH values, CO_2 can bond to alcohol groups. However, this reaction does not play an important role in industrial CO_2 absorption processes since the pH is not high enough. Other reactions present in this solution are the reaction of organic bases with water and water dissociation itself:

$$B + H_2O \rightleftarrows BH^+ + OH^- \qquad 3.9$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad 3.10$$

It should be also noted that tertiary amines cannot react with CO_2 in absence of water because they lack the proton needed for the deprotonation step. However, if water is provided in the system they show good reactivity with CO_2. The reaction in presence of water happens as:

$$CO_2 + NR_3 + H_2O \rightleftarrows NR_3H^+ + HCO_3^- \qquad 3.11$$

Methylaminoethanol is a secondary amine, therefore its reaction mechanism can be assumed the same for DEA[5] as proposed by *Laddha and Danckwerts (1980)[9]*:

$$CO_2 + R_2NH \rightleftarrows R_2NH^+CO_2^- \qquad K_2 \qquad 3.12$$

$$K_{-2}$$

$$R_2NH^+CO_2^- + B \longrightarrow R_2NCO_2^- + R_2NH_2^+ \qquad 3.13$$

$$K_b$$

The overall forward reaction rate with the assumption of quasi steady state concentration for zwitterions is suggested to be:

$$r(\frac{mol}{m^3s}) = \frac{k_2[CO_2][R_1R_2NH]}{1+\frac{k_{-2}}{\sum k_b[B]}} \qquad 3.14$$

Where B refers to any base contributing to the proton removal in the solution, mainly OH$^-$ and amine.

3.3 Fluid dynamics in stirred tank reactor

The flow pattern in a stirred tank reactor can be in different forms. Depending on the device's design i.e. the impeller type and baffles the flow can move upwards, downwards, radial or axial. The induced flow pattern changes significantly by different impeller shape and different blade angle. The standard suggested flow patterns for two general impeller types are as below figures:

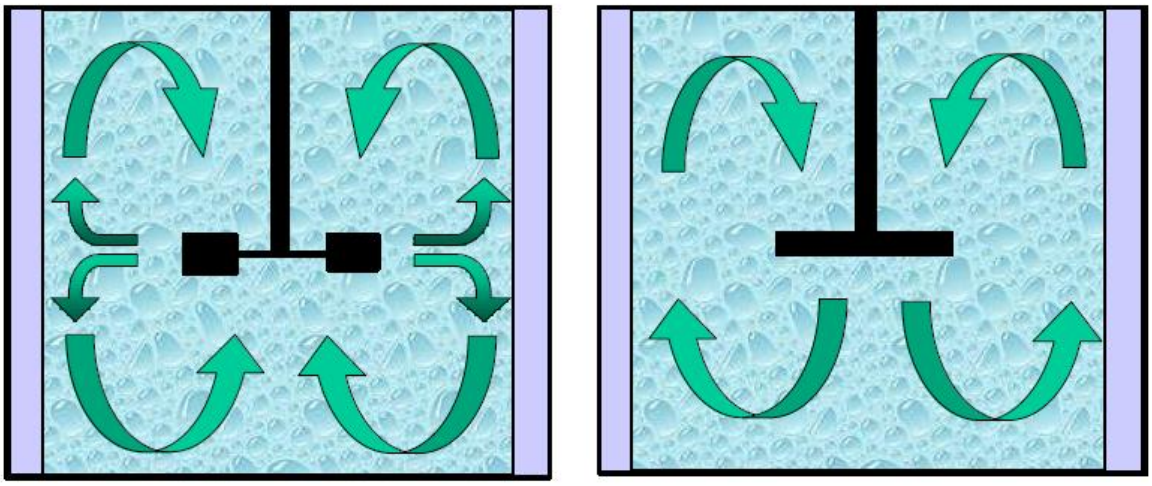

Figure 1 Radial impeller **Axial impeller**

3.1 Numerical modeling (1)

To determine the flow pattern in the present system numerical modeling is done by means of computational fluid dynamics and solving Navier-Stokes equations using finite volume method. In this method the whole computational volume is divided into a number of small building blocks called cells. By discretization of the domain it is possible to solve the partial

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[5] Diethanolamine a secondary amine with two ethanol molecules

differential equations as a set of algebraic equations around each cell which is solved later with iterative techniques.

3.1.1 Continuity equation

The material balance over a fluid element is called the continuity equation which for an incompressible flow (constant density) is

$$\frac{\partial U_i}{\partial x_i} = 0 \qquad 3.15$$

It should be mentioned that in the present system the maximum velocity of the gas is much less than the sound velocity which means a Mach number much less than 1. As a result, compressible flow assumption is valid.

3.1.2 Equation of motion

The momentum balance over fluid element for a Newtonian fluid is written as follows

$$\frac{\partial U_i}{\partial t} + U_j \frac{\partial U_i}{\partial x_j} = -\frac{1}{\rho}\frac{\partial P}{\partial x_i} + v \frac{\partial}{\partial x_j}\left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i}\right) + g_i \qquad 3.16$$

It states that momentum variations in each direction in the fluid should be balanced with the sum of forces acting on the fluid in that direction.

3.1.3 Simulating rotating flow

The stirred tank reactor is a case of rotational motion without changing the domain shape, coupled with a stationary part through interfaces i.e. stirrer and baffle zone, respectively. MRF[6] method (steady state) is a good primary way of calculating an appropriate initial condition for this simulation; however, due to presence of baffles in the tank (stationary parts) and the small distance between baffles and impeller blades, the interaction of baffles with impellers should be taken into account. After reaching a nearly converged solution using MRF method, calculations can be switched to sliding mesh simulation (fully transient).

In moving reference frame simulations, the domain is divided into two zones, stationary and moving. The moving zone equations are solved in a moving reference frame with two kinds of absolute or relative velocity formulation. A rule of thumb for choosing absolute or relative formulation for velocity in MRF method is if the most of the fluid domain is in motion then the relative formulation is recommended. However, in sliding mesh method the mesh moves in every time step and the flow at sliding interfaces are recomputed therefore only absolute formulation applies.

In order, to easily switch from MRF to sliding mesh during simulation, a non conformal mesh should be used which works for both methods. In a conformal mesh the interface between rotating and stationary zone is a single face between interface cells, while in a non-conformal mesh there are two overlapping faces between the zones. In Ansys meshing program it is possible to make a non conformal mesh by creating separate bodies at the

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[6] Moving reference frame

rotating zone and the stationary zone; it means that three separate solid bodies are present in this geometry; liquid rotating zone, gas rotating zone and the rest of the tank involving baffles which is considered the stationary zone. The sliding interfaces will be recognized as solid walls in FLUENT automatically which should be set to mesh interfaces manually.

