

CFD Modeling of Carbon Capture in Large-Scale for Structured Packed Bed Column

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Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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for Packed Bed Column

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Abstract

In this Ph.D. thesis, a novel 3D numerical model is developed to solve multiphase flow problem for carbon capture. The model solves the Navier-Stokes equations with commercial solver Ansys Fluent with higher accuracy and much better prediction. The proposed model was at first developed to solve the hydrodynamics problem inside the structured packed bed. In the hydrodynamic part, viscous resistance and inertia resistance for both gas and liquid were taken into account and were implemented by the User Defined Function (UDF). The structured mesh was done using ICEM-CFD. In this part, dispersion forces were also included by UDF. Hydrodynamics of the structured packed bed was validated in terms of liquid volume fraction and, a higher degree of accuracy was achieved. This achievement was done by implementing drag law in a novel way. Dispersion of the liquid inside the packed bed was modeled both by mechanical dispersion and by spread tensor. Pressure drop is a very important part of designing structured packing and, it has to be kept to a minimum. In the hydrodynamics study, this pressure drop was kept minimum, and a good distribution of gas and liquid was achieved.

The second part of the model is the chemical reactions. In this case, all the five reactions that occur in carbon capture were taken into account along with the hydrodynamics. Few studies like the effect of solvent concentration, the effect of pressure were studied by using this part of the model. Another novel aspect of the model is that it can predict gas-liquid interfacial area and enhancement factor for chemical reactions. As a result, it has become much easier to understand chemical reactions and calculate carbon removal easily.

The third part of the model is the heat transfer effect. Heat transfer effect was included by changing gas and liquid temperature and it was found that liquid temperature has a wider impact on carbon capture.

All the contributions to the knowledge were summarized in Chapter 7.

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I would like to dedicate my work to my mother Mrs Bilkish Begum and my wife Dr. Suraiya Sultana

Mohammad Ashraf Hossain

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Nomenclature

Symbol	Unit	Description
a_g	$m^2.m^{-3}$	Packing surface area per unit volume of packed bed.
E1,E2	-	Ergun coefficients
g	$m.s^{-2}$	Gravitational acceleration
s	m	Spread factor
f_e	-	Fractional wetted area.
Θ_1	-	Saturation of liquid
Θ_2	-	Saturation of gas
$S_{porous,1}$	-	Average momentum transfer at the wall for liquid phase
$S_{porous,2}$	-	Average momentum transfer at the wall for gas phase
$\bar{\tau}_1$	-	Averaged viscous stress tensor in liquid phase
$\bar{\tau}_2$	-	Averaged viscous stress tensor in gas phase
$\mathbf{R}_{l1}$	-	Average momentum transfer at the wall for liquid
$\mathbf{R}_{l2}$	-	Average momentum transfer at the wall for gas
$\mathbf{u}_1$	$m.sec^{-1}$	Velocity of liquid
$\mathbf{u}_2$	$m.sec^{-1}$	Velocity of gas
α_l	-	Volume fraction of liquid
α_g	-	Volume fraction of gas
$u_{d,1}$	$m.sec^{-1}$	Drift velocity of liquid
$u_{d,2}$	$m.sec^{-1}$	Drift velocity of gas
τ	Pa	Stress tensor
λ	$W.m^{-1}.K^{-1}$	Thermal conductivity
h	$J.sec^{-1}.m^{-2}.K^{-1}$	heat transfer coefficient between phases
C_p	$KJ.Kg^{-1}.K^{-1}$	Specific heat capacity
S_{lg}	$Kg.sec^{-1}.m^{-3}$	Mass source term between gas and liquid.
y_l	-	Mass fraction of liquid
y_g	-	Mass fraction of gas.
y_l^*	-	Mass fraction of liquid at interphase.
y_g^*	-	Mass fraction of gas at interphase.

Nomenclature

C_l	$Kg.m^{-3}$	Total concentration of liquid.
C_g	$Kg.m^{-3}$	Total concentration of gas.
D_g	$m^2.sec^{-1}$	Mass diffusivity of gas
D_l	$m^2.sec^{-1}$	Mass diffusivity of liquid.
k_g	$m.sec^{-1}$	Mass transfer co-efficient of gas
k_l	$m.sec^{-1}$	Mass transfer co-efficient of liquid.
$\vec{v}$	$m.sec^{-1}$	Phase velocity.
E	-	Enhancement factor.
h_l	-	Liquid hold-up.
T	K	Temperature
MWt	$gm.mol^{-1}$	Molecular weight
r	$mol.m^{-3}.sec^{-1}$	Reaction rate

Abbreviations

AC	Artificial Compressibility
GtC	Giga ton carbon.
CCS	Carbon capture and storage.

Subscripts

g	gas phase
l	liquid phase
int	interphase

Operators

∇	Hamilton (nabla) vector-type differential operator
∇^2	Laplacian second-order scalar-type differential operator

Chapter 1

Introduction and Objectives

The term multiphase flow is used in fluid dynamics when the fluid flow has more than one phase (gas, liquid, solid) or the same phase but with different chemical properties like oil droplets in water. In multiphase flows, two phases are considered. [One](#) is the primary phase, and the second one is the secondary phase. The Primary phase is continuous, and the secondary phase is dispersed in the ongoing phase. Multiphase flows are classified according to the phases or state inflows like gas-liquid flow, liquid-solid flow, etc. Depending on the application, multiphase flows can be in different names like slurry flows, debris flows, cavitating flows, etc. [\[2\]](#).

Multiphase flows can be divided into two [categories](#). The first one is the dispersed flows which consist of drops, bubbles, or finite particles. These are distributed on a continuous phase. On the other one is the [separated](#) flows. [These consist](#) of two or more serial streams of different fluids. These fluids are separated by interfaces. Multiphase flows are present almost everywhere. Starting with the environment, one can find multiphase flows in the rain, snow, fog, landslides, debris flows, mudslides, etc. The human body, all biological or medical flow like blood flow, are multiphase flows. Multiphase flows are also found in process industries, oil and gas exploration, coal mines, pharmaceuticals, etc. Multiphase flow is vital for many industrial processes like riser reactors, bubble column reactors, fluidized bed reactors, scrubbers, dryers, etc. With multiphase modeling analysis, flow dynamics and the contact area between phases can be improved [\[2\]](#).

1. Introduction and Objectives

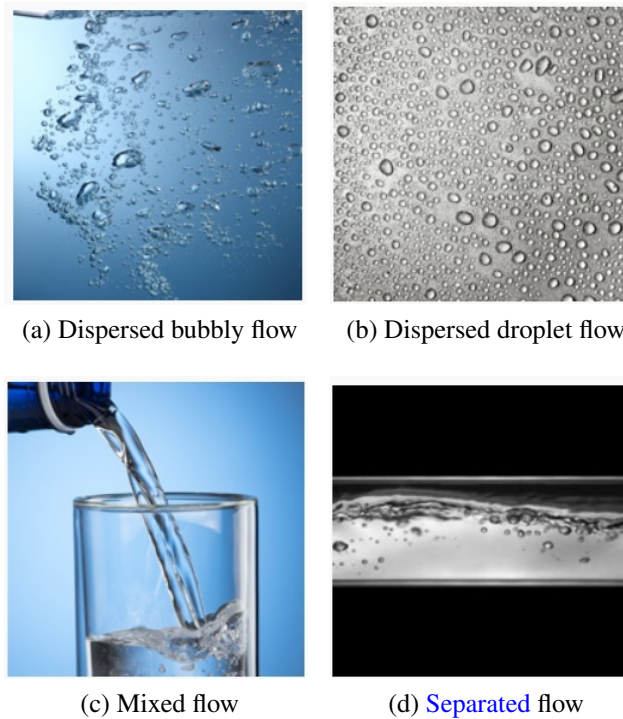


Figure 1.1: Different multiphase flows [1]

Different types of fluid flow are present in multiphase flows, namely bubbly flow, slug flow, chum flow, wispy-annular flow and, annular flow [3]. For co-current gas-liquid vertical flow, at first bubbly flow is formed and, bubbles of various sizes are formed. As the gas flow rate increases, many bubbles coalesce, and slugs of gas are formed, giving rise to slug flow. A thin liquid film is formed, and it separates spherical noses gas slug from the wall. At a higher gas flow rate, this flow pattern is destroyed and a chaotic type of flow, also known as churn flow, is created. With the further increase in the gas flow rate, separation is created and the liquid mainly flows on the wall and, on the other hand, gas in the core. In wispy-annular flow, the liquid is present in large drops, and the liquid film carries gas bubbles, and in the case of the annular flow, both gases flows through the center as a continuous phase, and liquid flows through the wall as a continuous phase [3].

1. Introduction and Objectives

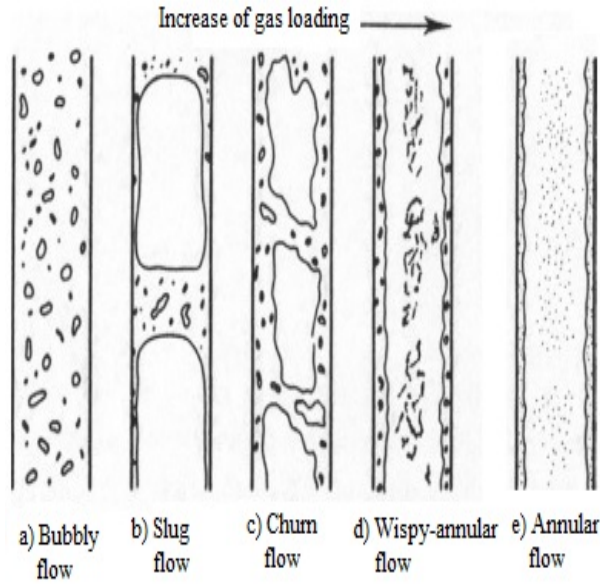


Figure 1.2: Different types of flows.

To study multiphase flows, the prediction of the complex fluid behavior is needed. It can be done by experiments or by numerical modeling. But, experimental studies are expensive, time-consuming. This problem can be solved by numerical modeling. With the increase of computational power these days, numerical modeling has become much easier and quicker. Computational fluid dynamics is an excellent option for numerical modeling. In CFD modeling, Navier-Stokes equations for each phase are solved to get the detail of the multiphase flow like the motion of all fluid particles, location of interface etc.[2].

In disperse flows, two types of models are present. trajectory models and two-fluid models. In trajectory models, the motion of the actual particles is used to assess the motion of the disperse phase. This model is good for granular flows. In two-fluid models, the disperse phase is treated as a continuous phase. Mass, momentum and, energy conservation equations are developed for the two-fluid flows. These equations are then solved computationally. Two-fluid models do not take into account the discrete nature of the disperse phase and take it as a continuous phase. Averaging processes are necessary in this case [2].

1. Introduction and Objectives

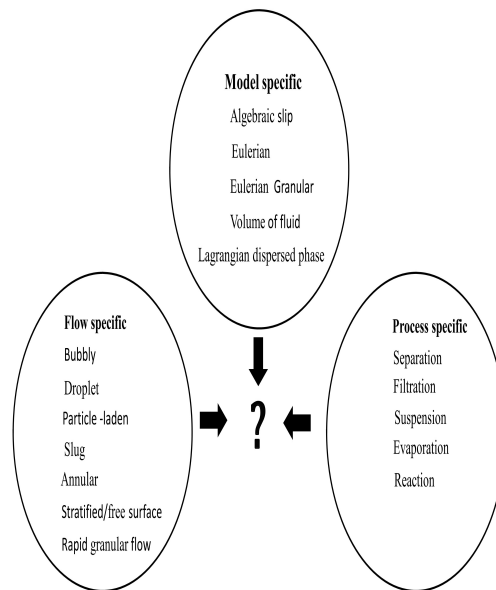


Figure 1.3: Modeling approach for multiphase flows.

In summary, for numerical modeling of multiphase flows, few things must be taken into account like the goal of the simulation, what are the important effects, take account hydrodynamics effects, take into account transport phenomena.