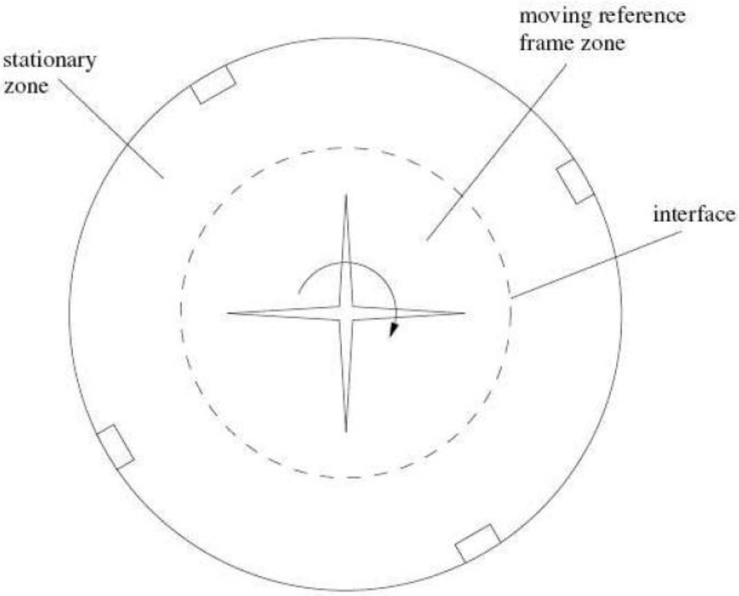

Figure 2 Moving and stationary parts in geometry

The MRF model is applicable in cases where flow at the interface between moving and stationary part is almost uniform (mixed out). This method applies an averaging at the flow moving out from the moving domain. Therefore, using this method with a turbulence model like LES is not appropriate. This is due to the fact that by averaging on the interface, the turbulent eddies forming with LES will be filtered out by the averaging. So, the choice of MRF or sliding mesh should be regarded while choosing the turbulence model.

3.1.4 Flow modeling

To simulate the flow depending on the level of turbulence in the system the flow model is chosen. In this simulation DNS (direct numerical simulation), k-ω SST and LES (large eddy simulation) are tested. DNS is the direct solution of Navier-Stokes equations which is the most accurate method of predicting the flow but a very high resolution grid and very fine time stepping in order of the smallest eddies size and life time is needed. Therefore, using this method is time consuming and expensive. Another method to simulate the flow is Large Eddy Simulation which calculates the large eddies while modeling the small scale eddies. K-ω SST model is a RANS model which suits a large range of Reynolds number from laminar to turbulent and is recommended to be used with sliding mesh and moving reference frame cases.

3.1.5 Multiphase modeling

To simulate the multiphase flow Volume of Fluid model can be used. This method is chosen due to large interface between two phases and it also makes it possible to follow the deformations on the interface. Using the VOF model, interface between gas and liquid is assumed as a transition region with varying volume fraction of phases in each cell of the interface region.

4 Experimental technique

To study the absorption and kinetic behavior of carbon dioxide with solvents such as amines, several experimental techniques are available. Stirred tank reactors, wetted wall columns and stopped flow technique are the most common ways of such kinetic study in most literature.

In this work, CO_2 is absorbed by aqueous solution of methylaminoethanol in a stirred tank reactor through the experimental part. The operation is done batch wise regarding both gas and liquid phase. A six-blade propeller is used to stir the liquid phase at the bottom of the tank and three impeller blades mounted on a shaft at the top of the tank for the gas phase mixing and keep the mixture close to homogeneity both in the gas and liquid phase. The impeller and propeller have separate shafts which makes it possible to stir each phase with different stirring speeds. The propeller speed is fixed specifically to avoid perturbations on the surface; this is intended to keep the gas-liquid interface constant in estimation of the absorption rate data, however, the surface condition and contact area is further studied in the CFD simulation of this system. The liquid and gas impeller speeds are set to 150rmp and 450 rpm, respectively.

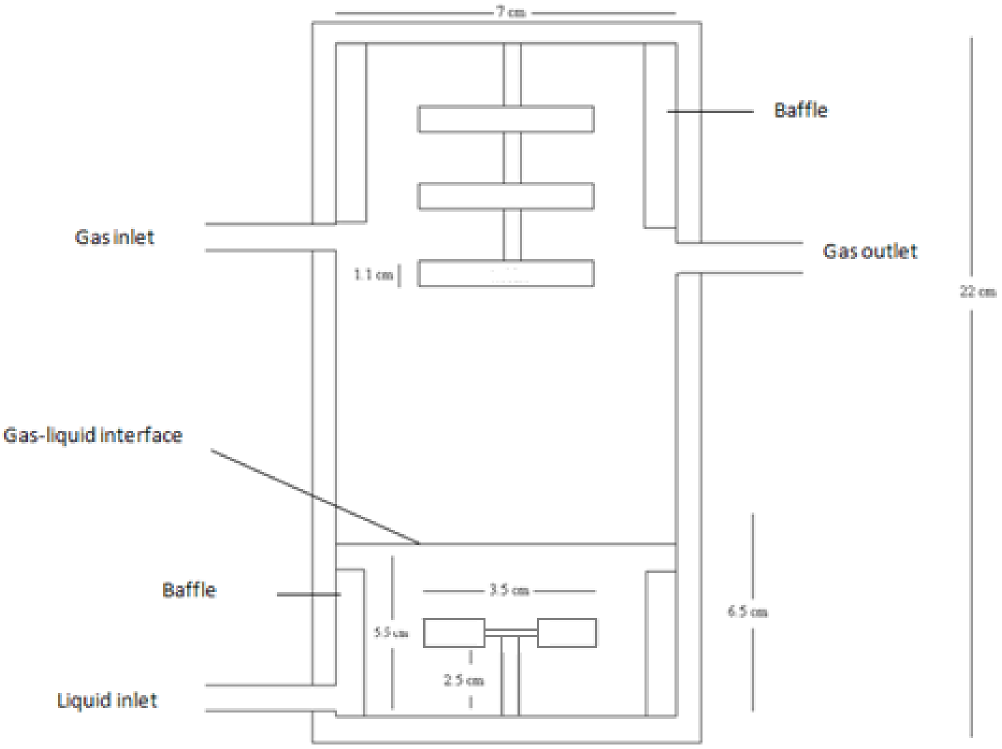

Figure 2 Stirred tank reactor used in the experiments

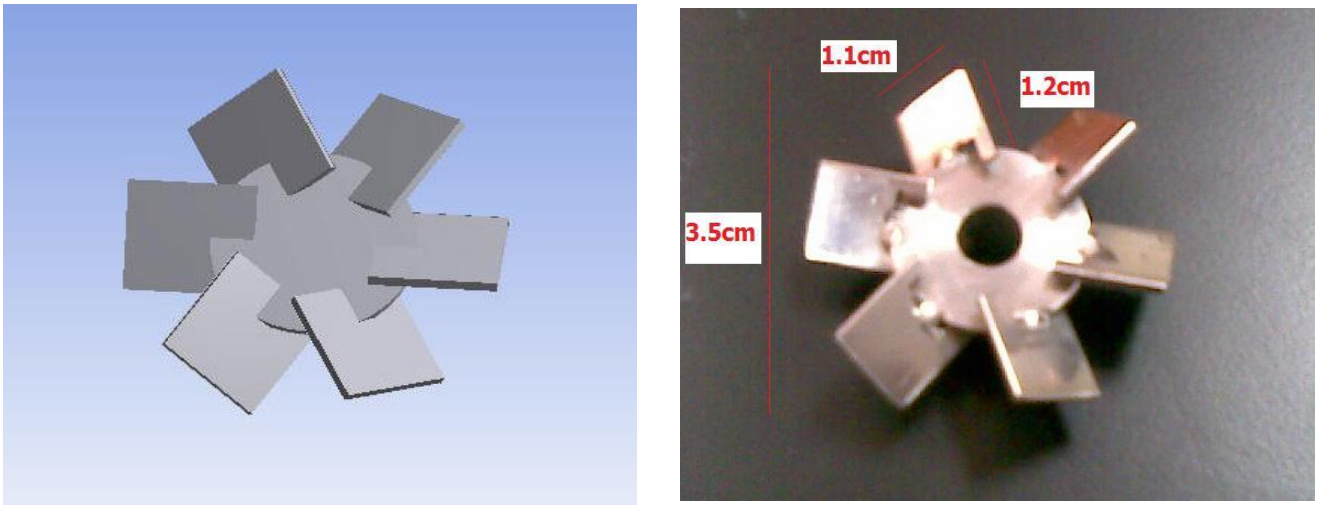

Figure 3 The liquid part propeller with 30° angle

The experiments are performed at constant temperature. In order to keep the temperature stable, the reactor is jacketed with circulating water which is kept in a certain temperature using a water bath. Bottom part of the tank is filled with fresh 200cc methylaminoethanol solution for each experiment. Each solution sample is well homogenized before being used in the reactor by continuous stirring. The gas mixer is used when nitrogen is present to keep gas diffusion resistance as low as possible. In all experiments the absorbed amount of CO_2 is much less than the MAE present in the solution, thus, the absorbed amount of CO_2 in all measured absorption rate data are intended to be at the initial stage of absorption where variations in amine concentration is presumably negligible; besides, the residence time is less than the required time to reach equilibrium in the system. The pressure drop is being recorded in the tank each 0.5 second in order to determine the absorption rate.

In such an absorption system the chemical reaction and flow are strongly coupled, therefore, the liquid flow should be adjusted in a way to make it possible for the mass transfer characteristics to be disentangled from the reaction kinetics. This is the reason making the CFD analysis valuable.

In order to use the generated results from experiments with this equipment several assumptions are made. The absorption rate of each case is calculated regarding the unbroken interface between the phases in a certain stirrer speed, and the deformations on the interface are neglected. It should be noted that the deformations on the surface can increase the mass transfer area and therefore the measured absorption rate per surface area of the interface. Another assumption is that the liquid surface renewal is fast enough to make the concentration gradient of amine in the liquid film caused by reaction of amine and CO_2 negligible. This means that the reaction would be pseudo first order regarding the amine concentration.

The pressure drop in the vessel is considered to be sum of absorbed carbon dioxide and the measured leakage of gas. The solution at the operating temperature and pressure has a vapor pressure of its compounds above in the gas phase, hence the vaporized amine and water can react with CO_2; nevertheless, the vapor pressure of water and amine in the experimental conditions are not significant compare to the CO_2 and N_2 and are neglected in the investigation. Both gas and liquid phases are assumed to be homogeneous ideal mixtures and all the possible impurities that might exist in either of the phases are neglected. In the gas phase before injection of CO_2 the vessel is filled with air and with several filling and purging the air is forced out of the vessel; so there might be still a small amount of air in the tank and the CO_2 which might be absorbed during this filling and purging is neglected. The methylaminoethanol can contain impurities which can affect the absorption process.

5 Simulation

5.1 Geometry

Geometry of the tank is built in the workbench design modeler. Since rotating parts exist in the tank moving reference frame (MRF) or sliding mesh should be used further in the flow modeling, therefore, the middle part of the tank involving the rotating parts (impeller and propeller) are defined as separate cylinder bodies in the geometry as it is shown in figure. This makes it possible to assign rotational speed to the moving parts later in the FLUENT program.

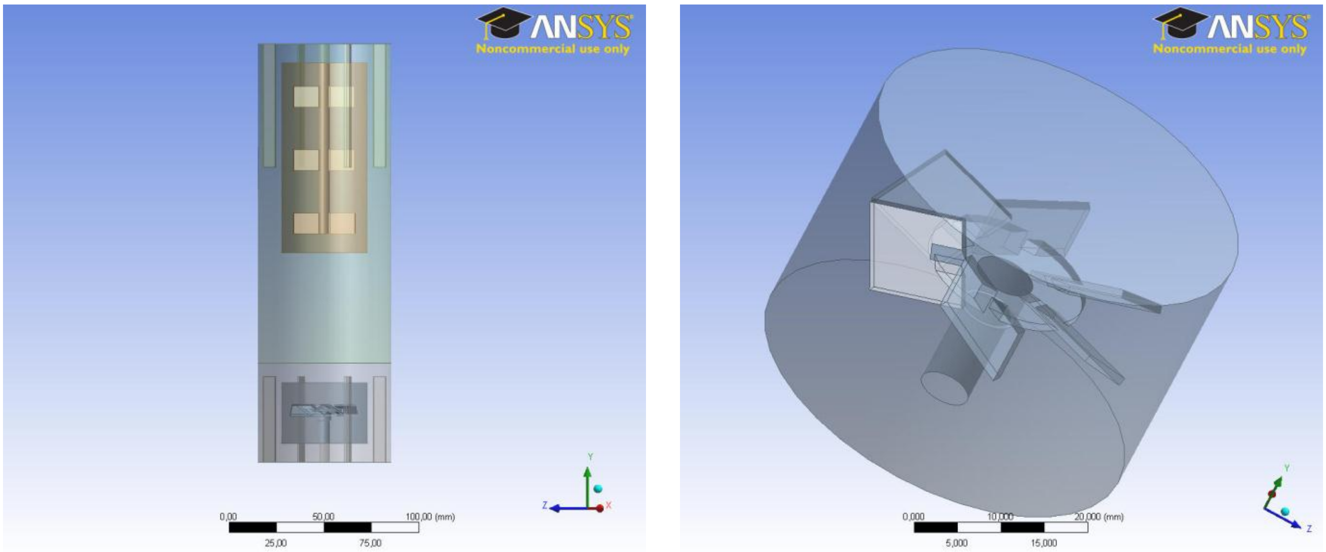

Figure 4 Geometry of the stirred tank reactor

5.2 Meshing

In the meshing program, default settings with a medium sized grid are chosen for producing the mesh, which gives a tetrahedral unstructured mesh in the whole tank. The reason is complexity of the geometry especially caused by the propeller blade angles and baffles. Existing of baffles affects the quality of the produced mesh specifically where the baffles are attached to the wall. In this region the aspect ratio and skewness of the cells goes beyond the allowed numbers. A very important part of this mesh is the interface region. In this area the cells should be fine enough to define the separation of gas and liquid well. A medium size mesh with 320751number of cells is used for this simulation.