1. Introduction and Objectives

1.1 Background and Motivation of the Research Work

Demand for energy throughout the world is growing up day by day with the rapid economic growth. As a result, energy demand is growing up, and since the industrial revolution, conventional fossil fuels are playing a vital role as a source in energy generation. Due to the increased use of fossil fuels, the environment is adversely affected, especially by carbon dioxide emissions. The temperature of the earth's surface has gone up significantly since the industrial revolution, and it is rising rapidly and causing a change in global climate change. This climate change has a severe impact on humans as well as other living species. CO_2 gases, produced by the combustion of fossil fuels, are greenhouse gases and contribute a lot to global warming. At present, 30 gigatons (Gt) of CO_2 is emitted into the world's atmosphere annually due to the combustion of fossil fuel and about 40% of it comes from the power plants alone [4]. According to the Emission database for global atmospheric research, in 2011, 33.4 billion tons of CO_2 was emitted to the atmosphere of the earth. It was 48% more than the emission of two decades ago. In pre-industrial time atmospheric CO_2 level was 280 ppm. In May 2013, it was increased to 400 ppm, which was an increase of more than 39%, and as a result, global surface temperature was increased by about 0.8 °C [5]. The International panel for climate change (IPCC) forecasted that by the year 2100, the mean global temperature may rise up to 1.9 °C [6].

According to the IPCC report at present, the concentration of Green House Gas (GHG) in the atmosphere is close to 400 ppm and if the emission of GHG continues like this scientists estimate that by 2050 it will be 500 ppm and by 2100 it will be 800 ppm. As a result, more global warming will happen, and it will give rise to seawater level, a severe decline in the world economy. Moreover, CO_2 emissions from fossil fuel will also contribute to the acidification of the oceans, and the nitrogen cycle in the atmosphere. Nitrogen will react with CO_2 and turn into more reactive oxidized forms. Even if the concentration of CO_2 is stabilized at 450 ppm by 2100, pH will be reduced by 0.1 but still coral reefs will be poorly doomed, and some sea animals cannot build shells in southern oceans. As a result, marine life will be affected a lot [7].

Between the years 2002-2011, the average CO_2 emission from fossil fuel and cement production was 8.3 GtC per year, and in 2011, it was 9.5 GtC per year, compared to 1990, it was 54% more. During 2002-2011, average CO_2 emissions from anthropogenic land use were 0.9 GtC per year. It is interesting to know that from 1750 to 2011, the CO_2 emission from fossil fuel combustion and cement industries was 375 GtC; at the same time, land use contributed to 180 GtC. From these CO_2 emissions, 240 GtC were accumulated in the atmosphere, 155 GtC were taken by the oceans and 160 GtC were taken by the terrestrial ecosystems. Finally, one can come to the conclusion that since pre-industrial times, CO_2 concentration has increased by about 40%. Using fossil fuel is the primary reason for it.

1. Introduction and Objectives

The second reason is the change in land use. Roughly ocean has taken 30% of it and as a result, oceans are becoming acidic [7].

In 2009, at the Copenhagen conference, all the participant countries agreed that the emission of global greenhouse gas (GHG) must be reduced by at least 80% by the year 2050 to keep global warming below 2 °C . It will also stabilize CO_2 concentration at the level of 450-550 ppm by the year 2050. It will ensure the stabilization of the global mean temperature increase between 2-2.8 °C. The present situation can be summarised as 240 GtC of CO_2 emissions have already been taken by the atmosphere and, 10 GtC per year are being released into the atmosphere. It will be a great challenge to reduce this emission [7]. CO_2 emissions can be drastically reduced by improving the efficiency of the power plants and reducing the requirements of energy [8].

There are three options to reduce carbon emissions a) Use of energy has to be reduced by improving efficiency, b) use other energy sources like renewables to replace fossil fuel c) Carbon capture and storage (CCS). The best option to reduce carbon is to go for renewable energy sources. But, at present renewable energy sources are not a good option compared to fossil fuel due to cost and feasibility. Therefore, the only option is to consider CCS to reduce CO_2 emission [9].

There are three main CO_2 capture systems for different kinds of combustion processes like post-combustion, pre-combustion and, oxyfuel combustion, and it is briefly discussed below:

1.1.1 Post-combustion: The post-combustion process CO_2 is removed from the flue gas after the combustion. This technology is a preferred option for retrofitting existing power plants. It is proved that for a small scale, this technology is capable of recovery of CO_2 at a rate up to 800 tons per day. For post-combustion CO_2 , the major challenge is its large parasitic load. It was estimated by the National Energy Technology Laboratory that the cost of electricity generation would be increased by 70% if the post-combustion the technique is used for CO_2 capture. This technology is used for coal-fired and gas-fired power plants.

1.1.2 Pre-combustion: In pre-combustion process, fuel is preheated before combustion. The fuel can be either gas or coal. For coal, a syngas is formed by involving a gasification process in a gasifier with the presence of low oxygen. The syngas consists of CO and H_2 and also free from other pollutant gases. Then, the syngas undergoes a water gas shift reaction and, CO gas is converted into CO_2 . It is used in coal-gasification power plants.

1. Introduction and Objectives

1.1.3 Oxyfuel combustion: In oxyfuel combustion, instead of air, oxygen is used for combustion. The amount of nitrogen gas is reduced due to this in the flue gas. Oxyfuel combustion is used both for coal-fired and gas-fired power plants.

There are different types of technologies available in carbon captures like adsorption-based CO_2 capture, membrane processes, cryogenic methods, hydrate process, and electrochemical techniques [10]. Different CO_2 separation technologies are discussed below:

1.1.4 Absorption: In absorption technology, a liquid sorbent is used to separate the CO_2 from the flue gas. This liquid sorbent can be regenerated by stripping. Few sorbents are like monoethanolamine (MEA), diethanolamine (DEA), and potassium carbonate. MEA is proved to be the most efficient sorbent with the efficiency of more than 90%. In recent years some other sorbents like piperazine and anion functionalized ionic liquid have also got considerable attention. Piperazine is found to react much faster than MEA, but its volatility is much higher than MEA, and its application in CO_2 capture is very expensive. One of the main challenges in absorption is potential amine degradation; as a result, the solvent is lost. Equipment corrosion is also a problem in absorption [5].

1.1.5 Adsorption: Adsorption technology is different than absorption in using sorbent. It uses solid sorbent instead of liquid. Solid sorbent binds CO_2 to its surface [5].

In selecting the sorbent's large specific surface area, higher regeneration ability and higher selectivity are the selecting criteria for sorbents. Some of the sorbents are activated carbon, calcium oxides, lithium zirconate, zeolites and, hydrotalcites [5].

Technology	Advantage
Absorption	Absorption efficiency is higher.
Adsorption	Absorbent can be recycled.
Chemical looping	CO_2 does not mix with Nitrogen gas.
Membrane separation	Higher separation efficiency is achievable.
Hydrate-based separation	The energy penalty is minor.

Table 1.1: Advantages of different separation technology

1. Introduction and Objectives

Technology	Disadvantage
Absorption	A lot of heat is needed to regenerate sorbent.
Adsorption	High temperature adsorption is needed.
Chemical looping	There is no large scale experience.
Membrane separation	Problems occur due to low fluxes and fouling.
Hydrate based separation	New technology is required by research.

Table 1.2: Disadvantages of different separation technology

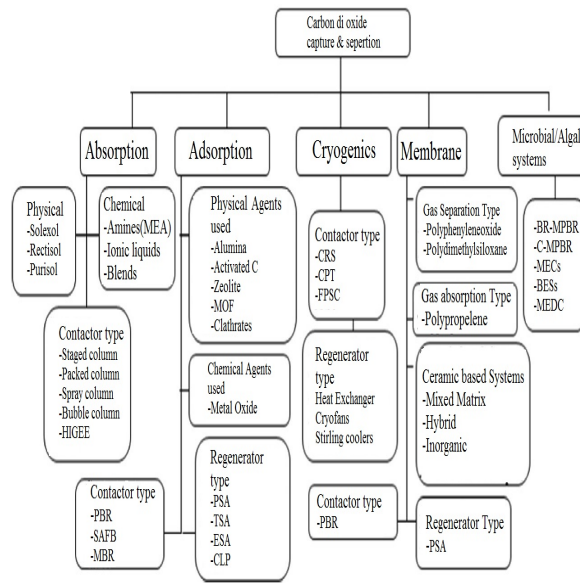


Figure 1.4: Various carbon capture technologies

[11]

CCS aims to develop more advanced CO_2 absorption technology to minimize energy consumption during the CCS process. Amine solution leads to corrosion on equipment, oxidative degradation of absorbents, flow problems due to high viscosity, and higher energy consumption. In the MEA absorption process, the MEA solution comes in contact with the flue gas in an absorber column and reacts with CO_2 present in the flue gas and thus, forms MEA carbonate in solution. This CO_2 rich MEA solution is then sent to stripper and reheated to release pure CO_2 . It is an expensive process as it needs a lot of energy input and a large process unit. The heating cost is responsible for up to 70% of the total operating cost. Using solid absorbents with a higher surface area can be a possible solution to this problem. Zeolites will be a good candidate for solid absorbent. Zeolites consist of nanoporous structures and have a higher surface area. But, in carbon capture, zeolites can be deactivated by moisture, and as a result, absorption capacity will be significantly reduced. Secondly, due to the presence of water vapor in combustion products,

1. Introduction and Objectives

zeolites will be ineffective. To make it work in CO_2 capture, moisture content must be removed [6].

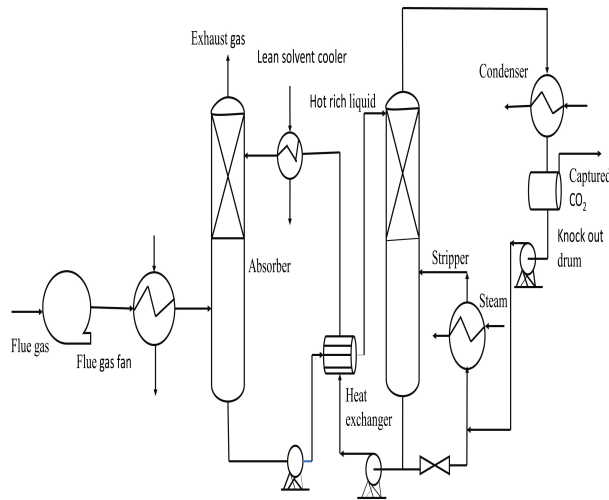


Figure 1.5: Schematic diagram of the solvent process for carbon removal.

[9]

Carbon capture technology has the main drawback in its process, and it is about the consumption of a certain amount of energy. This consumption of energy also contributes to producing more CO_2 [6]. To meet the target of carbon capture is very challenging as a large amount of it comes from the power plants themselves by the combustion of coal. Post- combustion capture (PCC) for coal-fired power plants is very cost-effective [12]. To solve this problem better [understanding](#) of liquid spreading in structured packings is necessary as based on liquid distribution and anyone will be able to determine what type of mechanism will be used.

1. Introduction and Objectives

1.2 Problem Statement

The primary outcome of this [Ph.D.](#) project is the successful development of a 3D CFD multiphase model to solve hydrodynamics problems for structured packings by taking into account dispersion forces. With this research work, it has now become possible to predict flooding inside the packing. Moreover, by taking account of chemical reactions, the model can predict the amount of carbon removal on any height of the packed bed column. The model is capable of working for any liquid and gas loading, which made it unique and the author can claim in confidence that the model is capable of replacing experiments for this type of application.