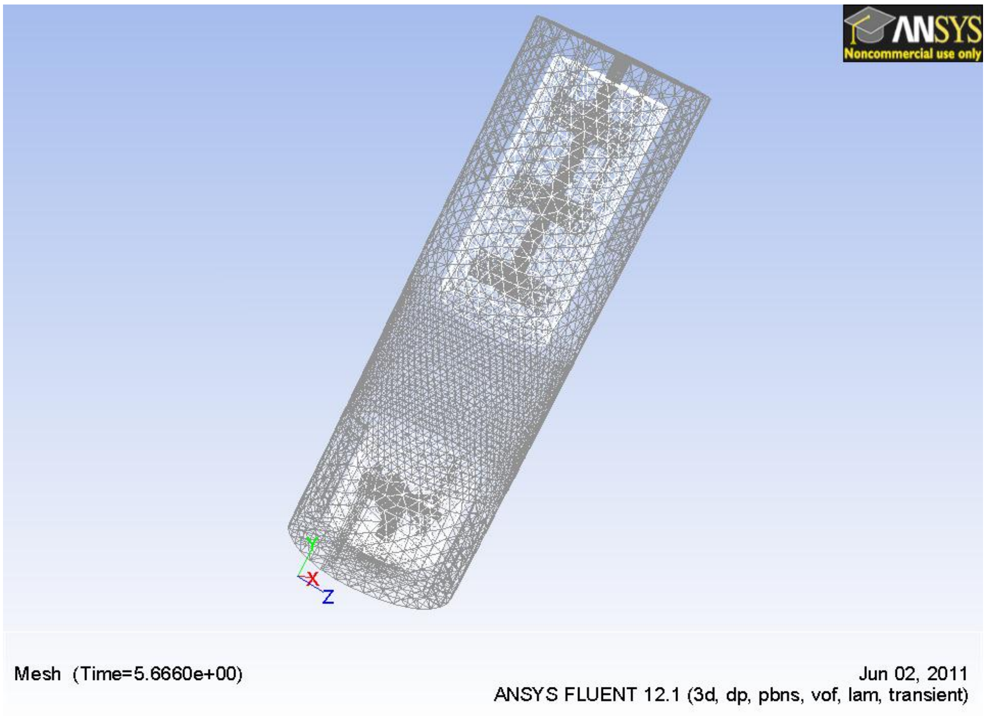

Figure 5 The produced tetrahedral mesh

5.3 Solution

According to the natural behavior of this system and the observed solutions there is no steady state solution for this system, therefore, the simulations are done in transient manner. Considering the rotational speed of impeller in the tank and by calculation of the Reynolds number and comparing that with turbulence data on the stirred tank reactors it is concluded that the flow in both gas and liquid parts are in laminar state during all experiments[10]. Thus, there is no need to use turbulence models at first glance.

$$Re = \frac{N_s D_s^2 \rho}{\eta} \qquad 6.1$$

<u>The turbulent region:</u>

$$\begin{gathered} Re \geq 10000 \ \ baffled\ tanks \\ Re \geq 5000\ unbaffled\ tanks \end{gathered} \qquad 6.2$$

Due to calculations the Reynolds number of the liquid part is about 3000 and in the gas part is 400 which a sign of being in the laminar region for this baffled tank as a rule of thumb.

The FLUENT settings for using VOF model are very important. The explicit scheme for VOF is problematic for convergence especially in this case which is a complex geometry and rotation in the system, plus, skewed cells in the grid. The discretization schemes used for pressure, volume fraction and gradient are body force weighted which is more appropriate for rotating flows, HRIC which leads to low numerical diffusion, and green-gauss cell based, respectively. In addition, the implicit body force option is used in this simulation because of the high difference between the densities of two phases and it helps to handle the forces in more robust numerical manner.

To figure an appropriate time stepping for the transient simulations, the time step is chosen due to the time it takes for moving cell to pass a stationary point. Regarding that the mesh is unstructured in this simulation a small size cell of the grid has been chosen for the grid spacing to determine the time step size. It is estimated as below:

$$\Delta t \approx \frac{\Delta s}{\omega R} \qquad 1.1$$

Δs = mesh spacing at sliding interface

ω = rotational speed

R = radius of interface

In the simulation a small time step size, 1 ms, has been chosen which is suitable for the rotational speed of both gas and liquid parts.

6 Results and discussion of experiments

6.1 Experimental data

Varying parameters in the experiments are temperature, CO_2 partial pressure and solvent concentration. MAE[7] is used as an aqueous solution in different concentrations of 1, 2 and 4 molar. CO_2 is also used in different concentrations of 10, 30, 50 and 100 percent as a mixture with N_2 which is an inert gas. The studied temperatures are 30,40and 50°C. The absorption rate of each experimental condition is summarized in table2.

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[7] methylaminoethanol

Table 2 Operating conditions in each experiment and absorption rates

CO_2 volume percent	Amine concentration mol/l	Temperature K	CO_2 absorption rate $mol/m^2 s$
100%	1	303 313 323	0.013 0.016 0.016
	2	303 313 323	0.018 0.023 0.025
	4	303 313 323	0.019 0.026 0.026
50%	1	303 313 323	0.005 0.008 0.008
	2	303 313 323	0.008 0.01 0.012
	4	303 313 323	0.01 0.013 0.016
30%	1	303 313 323	0.003 0.004 0.005
	2	303 313 323	0.005 0.005 0.005
	4	303 313 323	0.005 0.007 0.008
10%	1	303 313 323	0.0005 0.0008 0.0008
	2	303 313 323	0.0008 0.001 0.0008
	4	303 313 323	0.001 0.001 0.001

6.1.1 Temperature effect

The measurements are done in three different temperatures. Regarding the experimental data, the absorption rate slightly increases by temperature raise which is due to increase in chemical reaction rate constant. It is observable that the absorption rate changes with the same slope in the case of pure carbon dioxide and 50% carbon dioxide, however, there is a difference in slope of lower CO_2 concentrations; this indicates that reaction kinetics are controlling the absorption rate in higher concentrations of CO_2, while diffusion starts affecting the absorption rate in lower CO_2 concentrations, which shows a high mass transfer resistance in the gas phase.