In this thesis, to make the solution more accurate gas-liquid drag law is applied more efficiently, and as a result, the solution is much improved. So far, it was available in the 2D case, but now after the project, it can be used in confidence for a 3D case. For CCS, when the flue gas comes in contact with MEA in the packed bed column, the reactive mass transfer happens between the gas and liquid phases due to absorption. Hydrodynamic features like pressure drop, liquid saturation, liquid hold-up, etc play a vital role in the absorption process and as a result, packed bed performance highly depends on these parameters. For a large scale, CFD modeling predicting the liquid dispersion and liquid saturation is very important to predict the removal of CO_2 . This research made it possible to do it. A [user](#) defined function (UDF) was developed to take account liquid dispersion, liquid volume fraction, and reaction kinetics in C language. Commercial software package Ansys Fluent v14.5 was used to solve continuity and momentum equations. The analysis of the simulation results will give the following results:

- Correct presentation of liquid hold-up, pressure drop, and liquid saturation.
- Correct presentation of liquid and gas profile.
- Correct presentation of the reaction products of the MEA- CO_2 system.

The aims of this project can be summarized as follows:

1. To develop a 3D multiphase CFD model for large scale in taking consideration of liquid dispersion, hydrodynamic features like liquid hold-up, effective area, and pressure drop have to be calculated with the model as well. All these results have to be validated against experimental results.
2. To include mass transfer, chemical reactions, and heat transfer in the model to calculate the CO_2 removal across the column height. Further validation of the model at this stage will also be needed.

1. Introduction and Objectives

1.3 Thesis Structure

The thesis is divided into ten chapters.

Chapter 1 describes the background and problem statement of the research work.

Chapter 2 is for the literature review of models. It covers hydrodynamics studies, chemical reactions, and heat transfer effect in carbon capture.

Chapter 3 introduces the governing equations and solution techniques.

Chapter 4 introduces hydrodynamics modeling. This chapter validates the results with the experimental one. It also describes various hydrodynamic properties of the packed column.

Chapter 5 is about mass transfer and chemical reaction modeling.

Chapter 6 introduces heat transfer modeling. It explains what happens in carbon capture with the application of heat.

Chapter 7 is summarizing the conclusions of the present research work and the results of the contribution to the knowledge, including the future work.

1. Introduction and Objectives

1.4 Publications

1. 3D CFD modeling of liquid dispersion in structured packed bed column for CO_2 capture. Mohammad Ashraf Hossain, Seyed Ali Nabavi, Panneerselvam Ranganathan, László Könözy, Vasilije Manovic. Chemical Engineering Science 225 (2020) Article no: 115800.

2. 3D CFD modeling of reactive chemical absorption and effect of heat transfer in CO_2 removal in structured packed bed column. The paper is going through the editing stage and will be submitted to the journal very soon.

Chapter 2

Literature Review

Several key mechanisms are involved in carbon capture by MEA scrubbing by using structured packings. It starts with the distribution of liquid MEA through the structured packed bed. Section 2.1 is about the dispersion of liquid and the mechanism of distribution of liquid inside the packed bed. In the next step, MEA comes in contact with gas, and MEA reacts with CO_2 . Section 2.2 covers this reaction mechanism. In the process of carbon capture, heat also plays a vital role. Section 2.3 is about the heat transfer effect in the carbon capture process.

2.1 Multi-Phase Modeling of Liquid Dispersion

Liquid dispersion modeling has to consider the modeling of liquid spreading and the hydrodynamics inside the packed bed. Spreading of the liquid inside a packed bed column can occur from a single source or from multi-sources, depending on the requirements. In the hydrodynamics part of the modeling, normally wet pressure drops, liquid volume fraction, and liquid hold-up are studied. Liquid hold-up later helps to determine column dynamics.

2. Literature Review

determined in the dry bed of particles, and for wet pressure drop, a correlation is used. The main advantage of this approach is the effect of the liquid holdup on pressure drop is taken into account [16].

2.1.1.1 Pressure drop models

The pressure drop model of structured packings was fundamentally developed by Bravo et al. [17] from the separation research program [17]. This model (SRP I) was based on air-water pressure drop and for the drop of pressure prediction below loading conditions for structured packings. This model was further developed by Bravo et al. [18] by proposing a new correlation to predict efficiency and pressure drop for gauge and sheet metal structured packings. This improved model is reliable at low-pressure drop, but it does not work well above the loading point liquid hold-up is significant, and the model does not take it into account. Pressure drop prediction in structured packings was further improved by proposing using empirical capacity plots for pressure drop versus flow parameter by Fair et al. [27]. The main disadvantage of this approach is that for each size and type of the packing, a particular capacity plot is needed.

SRP I model was further improved by Rocha et al. [26] and named it as SRP II model. This model is based on the channel approach. They made modifications to effective gas and liquid velocity, contact time, and the characteristic dimensions of the packing. For the SRP II model, pressure drop at the flooding point is needed to predict liquid-holdup and pressure drop in the packing. A general suggestion was $1025 \text{ Pa}\cdot\text{m}^{-1}$ as the flooding pressure drop. SRP II model was further developed by Gualito et al. [22] to use for high-pressure systems. Gualito et al. [22] at first proposed a general model for structured packings made with metal, ceramic, and plastic, and then they improved the model to use it in low and high pressures. They mentioned that as the flooding pressure drop is very important in the SRP II model, it can be improved by using lower prediction values of liquid hold-up and pressure drop. For a higher pressure drop, the packing capacity is extended. Based on McNulty data [28] Gualito et al. [22] proposed a correlation between liquid superficial velocity and pressure drop at flooding.

The liquid hold-up is not significant in the pre-loading region of the packed bed as there is little interaction between gas and liquid in this region. But, above this point, liquid hold-up increases. In the SRP II model, the main disadvantage is that the model cannot predict the loading point. Fair et al. [21] used the method of Verschoof et al. [29] to predict this point.

Pressure drop up to the flooding point for two phases counter current flow in packed columns were also developed by Billet et al. [30] to study hydrodynamics. The effect of design, operational and physical parameters were considered in the model. This model was validated for a large number of packing type and was found working well for both

2. Literature Review

structured and random packing. This model was further developed by considering the effect of the liquid hold-up in pressure drop, flood points, loading and mass transfer efficiency [31, 32]. This model development was made on the assumption that for a counter current flow in a packed bed, the effective free space is equal to the multitude of vertical flow channels. In this model, the liquid hold-up is based on observations and dynamic hold-up and total hold-up are related to liquid flow regime as well as on the operating conditions. Based on the liquid hold-up a new model was proposed by Billet and Schultes [33] for high-pressure systems and systems with very low liquid viscosity. They considered liquid hold-up as a function of liquid velocity and liquid phase physical properties below the loading point. According to this model, if the gas velocity is increased, the shear stress at the gas-liquid interface also increases, and finally, column holdup and interface size also increase.

Hydrodynamics of the packed column was studied in detail by Mackowiak [34, 35] by presenting a model of a suspended bed of droplets to describe the gas velocity. This model was validated for different types of packing made with a different type of materials. The flooding gas velocity and flooding liquid hold-up can be calculated by this model. This model can handle liquid load up to $250 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$

Another model known as the Delft model is used to calculate hydrodynamics for sheet structured packings. This model was developed at the Delft University of Technology by Olujic [36, 37, 38]. This model is capable of evaluating performance and to optimize the geometry of structured packings. It assumes the surface is completely wetted and the liquid film exists with a constant thickness. The liquid hold-up is then calculated from the packing area and average film thickness. The liquid hold-up value calculated by this model is lower than SRP II model. According to this model, gas flows upwards through a triangular channel. This channel has constant dimensions, and gas has a zigzag flow. On the other hand, liquid flows downwards as a thin layer. As the flow changes direction, a diameter effect is introduced by Olujic [37], and he divided the hydraulic operation into two zones, namely the wall zone and bulk zone. According to experiments, the diameter effect is related to the number of direction changes of the gas in the bed. As a result, a new correlation is needed, and this gap was filled by Verschoof et al. [29]. They proposed an empirical correlation for different geometry of packings and a wide operating range. This model can be used with either Delft or SRP models to determine pressure drop. Further, the Delft model was described by Olujic et al. [38] in detail, and to predict the interfacial area of the packed bed with a large surface area, a new correlation was proposed. The main advantage is that this model does not require any adjustable parameters.

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2.1.1.2 Mass and momentum conservation models

Pressure drop, liquid hold-up, and flooding were predicted by Paglianti et al. [39] by developing a mechanistic model. The model is based on mass and momentum conservation. The model also considered both co-current and counter-current flow for structured packings. The model was first developed for simple geometry and then extended to complex geometry. The mechanistic model was also used by previous researchers [40, 41]. They considered packings as a bundle of channels and inclined angle equal to the corrugation angle. This model is based on several assumptions as 1) Gas load and gas-liquid interfacial shear stress does not affect packing fractional wetted area. 2) interfacial shear stress is not related to interfacial velocity, but to effective liquid velocity 3) Dynamic liquid hold up is based on Spiegel correlation [42]. By analyzing pressure drop, Brunazzi et al. [41] made two contributions. The first one is the distributed pressure drop due to loss both at channel walls and gas-liquid interface. The second one is the concentrated pressure drop due to the changes of flow direction at the interface between two adjacent packing, and it can be reduced by changing the gas flow direction. This model can be used for different types of packings to predict pressure drop and flooding.

The channel model with the combination of the Buchanan equation [20] was used by Brunazzi et al. [43] to study the flooding point for a specific loading in a packed bed. They used the channel model for dry pressure drop and the Buchanan equation for wet pressure drop. They commented that for higher liquid loads, a fixed value wet pressure drop may not give correct gas velocity. They proposed that liquid hold up at below the gas loading point should be taken to calculate flooding gas velocity. This model is applicable to both structured and random packing.

Based on the particle model, Stichlmair model [16] was further developed by Engel et al. [44] to calculate liquid hold-up, pressure drop, and flooding point for both structured and random packing. The big advantage of this model is that it only needs the dry pressure drop and the geometric parameters like void fraction and surface area. This model was validated for both structured and random packing with a large amount of physical and operating data. Using the correlation of gas-liquid interaction on a completely wetted packing surface, Ranke et al. [45] developed a physical-based model to describe hydrodynamics, pressure drop, liquid hold-up for the loading region of the flooding point.

Based on the open channel model, Rocha et al. [26] proposed a model to predict the pressure drop for ceramic structured packing. This model is based on three correlations, and all the correlations use the same general equation to calculate dry pressure drop. Then, it is corrected by liquid hold-up.

Few other models were also developed in the past based on different concepts. Iliuta et al. [23, 25] used double-slit model approximation to develop two-fluid mechanistic models to predict irrigated pressure drop, packing wetted area, and total liquid hold-up.

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This model does not need any adjustable parameter and can be used in the absorption column. Again, based on the theory of critical phenomena, Hanley et al. [46] developed a model to predict pressure drop for a two-phase flow. In this model, the pressure drop equation was a function of the liquid flow profile. Moreover, based on the macroscopic approach, Woerlee et al. [47] explained the hydrodynamics in an inclined flow channel for a two-phase counterflow. In this model, pressure drop by geometry and pressure drop by gas-liquid interface were considered separately, and three independent equations were proposed for a laminar film to explain liquid hold-up, phase velocity at the interface, and pressure drop as a function of gas or liquid phase properties.

Although a large number of literature is available for hydrodynamics study, there is a need for a 3D hydrodynamics study in terms of pressure drop, liquid saturation for a structured packed bed to avoid significant errors. The present CFD study on hydrodynamics provides it.

2.1.2 Liquid spreading modeling:

Liquid spreading happens due to mechanical dispersion, capillary dispersion, and overloading. For porous media, gas flow rate and porosity plays an important part in liquid spreading. Few approaches in modeling liquid dispersion were used as well in the past, like network models [48, 49], automata models [50, 51], random walk methods [52, 53, 54, 55], and general mathematical models [56]. All of these models used a source point for liquid distribution for CFD modeling. All the models used phase interaction but did not use mechanical dispersion, which is essential for porous materials [57]. Scott [54] proposed a statistical model based on a random hypothesis. This model can be used for low liquid rates and without the wall effects. Cihla and Schmidt [58] used a diffusion type equation. A radial spread factor is applied in this equation and the spreading of liquid in the packed bed was characterized by this. This idea was used by many authors. the idea of the diffusion model is that liquid flows as a film[59].

The most popular CFD method to understand the gas-liquid mechanisms are Euler-Euler and VOF methods. The advantages of the VOF method are: (i) all the typical flows (film, rivulet, and droplet) can be explained and observed. (ii) it is possible to get maldistribution of liquid (iii) the interaction force between the phases is not needed, and (iv) gas and liquid are treated as one mixture and is simple. The main disadvantages of this method are (i) it needs a very small grid size ii) it cannot simulate 3D large scale. The problem of the VOF method can be solved by a porous media model with an Eulerian method due to the lower requirement of computational resources. The porous media model with Euler-Euler method consists of the drag force between the gas and liquid for a two phase flow. For CFD simulations of gas-liquid two-phase flows in packed beds the available porous media models are the Attou [60], Lappalainen [61] and, Iliuta models

2. Literature Review

[24].

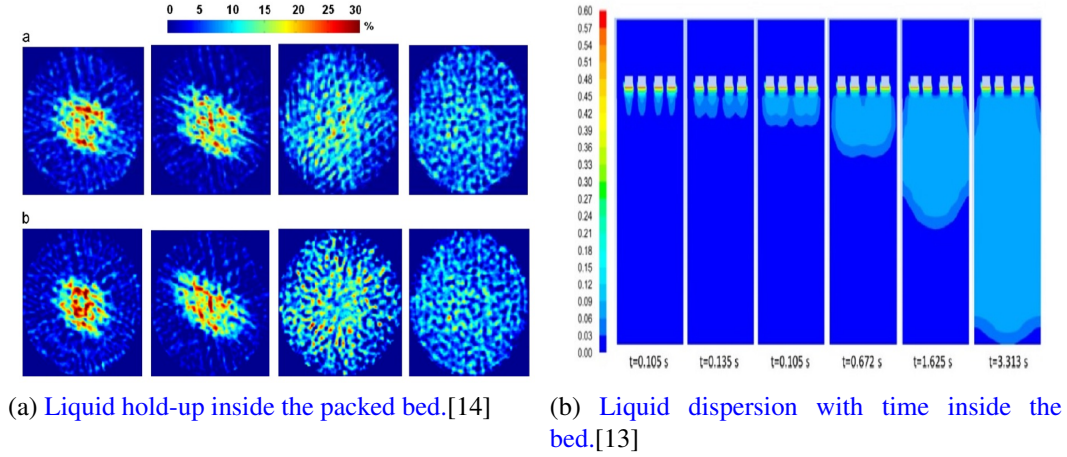


Figure 2.2: Liquid hold-up and liquid dispersion inside packed bed.

For the Attou model, it is assumed that a smooth liquid film flows on the spheres of the packed, and the gas flows through the empty space in the packing area. A stable interface separates the gas and liquid. And the phase interaction is described by the one-phase Kozeny-Carman equation. Finally, the form of each equation for the interaction becomes similar to the Ergun equation. Many researchers used this model [62, 63, 64]. Lappalainen et al. [61, 65] developed a porous media model based on the wetting efficiency and packing of spheres. The total interaction force for the gas and liquid is the difference between the drag force of the phases and the interaction force between the solids and liquid or gas. For drag force and the interaction force, Ergun equation is used. It is assumed that the packing materials are ideal spheres, and the liquid flows as a film on the surface of the spheres for both the Attou model and Lappalainen model. Moreover, in the Attou model it is assumed that a liquid film covers the solid spheres and in Lappalainen model it is assumed that part of the sphere surface is covered by the liquid and as a result a term wettability is used in this model. Iliuta et al. [24] developed a porous media model for the structured packing that contains columns. They had taken the flow as simplified two-parallel inclined slits, and slits are interconnected. Out of the two slits, one is a dry slit, and the other one is a gas-liquid wet slit. For laminar or turbulent flow, the slit wall experiences shear stresses. The pressure drop is equal across the dry slit and wet slit. For structured packing, this model is popular in CFD simulations [13, 14].

2. Literature Review

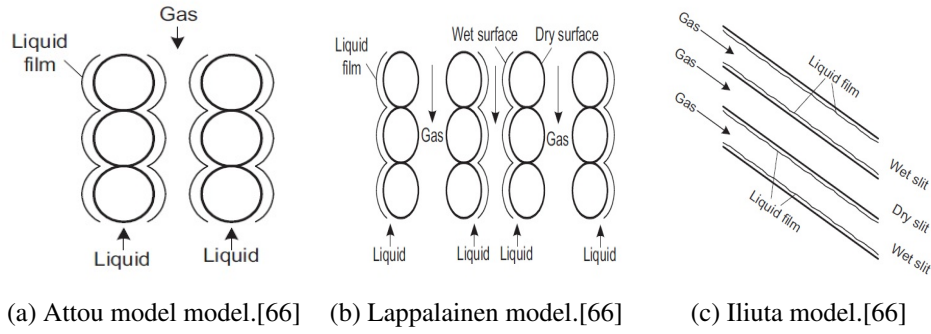


Figure 2.3: [Schematic diagram of different models for porous media.](#)

Since the drag law plays a vital role in the Eulerian-Eulerian method of CFD modeling of a liquid dispersion, there is a need to understand the influence of the drag law in gas-liquid multiphase flow in detail. At present, it is not available. The present work fills this knowledge gap.

2. Literature Review

2.2 Mass Transfer and Chemical Reactions

In post-combustion, carbon capture using monoethanolamine solutions in structured packed bed columns is one of the most accepted solutions. In the post-combustion stage, two columns are used. One is the absorber, and the other one is the stripper. The absorber is filled with structured packing material with a very high contact area. As both gas and liquid flow in a counter-current direction, the reactive mass transfer occurs with both the fluids.

The gas which has traveled through the absorber is clean gas free from CO_2 and is ready to be released into the atmosphere. However, the amine solution is enriched with CO_2 and enters the stripper. In the stripper, the weak bond between the CO_2 and amine is broken by applying heat, and the amine solution is again circulated in the absorber. This stage of CO_2 capture is the most expensive, and roughly 80% of the operating cost is engaged here. In this way, a full-cycle completes.

Over the past few years, due to the increase of computational resources, CFD has become a very useful and effective tool to model this reactive mass transfer in a packed bed column due to some outstanding benefits. It can eliminate expensive experiments, and it can be applied on any scale. Moreover, CFD can be very useful in optimization and thus can reduce the cost quite significantly.

CFD analysis for multiphase flows can be done in three different scales. 1) micro scale, 2) meso scale 3) macro scale.

In micro scale the computational domain is kept limited to few centimetres and liquid maldistribution can be understood by this. In meso scale, the computational domain is kept limited to several REUs (representative elementary unit), and in macro scale the whole reactor is being considered. In this study, macro scale was used by considering the whole packed bed as a porous medium. In modeling chemical reactions, both liquid dispersion and chemical reactions were implemented into the model by UDF, and Eulerian-Eulerian model was used for this purpose.

2. Literature Review

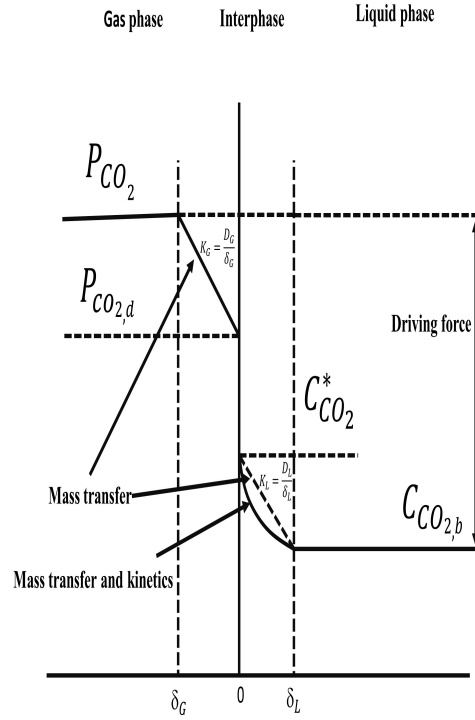


Figure 2.4: Mass transfer and reaction kinetics in MEA- CO_2 absorption system

In figure 2.4 P_{CO_2} is partial pressure of CO_2 at the interface, $C_{\text{CO}_2,b}$ is molar concentration of CO_2 in liquid phase (mol.L^{-1}), δ_L is liquid film thickness (m), δ_G is gas film thickness (m), D_G is diffusion coefficient in gas phase ($\text{m}^2.\text{sec}^{-1}$), D_L is diffusion coefficient in liquid phase ($\text{m}^2.\text{sec}^{-1}$), k_L is liquid side mass transfer coefficient ($\text{m}.\text{sec}^{-1}$), k_G is gas side mass transfer coefficient ($\text{m}.\text{sec}^{-1}$), $C_{\text{CO}_2}^*$ is interfacial concentration of dissolved CO_2 (mol.L^{-1}).

In chemical absorption, also known as reactive absorption liquid phase absorbs the gas with absorptive mass transport and reaction. Few chemical absorption systems are carbonate-based, amine-based, aqueous ammonia, and ionic liquid-based systems.

In CO_2 capture, chemical absorption occurs when CO_2 reacts with a chemical solvent and then forms a weakly bonded compound. By applying heat, this process can be reversed, and the solvent and CO_2 stream are separated. It is known as the regeneration stage [67].

In the absorber column, flue gas encounters the chemical solvent at a low temperature (40-60 °C). The chemical solvent becomes rich with CO_2 , and then it is compressed, heated in an exchanger, and then sent to the desorption column (stripper). The regeneration processes occur at low pressure (near to ambient) and high temperatures (100-140 °C). The regenerated solvent becomes lean and then again reused in the absorber [67].

2. Literature Review

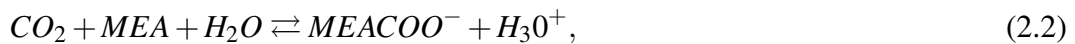
Few common amines are Monoethanolamine(MEA), Diethanolamine(DEA), Methyl diethanolamine (MDEA), Diglycolamice (DGA), Diisopropanolamine (DIPA), and Piperazine (PZ) or a mixture of amines that provides good reaction rates and needs less regeneration energy. MEA is preferred as it provides higher absorption capacity and faster reaction rates[67]. A special type of amine is sterically hindered amines (SHA). SHA forms more unstable carbamates and, as a result, less energy is needed for regeneration. Alternative solvents for chemical absorption are ionic liquids, potassium carbonate, and aqueous ammonia [67]. To achieve CO_2 capture, flue gases from post- combustion processes are treated by an absorption loop with basic solutions. The best solvents for this kind of treatment should have simultaneously a good resistance to thermal and oxidative degradation, high absorption kinetic, and low regeneration energy [68]. Two factors govern the absorption process between liquid and gas. a) mass transfer between the phases and b) chemical kinetics. Chemical kinetics depend on the solution that contains the dissolved reactive absorbent, but the mass transfer depends on the dissolved reactive absorbent and on the type of equipment. Diffusivities, fluid mixing, geometries determine the mass transfer. So, faster mass transfer and faster kinetics are essential for better performance [69].

2.2.1 Requirement for the Modeling

In chemical absorption, both thermodynamic and chemical reaction aspects are involved. In this process, both the chemical reactions and absorptive mass transfer occur simultaneously. In the reactive absorption process, the reaction velocity varies from very low to very high, known as slow reactions and instantaneous reactions, and multi-components are also involved in. The ideal model must be capable enough to handle all these challenges. It must also be easy enough to implement [67]. Surface tension plays a vital role in desorption by enhancing the diffusion process and increasing concentration gradient [70].

2.2.1.1 Modeling approach to the chemical reaction

Several chemical reactions are involved in the carbon removal process with MEA scrubbing. All the reactions are given below:



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Eq. (2.1) and eq. (2.2) are finite rate reactions and eq. (2.3) to eq. (2.6) are instantaneous reactions.