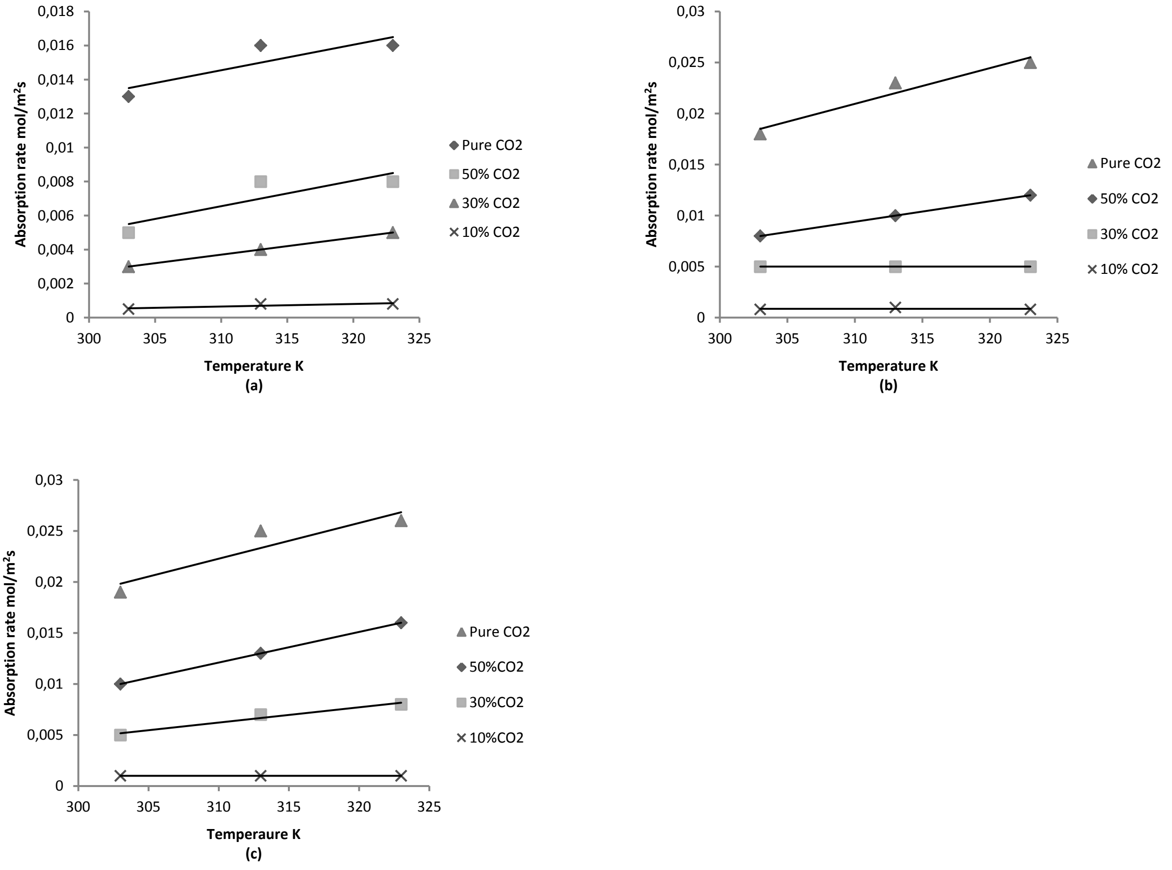

Figure 3 Absorption rate vs. temperature in a) 1 mol/l b) 2 mol/l c) 4 mol/l solutions

6.1.2 MAE concentration effect

Regarding the experimental results from absorption of CO_2 with different concentrations of MAE in the absorbent solution, it is observed that increasing the MAE concentration causes the absorption rate to increase. When pure CO_2 is present in the gas phase and no diffusion hindrance is present in the gas film altering the solution concentration from 2 to 4 does not have a significant effect on the absorption rate. If the reaction kinetic is considered to be in a fast reaction regime and first order regarding to MAE concentration then the absorption rate is expected to change linearly by increasing the MAE concentration. However, this is not happening in measurements. This shows that increasing the liquid bulk concentration does not affect the absorption rate linearly which can be due to several reasons; it could be an indication of a different reaction rate order regarding MAE concentration than one. It might also show that liquid film thickness is changing due to the viscosity change in the liquid by varying the MAE concentration. That would be a confirmation of high diffusion resistance in the liquid film which can be controlling the absorption process; plus, MAE has a rather high viscosity which can also intensify the diffusion resistance in the liquid; another probable explanation is that according to the reaction mechanisms, there is another reaction in the absorption process of CO_2 which is accompanying the reaction of CO_2 with MAE and that is the CO_2 hydration reaction (3.4). This reaction might occur on the surface before reaction 3.15 and this can limit the rate enhancement by reaction 3.15. In the lower CO_2 concentration case with 50% CO_2 the absorption rate still follows roughly the same slope which shows that gas diffusion resistance is still not high enough to control the absorption rate.

While reducing CO_2 to 30% the influence gas resistance is observed. Further reduction of CO_2 to 10% makes the gas film resistance enough to take complete control of the absorption rate and changing the solution concentration has practically no effect on the absorption rate.

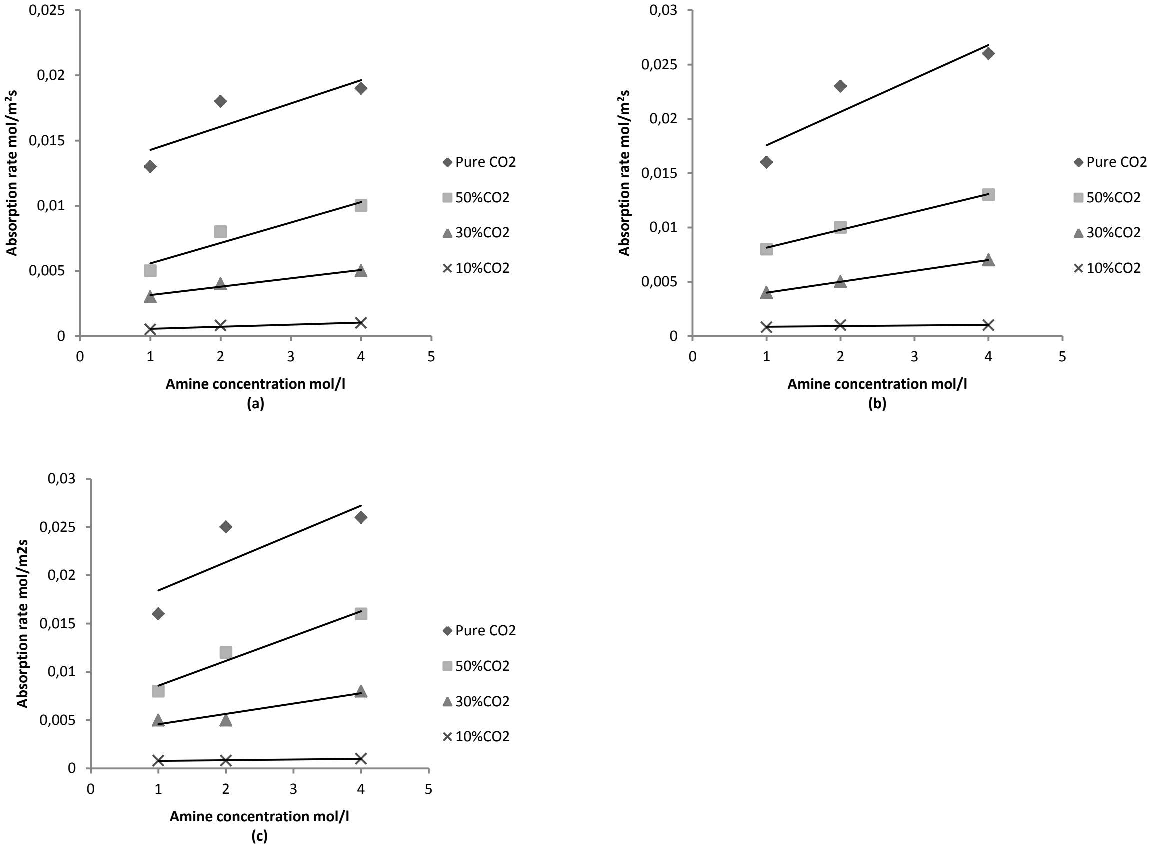

Figure 4 Absorption rate vs. amine concentration at a) 303K b) 313K c) 323K

One might think that the stirrer speed can be an effective parameter in this system. The stirrer speed which is kept constant in the reported data is considerable indeed. It is also observed in the experiments[8] that the absorption rate is clearly dependent on the stirrer speed which helps to realize that the reaction is occurring in the fast reaction regime and diffusion is the controlling factor.

6.1.3 CO_2 partial pressure effect

The influence of gas phase concentration variation is studied by changing the volume percent of CO_2 in the gas mixture. The inert gas used to dilute the gas phase is nitrogen which is not

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[8] The data with different stirrer speed is not recorded but its effect has been observed in the laboratory by the author

absorbed to the solution and is not involved in any reaction in the present system. The homogeneous mixture of gas is provided in flasks before entering the sealed tank. It should be noted that the total pressure is approximately the same in each experiment and only the partial pressure of gases are changing. This parameter obviously controls the absorption rate. This indicates that the partial pressure of the gas highly influences the absorption rate.

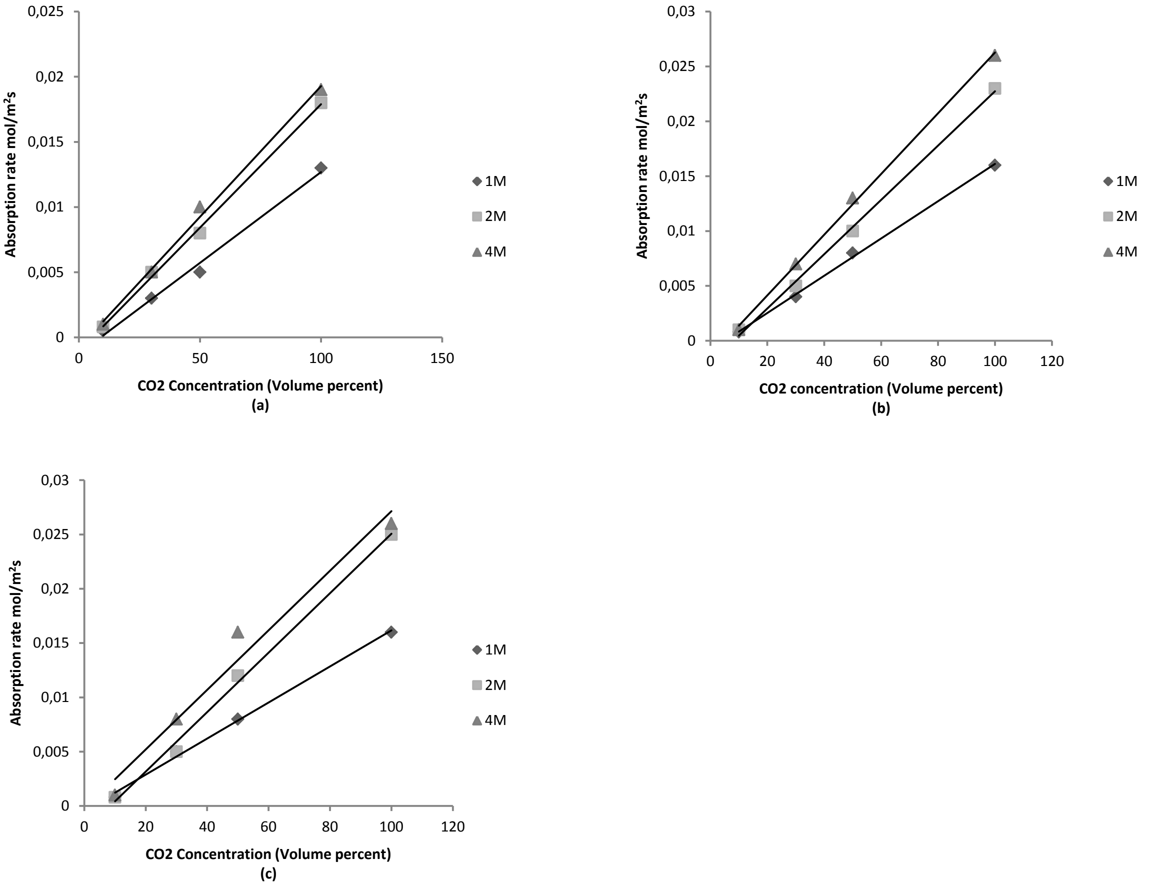

Figure 5 Absorption rate vs. CO2 concentration at a) 303K b) 313K c) 323K

6.2 Simulation results

6.2.1 Flow pattern

The flow pattern is simulated using FLUENT. The initial velocities are set to zero. From the Reynolds number calculations the flow was considered laminar. By using the DNS modeling it is obvious that contrary to the rule of thumb which predicts the flow to be laminar there is turbulent behavior in the system. This turbulence region is mostly seen on the upper part of the liquid tank above the impeller. This behavior can be explained by the fact that on the upper part there is no wall or impeller shaft to stabilize the flow which causes chaotic manner in this region. There are swirls forming and dying out in this part.