Two types of approaches can be used to model the absorption process in a packed bed. One is equilibrium-stage modeling and the other is rate-based modeling. In the equilibrium-stage modeling, both the liquid and gas phases are well-mixed, and all the segments are considered to be in equilibrium. Only the mass, enthalpy are considered in this approach and are much simpler [71].

In rate-based approach, a finite rate of absorption is considered. As a result, physical properties and mass and heat transfer rates are very important in this approach. Heat and mass transfer are explicitly considered in rate-based models. Concentration gradients of the fluid are used to calculate mass transfer. Temperature gradients are used to calculate the heat transfer. Two film models can be used to describe the mass transfer that occurs at the gas-liquid interface. This model assumes that mass transfer and heat transfer happen only in the liquid and gas phase, and at the same time, bulk phases are ideally mixed, and there is no gradient of concentration or temperature. There is a thermodynamic equilibrium state in the gas-liquid interface. To describe the physical and chemical properties of the fluids, heat, and mass transfer, rate-based models need many input parameters. Transport properties and mass transfer correlations are also needed in this model [71].

A quick mass transfer is assumed in equilibrium models. As a result, these models are more applicable for high reaction rate solvents like primary amines. Mole fractions, equilibrium equations, material and heat balances are used in this model [67].

Non-equilibrium models predict mass transfer resistance and real reaction rates. The enhancement factor is approached in this type. It is done either experimentally or based on simplified assumptions [67].

Reaction kinetics can be considered by both models, or it might not be considered. Kinetics should be considered as a dominating factor if the mass transfer rate is faster than the reaction rate. The equilibrium stage can consider bulk phase reaction kinetics or both the bulk phase and film kinetics. However, this type of approach is physically inconsistent with reaction kinetics [67].

Usually reactive absorption for columns is modeled with an equilibrium state, but absorption is a phenomenon controlled by rate. As a result, mass and heat transfer are driven by gradients of the chemicals and temperature. Due to this reason, equilibrium-based models are usually not adequate.[72].

Only rate-based models can consider resistance to mass and heat transfer. In this model, mass and heat fluxes along the interface are considered. To predict the accelerat-

2. Literature Review

ing effect of chemical reactions on mass transfer, additional rigorous predictive models are required. These effects can be described well by enhancement factors for a single irreversible reaction. For simple reaction, enhancement factors derived from theoretical derivations are exact else, they are based on several simplifications like gas-phase resistance is negligible, absorption is isothermal, through the interface, only one component is transported [72].

In the reaction process, several components from both liquid and gas phases are present. These components are comprised of both neutral molecules and electrolyte species. As all the components take part in complex and parallel reactions, multicomponent mass transfer and multiple reactions arise. As a result, a specially developed model that considers mass transfer resistance, electrolyte thermodynamics, reaction systems, and column configuration is required [72].

Gas-liquid hydrodynamics can be described by three frameworks, namely two-film theory, penetration theory, and surface renewal model. According to film theory, a stagnant film of both gas and liquid is assumed on the two sides of the liquid-gas interface. In this layer, resistance to the mass transfer is concentrated, and mass transfer occurs by molecular diffusion. According to penetration theory, the gas-liquid interface is not stagnant, and fluid elements raise from the liquid bulk to the interface, where it remains for a time and then finally travels back to the solution. The surface renewal model is a modification of the penetration theory. It assumes a distribution of the contact time of the liquid elements. It considers mass transfer through a laminar layer [73].

To reduce the complexity in solving mass and energy balance equations, the enhancement factor is introduced. It is defined as the ratio of mass transfer from chemical absorption to physical absorption. As it is a relative factor, it indicates the improvement of the reactive solvents over the non-reactive solvents. For numerical solutions, the enhancement factor is preferred as it reduces computational load. Several enhancement factors were developed in the past based on eddy diffusivity, fast kinetics, and concentration of the species and Hatta number [73].

Hatta number is a relative parameter to compare the rate of reaction in a liquid film to the rate of diffusion. A higher Hatta number will indicate a higher reaction rate compared to diffusion. As a result, the reaction will take place mostly in film [73].

Based on the Hatta numbers, three different regimes of reaction rates can be defined as below: i) Instantaneous / very fast reaction ($Ha > 10$). The reaction is very fast and occurs at the gas-liquid interface. Mass transfer will not be enhanced further with the increase of the reaction rate. The mass transfer in the liquid film only depends on the concentration and diffusion coefficients of the components. ii) Intermediate reaction ($1 < Ha < 10$). The reaction occurs in the liquid film, and a concentration gradient is created. This gradient enhances mass transfer. Mass transfer in the liquid film depends on the reaction kinetics

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and diffusion coefficients. iii) Slow reaction ($Ha < 1$). In this region, the reaction is slow and it occurs in the bulk phase [73].

2.2.1.2 Modeling approach to mass transfer

Structured packings have been widely used in chemical and petrochemical processes for separation purposes, especially in distillation. Accurate prediction of the mass transfer efficiency is essential for the successful design and operation of packed columns. The mass transfer process in packed columns is dependent on many factors, such as vapor/liquid rates, physical properties, and vapor-liquid equilibrium value. All these factors change from location to location along the column [74].

The effective interfacial area may be affected by the vapor flow due to a) improvement of packing wetting by increasing liquid hold-up b) instabilities in liquid flow resulting in higher interfacial area. These effects are especially significant at high vapor rates. The interfacial area may more dependent on the relative surface tension gradient than on absolute values [74].

Modeling and prediction of gas-liquid mass transfer, especially for mass transfer with chemical reaction, are rare due to the complexity of multiphase fluid flow and transportation. Chemical absorption is comprehensively considered as a good choice for its advantages of high efficiency, low cost, and mature technology. The mass transfer can be enhanced due to a large contact area and intensive mixing between gas and liquid phases [75].

An increase in liquid flow velocity would create thinner liquid films or smaller liquid droplets, offering an enhancement in the gas-liquid interfacial area and a reduction in the mass transfer resistance. Schmidt number describes the ratio of viscosity to diffusion. With larger gas Schmidt number and a liquid Schmidt number, the smaller diffusion reduction of mass transfer. Weber number of the liquid phase reflects the effect of surface tension of liquid phase. It is associated with the shape of liquid droplets or film [75].

The texture has a significant influence on the mass transfer efficiency. Mass transfer is significantly higher on a textured surface than with a flat inclined plate. Counter gas flow also affects the mass transfer, but the impact of texture is significantly higher [76].

The liquid film controls the resistance. When the gas flow rate is increased to a certain degree, the liquid film struck into liquid drops; as a result, effective mass transfer area is increased. The effective mass transfer area increases along with the increase of liquid and gas flow rates [77].

The higher liquid mass transfer coefficient plays a big role in determining the increasing absorption performance. If the liquid load is increased, the mass transfer coefficient also increases [78].

Mass transfer of CO_2 into liquid phase is significantly influenced by the chemical reac-

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tion. If CO_2 reacts closely to the gas-liquid interface, the reaction will be fast and the concentration of CO_2 far from the interface is zero [79].

Both the wetted area and effective mass transfer area are very important in predicting mass transfer for packed beds. The surface area of dead zones is included in the wetted surface area, and the surface of the liquid film is included in the effective mass area. Like the surface of drops, jets, and sprays [80].

Diffusion through the gas film proceeds at a rate that is proportional to the difference between solute concentrations in the gas on the outside and inside of the gas film. Diffusion through the liquid film is controlled by the difference between the concentration of solute in the liquid at the interface and its concentration on the other side of the liquid film. Since the surface films are very thin, the actual amount of solute contained in them at any one time is usually negligible compared to the amount diffusing through them. That all the solute which passes through one film must also pass through the other, and the two films may be considered as two diffusional resistance in series [81].

The design of structured packed columns requires a detailed description of the hydrodynamics and mass transfer on the surface of packings. This is since the efficiency of the structured packed column is highly dependent on the flow behavior of the liquid phase inside the packing, which can change rapidly over the range of only a few inches. It is well known that the local flow behavior of a liquid phase includes film, rivulet, and droplet flows and is governed by the liquid and gas loads as well as by system parameters, including the contact angle [82].

The film wetted area is a significant parameter affecting the heat and mass transfer of the falling film. When the falling film was very thin, the width changed slightly, and the film expanded along the flow direction. Then, with the increase of film thickness, the width decreased dramatically, which results in a serious decline in the wetted area. With a higher contact angle, the film also decreases [83].

Several mass transfer models are available to predict the mass transfer in packed bed as below:

- a) Liquid distribution model: According to this model, it is assumed that all the liquid rivulets travel only in an upward direction.
- b) Effective mass area model: In this model, the width and the thickness of the liquid rivulet is calculated, and then the surface area of the liquid rivulets are calculated and the effective area for mass transfer is assumed to be the same as the rivulet surface area.
- c) Mass transfer coefficient model: The overall mass transfer coefficient for a chemical absorption system can be determined as :

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{HEk_L^0} \quad (2.7)$$

in eq. (2.7) K_G is the overall mass transfer coefficient, k_G is gas-phase local mass

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transfer coefficient, k_L^0 is liquid phase physical liquid mass transfer coefficient, E is the enhancement factor, H is Henry's constant.

2.2.1.3 Modeling approach to reaction kinetics

In choosing the reaction scheme, two mechanisms are proposed firstly, zwitterion mechanism and secondly termolecular mechanism. Zwitterion mechanism is a two steps mechanism, and it is about the formation of zwitterion when CO_2 reacts with MEA. Then this zwitterion forms carbamate. The overall reaction rate can be presented as a function of the concentration of CO_2 , MEA, and H_2O . According to the termolecular mechanism as CO_2 reacts with MEA; it forms a loosely bound product rather than zwitterion, and is a single-step mechanism. The concentration of water in MEA is larger than the other species, and as a result, the transport property model is required to determine various physical and thermal properties like pressure drop, liquid hold-up, mass transfer coefficient, thermal conductivity [71].

The increasing pure MEA content leads to the acceleration of absorption in the bottom part of the porous zone while it inhabits the reaction in the upper part of the column. The reaction rate is dominated by pure MEA content in the bottom part of the porous zone and then decreases gradually towards the top of the absorber filing. The reaction rate is mostly dependent on reacting species content and reaches its maximum value at the bottom of the column, where CO_2 concentration is the highest. CO_2 capture efficiency is mostly influenced by the liquid to gas ratio [84].

2.2.1.4 Mass transfer models for packed bed

Several empirical and semi-theoretical models to predict the mass transfer in a structured packed bed column were proposed and tested before by different authors. Xu et al. [74] developed a model to predict the mass transfer efficiency of the structured packed bed based on Billet model [85]. This model was validated with experimental results.

Shetty et al. [86] proposed a fundamental approach to calculate mass transfer coefficients, interfacial area, and liquid hold-up without using any adjustable parameters. They investigated the complex nature of the surface and the liquid flow mechanism on the surface. Finally, they were able to calculate the liquid mass transfer coefficient. The main advantage of this approach is that it is possible to get rid of assumptions.

Depending on the wetted surface area and the total area of packing, Onda et al. [87] developed a model to predict liquid side mass transfer coefficient and interfacial area. This model was further developed by Bravo et al. [17] by making the wetted surface area as a function of the physical properties of the liquid, liquid flow rate, and the packing geometry. In this model, the effective interfacial area was considered equal to the surface

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area of the packing and liquid side mass transfer was based on penetration theory.

Barovo model was again developed by Nawrocki et al. [88]. In this model, the gas side mass transfer coefficient was calculated based on the wetted wall column, and the liquid side mass transfer coefficient was calculated by penetration theory. Penetration theory was also used by Murrieta et al. [89] to predict the liquid side mass transfer coefficient based on exposure time.

Based on falling liquid film with the gas phase, Del Carlo et al. [90] proposed a model that includes the physical properties of the liquid and the geometrical characteristics of the packings. This model does not need any adjustable parameter, but it relies on semi-empirical equations.

2.2.1.5 Chemical reaction models for carbon removal:

For chemical reactions, several models were developed based on enhancement factor, without the enhancement factor and based on equilibrium and non-equilibrium.