After several rotations of the impeller the LES model is used to determine the turbulence viscosity and check if the time and grid resolution is enough for modeling turbulence. However, the turbulence viscosity is much higher than the molecular viscosity and therefore large eddy simulation is preferred. Then, to simulate the flow k-ω SST model is used to gain a developed profile for two rotations of the impeller using the average velocity of the k-ω the simulation is switched to LES afterwards.

After several rotations and reaching a developed velocity profile in the tank, the velocity vector plot shows a much higher velocity in the gas phase and lower velocity in the liquid phase which is due to different rotational speeds used. The flow pattern in the gas phase confirms that the assumption of no resistance in the gas phase is valid due to the high gas circulation rate close to the liquid interface.

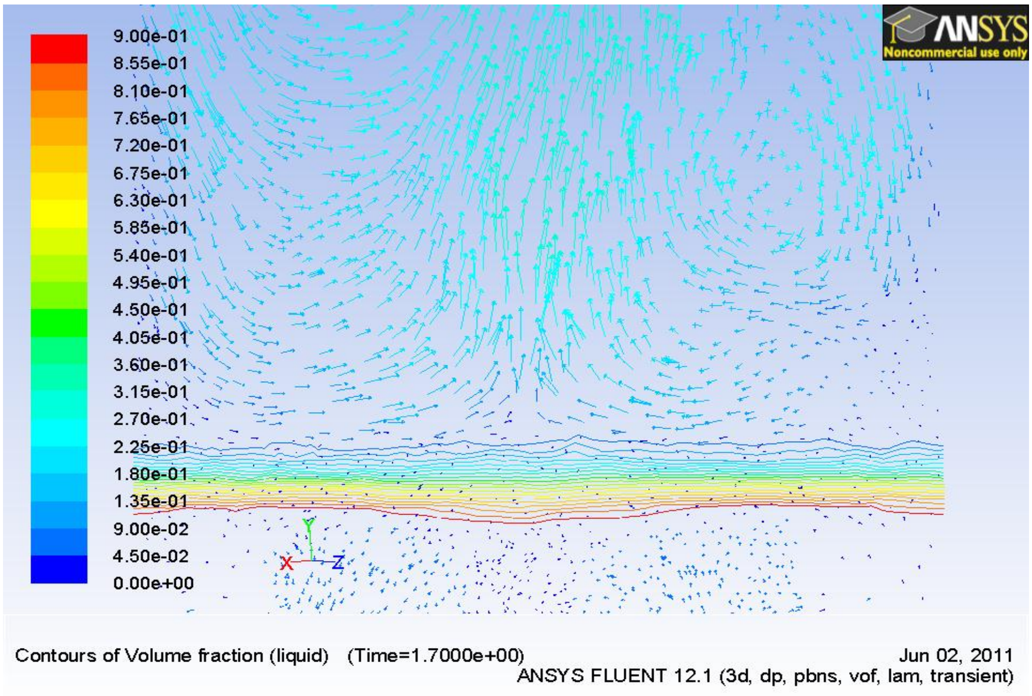

Figure 6 Velocity vector close to the gas liquid interface

Sampling the velocity magnitude in a bounded plane inside the liquid flow and also tracking the interface positions in transient simulations shows that after several rotation of the impeller, flow pattern reaches a steady status with a very small deformation on the liquid surface. In a low rotational speed (150 rpm) the surface stabilizes in a few rotations, however, in higher rotational speeds (450rpm) the deformation on the surface is significant. Tracking the gas-liquid interface simulation is evidence which makes the assumption of constant gas-liquid surface area on the interface valid for the reaction simulation in rotational speed of 150 rpm. In this speed of rotation the surface increase is less than 1 percent. While, in higher rotational speed of 450rpm the liquid surface increases more than 10 percent.

In the multiphase simulation the velocity profile on the liquid surface region is too small compare to the rest of the liquid. To check the liquid flow results the liquid part of the tank is simulated separately as a single phase with a zero shear wall on the surface. The results show differences on the upper part of the liquid compare to the multiphase simulation. The velocity of the liquid on the surface is higher. Regarding that a low quality mesh is used in the multiphase case, especially a high difference between the outer cylinder and the inner cylinder of the sliding mesh, the unexpected results on the surface can be explained by the poor meshing.

6.2.2 Exposure time

To determine the exposure time of liquid elements on the surface of the liquid part several massless particles are injected on the liquid surface of the single phase simulation. To save time and avoid huge amount of particle track data the particles are injected only at a quarter of the tank at different places on a plane at the surface.

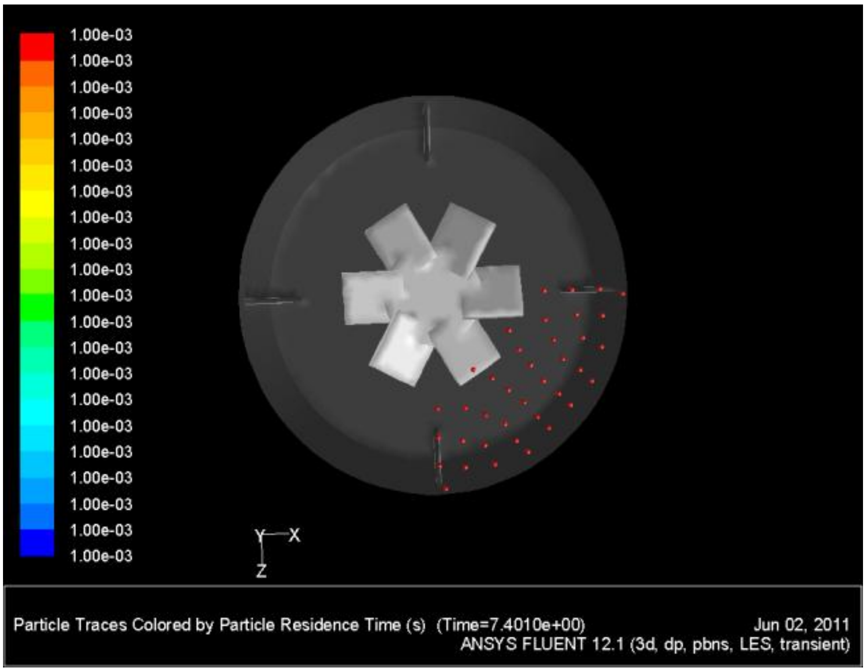

Figure 7 Injected particles at interface

By saving the particle history data at each time step it is possible to follow the particles moving along the flow lines. The figures below show descending of the particles from the surface.