Lars et al. [72] developed a model by considering heat and mass resistances by the film theory by explicit calculation of the interfacial fluxes. Relevant reactions and diffusion kinetics are combined with the film model. For electrolyte solutions, a specific feature is added. They had avoided using of enhancement factor concept by implementing reaction rates as source terms into the transport equations by film phenomena and liquid bulk behavior. Although they had validated and found a good arrangement with experimental results choice of proper kinetic description is not very clear with their model.

Jozsef et al. [73] developed a general approach to calculate enhancement factors for a wide range of loadings and temperatures. They started with two film approaches and then extended it to the surface renewal model. They used the model for MEA solution for CO_2 removal and found results are improved compared to the film model. This study is a very good example that it is not a good idea to exclude the enhancement factor as other authors had suggested before; rather for MEA- CO_2 reaction, it provides a better result and can be used with confidence in this type of reaction. It also improves computational cost for this type of problem [73]. The equilibrium based approach was also used by Mores et al. [91]. They used the two-film model, and mass transfer coefficients were calculated based on Onda model.

Jose et al. [92] showed that gas velocity and density have a greater influence on the interfacial area, and gas kinetic energy also affect liquid drop dispersion. The effective transfer area is proportional to the liquid load. Within a single phase, the transfer rate depends on the gradient of concentration, the turbulence that is present in the phase, and on fluid physical properties. The individual mass transfer coefficients depend more on the system rather than the geometric character of the packing. On the other hand, the effective interfacial area for mass transfer of the interfacial area at any given point in the

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bed should depend on the kinetic energy of the phases, packing surface wettability.

Chinmay et al. [93] developed a rate-based model by considering multicomponent mass transfer, chemical reactions, and heat transfer. They used Aspen. Reactive absorption does not need elevated pressure like physical absorption. They did not use enhancement factors in the model. Hydrodynamics was included by correlations for liquid holdup and pressure drop. They commented that the model is capable of predicting concentration and temperature for a wide range of operating conditions.

Apart from numerical modeling, in the past, researcher had worked in the post-combustion carbon capture both experimentally. Haunling et al. [94] used ammonia scrubbing for CO_2 removal. They did experimental work. They concluded that with Ammonia scrubbing, the CO_2 removal efficiency can be as high as 98%. But, due to the nature of the high corrosion of ammonia this approach is not very cost-effective. To overcome these problem, aqueous solutions of ethanolamine, particularly mono ethanolamine (MEA), is used for CO_2 removal because of its low volatility, thermal stability, and high reactivity. For the rational design of absorption equipment, the knowledge of chemical kinetics between CO_2 and MEA is very important. Post-combustion capture with MEA is a reactive absorption process. Although many workers worked on it, there is a considerable discrepancy between previous results.

Leila et al. [95] developed a model based on two-film theory for mass transfer and a rate-based model for chemical reactions by using Fortran Boundary Value problem solver (BVP). One of the big problems of it is due to guessing it is very obvious to bring a significant amount of errors in the model. FORTRAN programming was used by Ahmed et al. [96] to study reaction kinetics in CO_2 capture. Lawal et al. [97] used Aspen to model CO_2 capture using two different approaches, equilibrium and rate-based, to understand the dynamic behavior of the absorber. They concluded that the rate-based approach yielded better predictions compared to the equilibrium-based approach. But, the main problem of this type of study is due to too many input parameters and adjustable parameters, this approach is not quite robust and reliable.

These types of problems can be easily overcome by CFD modeling as it is quick, less expensive, and can work on any geometry with minimum input parameters. As a result, several researchers used this for CO_2 capture modeling.

Dadiusz et al. [84] did a 2D axisymmetric CFD model for CO_2 capture. They used amine solvent with counter-current two-phase flow. For hydrodynamics, a two-fluid Eulerian model was applied, and they also included chemical reactions. They concluded that CO_2 capture efficiency is mostly influenced by the ratio of liquid to gas mass fluxes. They also did experimental work and validated their model. However, inside a structured packed bed column, flow is three-dimensional. So, a 3D model is needed.

An effort to fill this gap was made by Daniel et al. [98]. They developed a 3D model

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for small scale. They used the VOF model by taking into account the hydrodynamics, physical mass transfer, and reaction kinetics for micro scale in the structured packed bed. They used Higbie's penetration theory to describe physical mass transfer. They concluded that as the concentration of MEA increases, the enhancement factor also increases, and the model is able to describe reactive enhancement factor successfully. From their work, it was understood that the CFD model is a very good tool to understand reaction kinetics and associated parameters for the 3D case. However, their work was done on a micro scale. There is still a gap in knowledge for chemical kinetics in macro i.e. large scale, by taking account of the whole reactor.

Large scale 3D CFD modeling was done by Pham et al. [13]. They used 3D Eulerian-Eulerian CFD model to investigate hydrodynamics, mass transfer, and chemical reaction for MEA with multiple inlets in the structured packed bed. They concluded that the higher mass transfer coefficient leads to higher CO_2 removal. Although by their work, it is possible to understand the reaction kinetics and CO_2 removal rate in the whole reactor, there is still a knowledge gap in 3D large scale CFD modeling. For chemical reaction modeling, they used a reduced model based on molar concentration without hydrodynamics. Hydrodynamics studies they did separately but not in the chemical reaction. Probably it was done to reduce the complexity in CFD modeling. Secondly, it was found that for large scale modeling, drag law plays a very important part in hydrodynamic behavior. So, it is very obvious that in a chemical reaction it will play a vital role as well in carbon capture. It is clear that drag law will be very important to calculate the CO_2 removal rate across the column height. A lack of modeling approach without it will lead to a significant error. Lastly, although for multiple inlets, one can get an idea about the CO_2 removal there is still a need to find a relationship in CO_2 removal for single inlet and multiple inlets as it will play a vital role in cost as well as gas loading. [These knowledge gaps were filled by present research.](#)

2.3 Heat Transfer and Chemical Reactions

Heat transfer in a packed bed takes places through the solid particles and the fluid-filled voids. Radiation, conduction, and convection are involved in this process and are discussed as below:

- radiation between adjacent voids;
- radiation between two particles between the surfaces;
- convective heat transfer between fluid and solid particles;
- conduction through the fluid in void space;

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- conduction through the stagnant fluid between two points or non-contacted particles;
- conduction through the stagnant fluid between two areas contacted area;
- conduction through the contact area between two areas contacted particles;

At low temperature (< 450 K) the last three mechanisms is dominant for heat transfer [99].

2.3.1 Mechanism of heat transfer inside packed bed:

If the thermal conductivity ratio between solid and fluid is low, the dominant heat transfer mechanism will be solid-fluid-solid conduction between contacted particles. If this ratio is increased, the dominant heat transfer mechanism will be solid-solid conduction between contacted particles. If this ratio is less than 10, heat transfer will be occurring mainly in the fluid phase [99].

Numerically solving the Navier–Stokes equations and the local energy equations in the fluid and solid phases is the most direct approach to predict heat transfer and fluid flow in a packed bed. In that case entire geometry (both the fluid and solid phases) is meshed into elementary volumes. Different methods like finite element, the finite volume can be used to discretize the partial equations on each elementary volume. Heat, mass, and momentum balances are non-linear equations and are coupled to solve until a fixed convergence is achieved [100].

The fluid inside the packed bed does not contribute to radiation. It occurs between the surfaces of particles and the wall. On the other hand, convective heat transfer between the fluid and particle surface and between fluid and walls depends on the local superficial velocity [100].

By using CFD codes, it is possible to solve mass, flow, and energy balances in complicated geometries like a packed bed. In a large number of control volumes, the differential forms of these control volumes are applied. The computational domain is made of the total number of these control volumes. After implementing the boundary conditions, the flow and energy balanced are solved by numerical iterations. The accuracy of the solution largely depends on the number of control volumes and the size of the cells [101].

For a non-isothermal bed, the temperature profile is developed along the axial coordinate of the bed, and the temperature field is not periodic. The momentum and energy balances must be decoupled to use the periodic flow boundary conditions. Flow parameters, such as viscosity and density, are assumed independent of temperature for this type of boundary condition [101].

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In porous media, convection heat transfer from the fluid to the wall becomes weak due to viscous dissipation. The temperature of the fluid in the bottom part of the channel is higher than the core region of it [102]. There are two models for the convection heat transfer in porous media 1) local thermal equilibrium model 2) local thermal non-equilibrium model. For the local thermal equilibrium model, it is assumed that the fluid temperature is equal to the solid phase temperature. It can also be explained as the local thermal equilibrium between the fluid and solid phase at any point of the porous media [102].

There are two different types of models for fixed-bed CFD simulation. For the first type, the bed is taken as an effective porous medium with parameters for dispersion and heat transfer. Reactions take place in the porous medium and are represented by source terms in the conservation equations. The velocity field is averaged, and the axial component of it varies radially. The disadvantage of this approach is that due to the continuous lumping of transport processes; an effective viscosity for the bed is needed [101]. In the second type of fixed bed CFD simulation, the geometrical complexities of the packed bed are not simplified or replaced by an effective medium like the first case. Although the governing equations for fluid flow are simple, grid generation and geometric modeling are complicated and need a greater amount of computational resources. As a result, this approach applies to a small scale [101].

To control the temperature of the packed bed, knowledge of the heat transfer bed characteristics of a packed column is important. Pauline et al. [103] performed 2D CFD modeling of heat transfer in a packed bed column for laminar and turbulent flows. They used porous media, and both the radial and axial distribution of temperature were examined. The flow was taken as isothermal, and a constant value of viscosity, density, thermal conductivity, and specific heat was taken. They showed that at a specific position of the column, the gas temperature inside the column is equal to the wall temperature. They also commented that heat transfer is a function of axial position, and it depends on the length of the heating. They also commented that better arrangement could be obtained between the numerical and experimental results if the density, viscosity, specific heat, and conductivity parameters are presented by the models of an incompressible ideal gas [103].

Forced convection heat transfer in porous media is influenced by the transverse thermal dispersion. The effect of viscous dissipation increases in porous media as the contact surface between the fluid and solid particles is very high [102]. As the heat transfer mechanism is influenced by a porous structure, the knowledge of porous structure is important. Heat exchange in a packed bed occurs through the adjacent wall of the bed. Various operating conditions influence the heat transfer between the solid-fluid system [104]. The effective thermal conductivity of a packed bed can be divided into three components. 1) Effective thermal conductivity due to stagnant fluid and consists of four distinct heat

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transfer mechanisms a) conduction through the solid b) conduction through the stagnant fluid/gas phase c) radiation between the solid surfaces d) conduction through the adjacent particles. 2) The second component of the effective thermal conductivity is due to the turbulent mixing of the fluid through the packing in parallel to the wall. Turbulent mixing increases the effective thermal conductivity. 3) The third component is the motion of the fluid [104].

If the wall temperature is uniform in the packed bed, heat transfer occurs because of three basic methods. Due to the temperature gradient between the bed and conduit wall, heat is transferred to the bed particles by conduction and convection. Heat is transferred from the bed to the fluid flowing through the bed is by forced convection. This heat transfer is affected by the mechanism of the fluid flow adjacent to the solid surface. Heat transfer takes place only when there is a temperature difference between the conduit wall and the fluid flowing through the conduit [105]. When heat transfer takes place, the temperature of the moving fluid is the same as the temperature of the solid particles that made the bed. At some distance from the bed, fluid temperature is the same as the undisturbed stream known as the thermal boundary region [105].