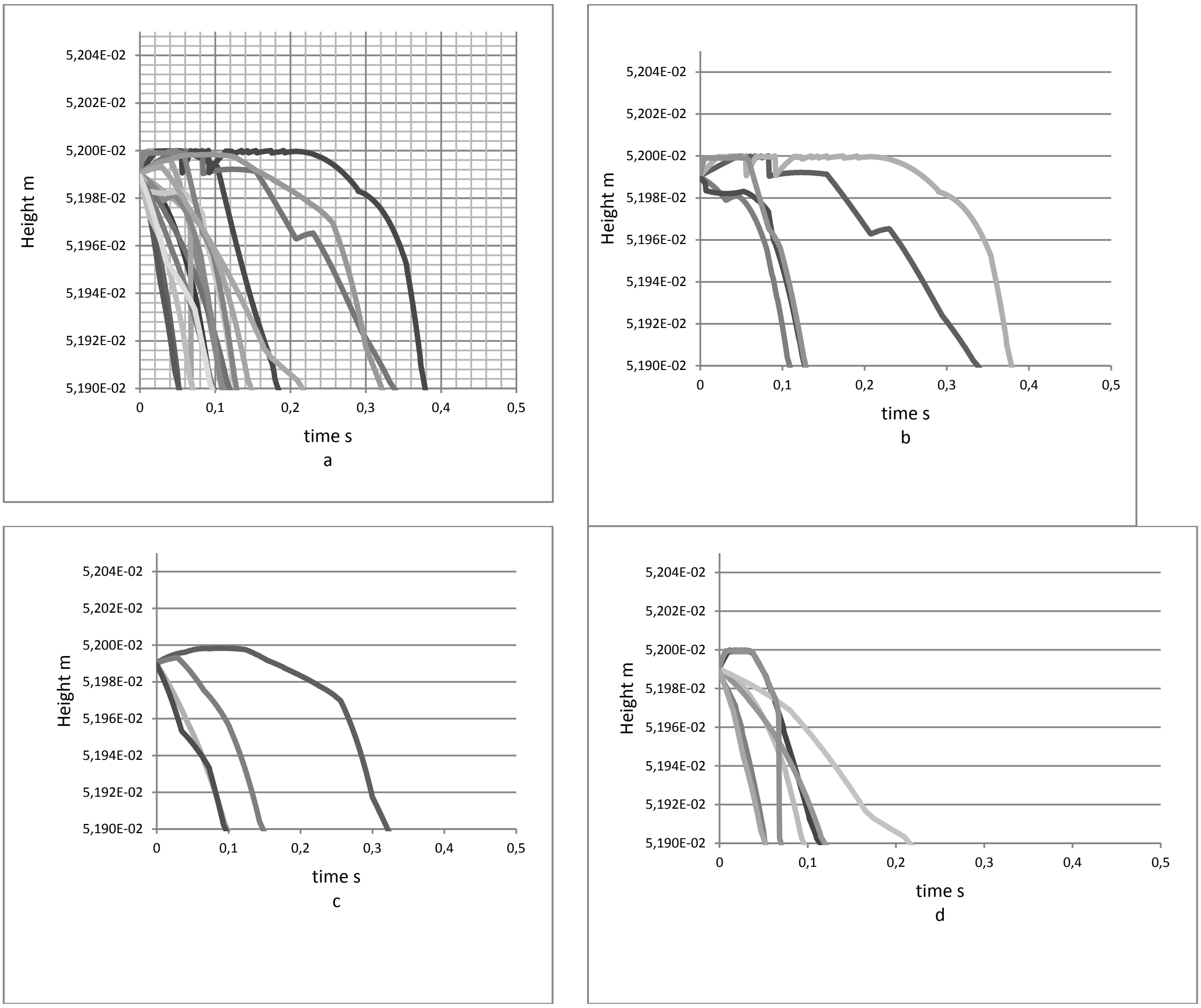

Figure 8 descending of particles from the surface (h=0.052m) into the bulk liquid in time a)particles in different positions b)particles close to reactor walls c)particles at 0.5 cm distance from the wall d) particles with 1 cm or more distance from the walls

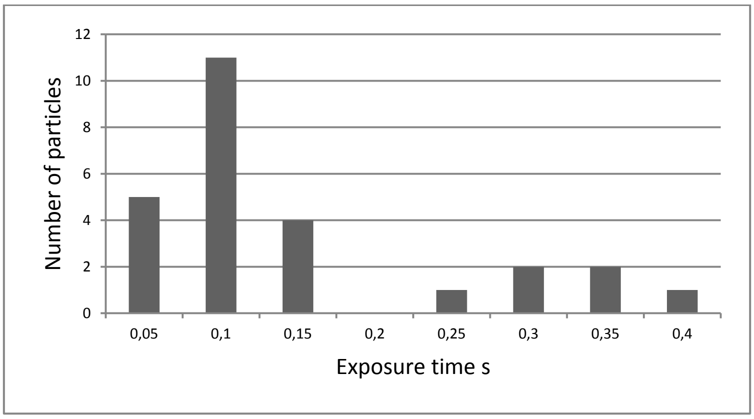

Figure 9 Number of particles vs. time range of exposure time

From the particle track data it can be concluded that the particles very close to the walls and especially baffles descend slowly. The particles spend the longest time on the surface before they reach the middle where the impeller is affecting the flow strongly and then the descending speed increases. Assuming the particles to be exposed to the gas phase in 20 µm from the surface it can be shown that most of the particles spend a time between 0.05-0.15s on the surface. Considering 0.1s as an average exposure time for the liquid elements on the liquid surface and using the penetration theory formulation, the penetration depth (eq.3.1) and the liquid mass transfer coefficient (eq.3.2) are 25µm and 1.6e-04, respectively.

7 More to investigate

To investigate this problem further the Maragoni effect should be considered. This effect which initiates instabilities on a surface caused by concentration difference on the surface can induce a mass transfer phenomenon called cellular convection. The exposure time needed for this effect to start instabilities is reported 0.01s for MEA solutions in the work of *Krzysztof*. The Maragoni effect in a stirred tank reactor with a flat interface is studied in the work of *Marius Rosu et al.* and it is reported that in absence of any surfactants and surface contaminations the mass transfer coefficient can be enhanced up to 3 times due to the cellular convection.

8 Conclusion

In this study a stirred tank reactor is used to measure the absorption rate of carbon dioxide by aqueous solutions of methylamino ethanol. To evaluate the effect of liquid movement on the absorption rate and determine the mass transfer coefficient and the penetration depth, the exposure time of the fluid element on the surface is determined. This exposure time has an average value of 0.1s which corresponds to a penetration depth of 25µm. By using CFD tools, regarding the usage of sliding mesh and LES simulations, a high computational power is needed, plus, a high resolution mesh. The grid size and quality has a high effect on the results which is due to using the sliding mesh and also the nature of turbulence in the stirred tank system.

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