In a packed bed, the forced convective heat transfer is influenced by many parameters like Reynolds number, Prandlt number, void fraction, the ratio of tube diameter to sphere diameter, local flow conditions, the effect of radiation, natural convection, surface roughness, and the ratio of bed height to sphere diameter [106]. The thermal conductivity of a packed bed depends on the fluid flow and heat transfer conditions and on the size and shape of the particles. Effective conductivity of the stagnant gas is influenced by Several heat transfer mechanisms 1) conduction through the gaseous phase 2) conduction through the solid phase 3) heat radiation through solid-solid and through the void area to the next layer 4) conduction through the contact area and 5) the pressure-dependent conductivity caused by the smoluchowski effect [106]. Wall to fluid heat transfer occurs due to heat flux penetration through the wall of the packed bed. Heat must pass the wall boundary layer established by the streaming fluid. This thickness depends on the Reynolds and Plandelt numbers. Similarly, a thermal boundary layer exists at this layer, and it causes temperature difference [106].

Parameters that influence the heat transfer: a) Heat transfer through radiation: Heat transfer by radiation generally depends on the temperature level, T , on the optical properties of the surface of the particles, on the optical properties of the continuous phase [107]. b) Pressure dependence of the thermal conductivity: Thermal conductivity of gas does not depend on pressure. This remains true if the mean free path of the gas molecules is small compared to the geometrical dimensions of the corresponding voids. The ratio of these two numbers is known as the Knudsen number. If the Knudsen number is large, the thermal conductivity of the gas depends on both the dimensions of the voids and the mean free

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path of the gas molecules [107] c) Solid-solid heat transfer due to flattening: Flattening of particles can occur due to the application of external mechanical load or to the weight of the bed [107]. Particle shape and size distribution influence the thermal conductivity of packed beds. If the temperature is increased, the thermal conductivity also increases. At higher temperatures, thermal radiation becomes a more dominant mechanism of heat transfer in a packed bed [107].

When fluid passes through an empty pipe, the heat transfer coefficient is infinite at the inlet but further down the pipe along the inlet, the heat transfer coefficient decreases, and finally, it appears as an asymptotic value. This is not a likely cause for the heat transfer in a packed bed as the heat transfer coefficient depends more on the fluid flow near the wall rather than the temperature distribution [108]. The energy released by the exothermic chemical reactions in a packed bed must be cooled at the walls; as a result accurate correlation between heat transfer coefficient from packed beds is needed. Experimental data for the Nusselt number as a function of Reynolds number often shows disagreement between one study to the other [108].

2.3.2 Different heat transfer models for packed bed column:

Few mathematical models are available for predicting the effective heat transfer in a packed bed. At first, the cell model. It consists of two contacting spheres. It is assumed that heat conduction occurs in two parallel paths. One is the conduction through solid and fluid phases, and the other one is the conduction through the fluid-filled voids. This model was used by Kunii et al. [109]. This model was further developed by Schlunder et al. [110] by considering cylindrical cells. This cylindrical cell contains two contacting particles with deformable shapes. Both two models are based on a representative geometric unit. Due to empirical equations, representative geometric unit needs a large number of parameters determined by experiments. Another drawback is that if the thermal conductivity ratio between the solid and fluid is very high (greater than 1000), these models underestimate the effective thermal conductivity [111]. Jian et al. [99] studied flow and heat transfer performances in uniform and non-uniform packed beds. They showed that the effect of packing form and particle shape has a great influence on the flow and heat transfer. Overall, heat transfer is the best for the long ellipsoidal particle model. Local behavior and macroscopic characteristics of flow and heat transfer are largely affected by the internal structure of the packed bed, and this effect can be predicted by CFD. Cheng et al. [111] did the modeling by considering three mechanisms, including conduction through the solid particles and stagnant fluid that is present in the non-contracted particles, conduction through the solid particles, and stagnant fluid, conduction through the contact area between contacted particles. In the presence of a stagnant fluid, the effective heat transfer can be evaluated based on two aspects i) heat transfer between particles that

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are obtained in simplified conditions ii) conductivity of particles in the packing that is obtained by packing structure [111]. Argento et al. [112] solved this problem by applying the packing structure concept in the model to predict the effective thermal conductivity. Only the heat transfer between the particle contact area was considered and the effect of liquid was totally ignored. As a result, this model applies to the compressed packed beds that are filled with particles with large deformation. Romkes et al. [113] used CFD modeling to predict particle to fluid heat transfer of a single free sphere for a composite structured packing (CSP). In their modeling the temperature of the surface of the particle was set to surface temperature, and the fluid at the boundary of the domain was set to a lower bulk temperature. They commented that CFD could predict heat and mass transfer characteristics with an average error of 15%.

Tal et al. [114] developed CFD-DEM models to predict momentum and heat transfer between fluid and solid particles. They examined the influence of particle roughness on heat transfer. Discrete Element Method (DEM) uses Newton's second law to solve the motion of discrete particles, and the fluid flow is solved by locally averaged Navier-Stokes equations known as computational fluid dynamics (CFD). Heat transfer mechanisms like particle-fluid convection, radiation, and direct conduction were examined. They commented that heat transfer predictions are significantly influenced by the average surface roughness slopes, and particles with high roughness cannot be predicted with DEM only.

The effective radial thermal conductivity describes heat transfer resistance through the packing and fluid inside the bed. It lumps together all heat transfer mechanisms. Due to the extra resistance heat transfer coefficient near the wall causes a temperature jump [115]. At a low Reynolds number, actual temperatures and velocities are required to determine the effective heat transfer parameters in fixed bed reactors. It must be done without disturbing the geometry. Computational fluid dynamics could be a means to obtain this result [115].

To improve the performance of a packed bed reactor, knowledge of temperature profile and heat transfer rates are essential. Roughly, the fluid temperature can be measured with little difficulty, but the measurement of the solid surface temperature is very difficult. The temperature distribution inside the bed must be estimated in terms of the heat transfer coefficient between and the packed bed wall [116].

Magnico et al. used an Eulerian and a Lagrangian approach to model the hydrodynamics and transport properties of packed beds. He studied heat transfer prediction, near-wall treatment. Wall-to fluid heat transfer models were used. He had established a relationship between the local flow field and the local wall heat flux in a packed bed of spheres. He concluded that local heat transfer rates do not correlate statistically with the local flow field [117]. Hydrodynamics properties were also studied by Yaghoub et al. [118] used 2D CFD techniques to investigate hydrodynamic and heat transfer phenomena

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in a gas–solid fluidized bed reactor by taking few assumptions as 1. Gas-phase is ideal and incompressible. 2. Heat transfer between different solid phases is negligible. 3. Solid particles release constant heat flux. They commented that the Eulerian-Eulerian model is suitable for modeling the industrial fluidized bed. Particles with smaller diameters have a lower volume fraction at the bottom of the bed and a higher volume fraction at the top of the bed. Augier et al. [119] also used CFD to predict heat and mass transfer coefficients in a lot of different packed bed configurations. They used hydrodynamics and solved the transport equation for temperature. They compared the Nusselt number with the Reynolds number for different porosity.

Apart from 2D CFD modeling, Michiel et al. [101] performed 3D Computational fluid dynamics (CFD) analysis of simultaneous flow and heat transfer through realistic spherical packings in the wall region Of a fixed-bed reactor and concluded that there is no statistical relationship between the local flow features and the wall heat flux and large-scale flow structures in the bed is related to local patterns of wall heat flux. Also, Xueyn et al. [120] carried out a 3D CFD simulation to investigate the local flow and heat transfer in a 120-sphere random packed bed of 120 spheres. They used the finite volume method for low Reynolds number steady-state incompressible flow to understand flow behavior and heat transfer effect. The void fraction distribution is highly inhomogeneous in a randomly packed bed; as a result wall effect happens. With the increase of Reynolds number, flow inhomogeneity also increases. They also commented that for low void fraction, a higher temperature gradient comes into effect [120]. Simon et al. [115] studied fluid flow and heat transfer in a fixed bed of tube to particle ratio 2.86 by solving the 3D Navier–Stokes and energy equations. They used finite element code, ANSYS: FORTRAN. The eight spheres form the model geometry. They used CFD to calculate the wall heat transfer coefficient, and the radial effective thermal conductivity ratio, by using air as the fluid. They also carried out a study on how pressure and wall temperature depend on effective heat parameters [115]. 3D modeling was also used by Ahmadi et al. [121] to study hydrodynamic and heat transfer characteristics of a randomly packed bed with cylindrical particles. They concluded that CFD could be used to confidently discuss the flow and heat transfer behavior.

Laguerre et al. [100] used two modeling approaches to study transient heat transfer in a packed bed of spheres by free convection and compared with experimental results. For the first approach, they used computational fluid dynamics software to solve the Navier–Stokes equations and the local energy equations in the fluid and solid phases. They also included radiation between the solid surfaces [100]. For the second approach, the authors developed a heat transfer model based on the dispersed particle by taking into account convection, conduction, and radiation between particles [100], and they commented that Free convection heat transfer occurs in the fluid between the particles. Due to

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low Fourier's number, if the particle size is large and the thermal conductivity and velocity of the fluid are low, the surface temperature of a particle can differ significantly from its core temperature for a long-time-interval and due to low Biot number, it can also be very different from the fluid temperature [100].

In summary, based on the literature survey, several key areas of knowledge gaps were identified. Firstly, in hydrodynamics, since the drag law plays a vital role in Eulerian-Eulerian method of CFD modeling of a liquid dispersion, there is a need to understand the influence of the drag law in gas-liquid multiphase flow in detail. At present, it is not available. It is done in this study by improving gas-liquid drag force modeling in a 3D CFD model. For chemical reactions, the main knowledge gap is about how to increase reactive mass transfer and how to maximize carbon capture. In this work, it is done by proposing a hypothesis that enables tracking of all the components of the reactions. Finally, the influence of heat in carbon capture is not available in the presence of chemical reactions and hydrodynamics. This knowledge gap was filled by introducing the heat transfer effect in the CFD model.

Chapter 3

Governing Equations and Solution Method

In CFD modeling, Navier-Stokes equations are solved in a controlled volume. In this chapter, momentum equation, mass conservation equations, and energy conservation equations are derived in sections 3.1, 3.2, and 3.3, respectively. Section 3.4 is about the mass source terms, and these terms were implemented by UDF along with hydrodynamics.

3.1 Momentum equation

The momentum equation is the law of conservation of momentum in a mathematical formulation. In fluid dynamics, momentum equations are widely used to study the forces on fluid particles.

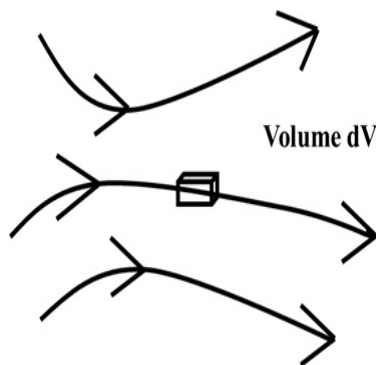


Figure 3.1: Infinitesimal fluid element

Let us consider an infinitesimal fluid element with volume dV is traveling with velocity V as shown in figure 3.1. As it moves, it will experience forces acting on its surfaces,

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as shown in figure 3.2.

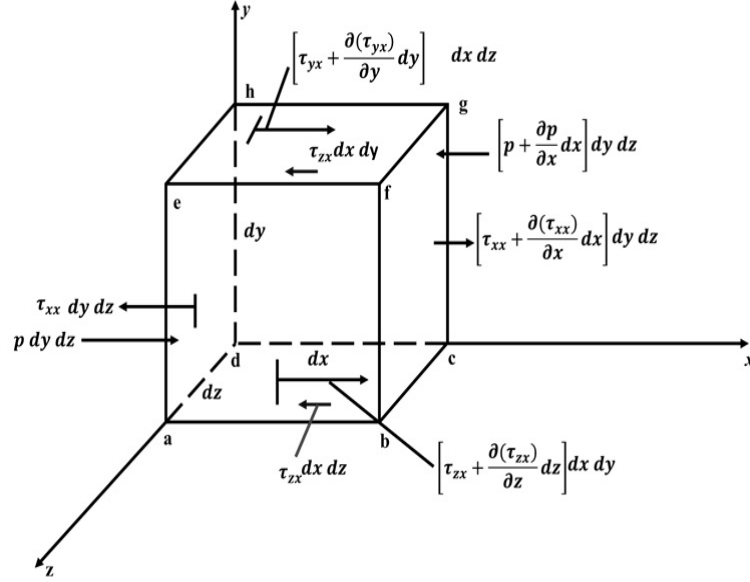


Figure 3.2: Forces in x direction on infinitesimally small moving fluid element.

The conservation of momentum is based on Newton's second law of motion to the differential volume of fluid. For the moving fluid element, x- component of forces according to Newton's second law is given by

$$F_x = ma_x, \quad (3.1)$$

now, moving fluid element will experience two types of forces firstly body forces and secondly surface forces. Body forces act directly on the volumetric mass of the fluid element. Forces of this type are gravitational forces, electric and magnetic forces. On the other hand, surface forces act directly on the surfaces of the fluid element. Surface forces can be divided into two parts. The first one is the pressure distribution on the surface of the fluid element by the outside fluid surrounding the fluid element. The second one is the normal and shear stress acting on the surface of the fluid element imposed by outside fluid by friction. Let us consider the body force per unit mass of the fluid is $\vec{g}$ which has the x-component g_x . The volume of the fluid element is $(dx dy dz)$. The body force of the fluid element in x-direction is given by

$$F_{x,body} = \rho g_x (dx dy dz), \quad (3.2)$$

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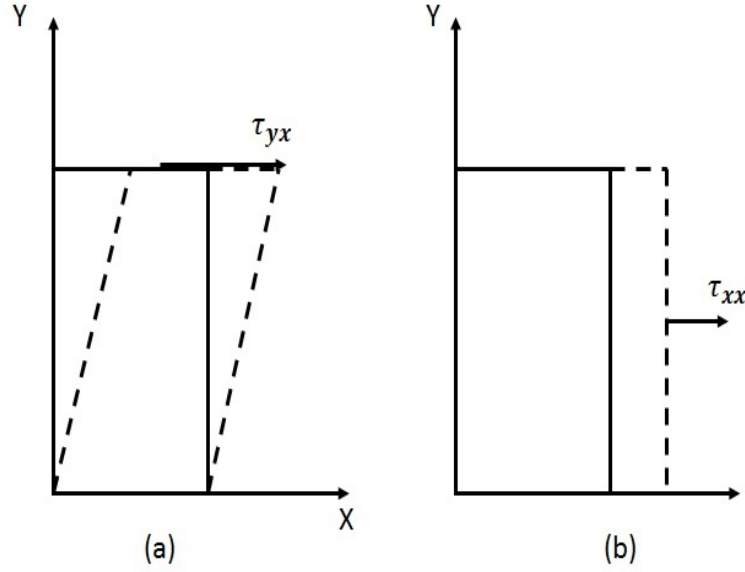


Figure 3.3: Shear and normal stress.

in figure 3.3, shear stress is denoted by τ_{yx} and normal stress is denoted by τ_{xx} . From figure 3.2, for the moving fluid element, the net surface force in x-direction can be derived as

$$F_{x,surface} = [p - (p + \frac{\partial p}{\partial x} dx)] dydz + [(\tau_{xx} + \frac{\partial \tau_{xx}}{\partial x} dx) - \tau_{xx}] dydz + [(\tau_{yx} + \frac{\partial \tau_{yx}}{\partial x} dy) - \tau_{yx}] dx dz + [(\tau_{zx} + \frac{\partial \tau_{zx}}{\partial z} dz) - \tau_{zx}] dx dy, \quad (3.3)$$

and adding, eq. (3.2) to eq. (3.3), the total force in x- direction

$$F_x = (-\frac{\partial p}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z}) dx dy dz + \rho g_x (dx dy dz). \quad (3.4)$$

The mass of the fluid is constant and can be written as

$$m = \rho dx dy dz. \quad (3.5)$$

Since the acceleration of a fluid element the rate of change of its velocity with respect to time, the component of acceleration in x-direction denoted by a_x is simply the rate of change of u with respect to time and, this change can be represented by a substantial derivative as

$$a_x = \frac{Du}{Dt}, \quad (3.6)$$

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now, by combining eq. (3.1) to eq. (3.6) one can write

$$\frac{Du}{Dt} = -\frac{\partial p}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} + \rho g_x, \quad (3.7)$$

in the same way, y and z- component will be

$$\frac{Dv}{Dt} = -\frac{\partial p}{\partial y} + \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} + \rho g_y, \quad (3.8)$$

$$\frac{Dw}{Dt} = -\frac{\partial p}{\partial z} + \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} + \rho g_z. \quad (3.9)$$

Eqs. (3.7) to (3.9) are the momentum equations in non-conservation form. These are scalar equations and are called Navier-Stokes equations. Eqs. (3.7) to (3.9) can be written as

$$\rho \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right) = -\frac{\partial p}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} + \rho g_x, \quad (3.10)$$

$$\rho \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right) = -\frac{\partial p}{\partial y} + \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} + \rho g_y, \quad (3.11)$$

$$\rho \left(\frac{\partial w}{\partial t} + u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right) = -\frac{\partial p}{\partial z} + \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} + \rho g_z. \quad (3.12)$$

Eqs. (3.10), (3.11) and (3.12) are known as Cauchy's equations. Sir Issac Newton stated that shear stress in a fluid is proportional to the rate of change of strain, and such fluids are called Newtonian fluids. For such fluids, Stokes obtained

$$\tau_{xx} = \lambda \nabla \vec{V} + 2\mu \frac{\partial u}{\partial x}, \quad (3.13)$$

$$\tau_{yy} = \lambda \nabla \vec{V} + 2\mu \frac{\partial v}{\partial y}, \quad (3.14)$$

$$\tau_{zz} = \lambda \nabla \vec{V} + 2\mu \frac{\partial w}{\partial z}, \quad (3.15)$$

$$\tau_{xy} = \tau_{yx} = \mu \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right), \quad (3.16)$$

$$\tau_{xz} = \tau_{zx} = \mu \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right), \quad (3.17)$$

$$\tau_{yz} = \tau_{zy} = \mu \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \quad (3.18)$$

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where μ is the molecular viscosity coefficient, and λ is the bulk viscosity coefficient. Putting all these values to eq. (3.10) to eq. (3.12) one can get, for incompressible fluid as

$$\rho \cdot \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right) = -\frac{\partial p}{\partial x} + \rho g_x + \mu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right), \quad (3.19)$$

$$\rho \cdot \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right) = -\frac{\partial p}{\partial y} + \rho g_y + \mu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} \right), \quad (3.20)$$

$$\rho \cdot \left(\frac{\partial w}{\partial t} + u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right) = -\frac{\partial p}{\partial z} + \rho g_z + \mu \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} \right). \quad (3.21)$$

In vector form, it can be written as

$$\frac{\rho D \vec{V}}{Dt} = -\nabla P + \rho \vec{g} + \mu \nabla^2 \vec{V}, \quad (3.22)$$

eq. (3.22) can be written as

$$\frac{D(\rho \vec{V})}{Dt} = -\nabla P + \rho \vec{g} + \mu \nabla^2 \vec{V}, \quad (3.23)$$

by using material derivate, one can obtain

$$\frac{D(\rho \vec{V})}{Dt} = \frac{\partial(\rho \vec{V})}{\partial t} + \vec{V} \cdot \nabla(\rho \vec{V}), \quad (3.24)$$

hence, from eq. (3.24), one can get

$$\frac{D(\rho \vec{V})}{Dt} = \vec{V} \frac{\partial \rho}{\partial t} + \rho \frac{\partial \vec{V}}{\partial t} + u \frac{\partial(\rho \vec{V})}{\partial x} + v \frac{\partial(\rho \vec{V})}{\partial y} + w \frac{\partial(\rho \vec{V})}{\partial z}, \quad (3.25)$$

again, from eq. (3.25) one can write

$$\begin{aligned} \frac{D(\rho \vec{V})}{Dt} &= \vec{V} \frac{\partial \rho}{\partial t} + \rho \frac{\partial \vec{V}}{\partial t} + u \left(\rho \frac{\partial \vec{V}}{\partial x} + \vec{V} \frac{\partial \rho}{\partial x} \right) + \\ &+ v \left(\rho \frac{\partial \vec{V}}{\partial y} + \vec{V} \frac{\partial \rho}{\partial y} \right) + w \left(\rho \frac{\partial \vec{V}}{\partial z} + \vec{V} \frac{\partial \rho}{\partial z} \right), \end{aligned} \quad (3.26)$$

again, from eq. (3.26), one can obtain

$$\frac{D(\rho \vec{V})}{Dt} = \left[\vec{V} \left(\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + v \frac{\partial \rho}{\partial y} + w \frac{\partial \rho}{\partial z} \right) + \rho \left(\frac{\partial \vec{V}}{\partial t} + u \frac{\partial \vec{V}}{\partial x} + v \frac{\partial \vec{V}}{\partial y} + w \frac{\partial \vec{V}}{\partial z} \right) \right]. \quad (3.27)$$

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By using the material derivative, eq. (3.27), can be written in vector form as

$$\frac{D(\rho \vec{V})}{Dt} = \vec{V} \frac{D\rho}{Dt} + \rho \frac{D\vec{V}}{Dt}. \quad (3.28)$$

3.2 Mass conservation equation

According to the mass conservation law, mass cannot be created or destroyed. Mass conservation equations make of relationship of rate of change of mass in a unit volume with all the incoming and outgoing species within this volume at a given time. It is shown in figure 3.4.

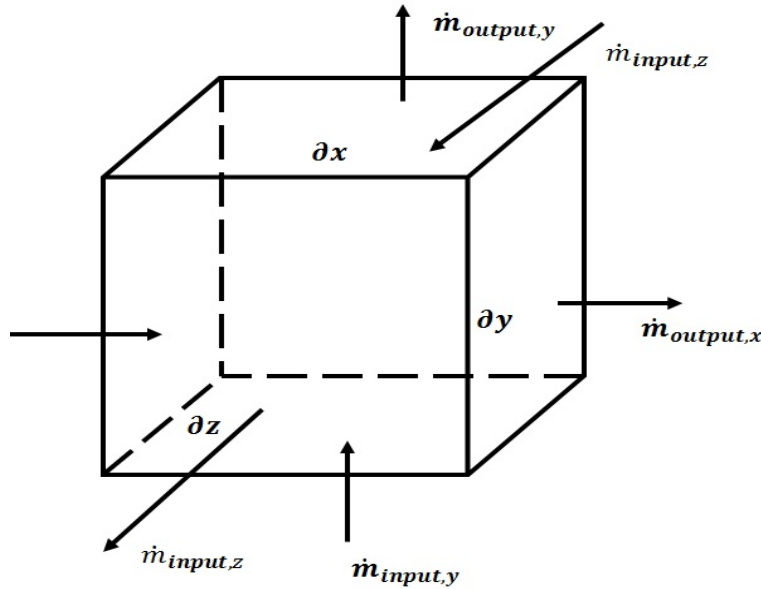


Figure 3.4: Mass flux through differential volume

To derive the mass conservation equation, let us consider a differential fluid volume dV with density ρ . The velocity vector at the centre of the volume is given as $\vec{V} = u\vec{i} + v\vec{j} + w\vec{k}$. In x-direction, the mass flow rate $\dot{m}$ leaving the differential volume is calculated by multiplying mass flux with the area of the face. Hence, the mass flow rate leaving the differential volume in the x-direction is given by

$$\dot{m}_{out\ put, x} = [(\rho u) + \frac{\partial(\rho u)}{\partial x} \frac{\partial x}{2}] \partial y \partial z, \quad (3.29)$$

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similarly, the mass flow rate entering the differential volume in x-direction is given by

$$\dot{m}_{input,x} = [(\rho u) - \frac{\partial(\rho u)}{\partial x} \frac{\partial x}{2}] \partial y \partial z, \quad (3.30)$$

for y-direction, it will be

$$\dot{m}_{output,y} = [(\rho v) + \frac{\partial(\rho v)}{\partial y} \frac{\partial y}{2}] \partial x \partial z, \quad (3.31)$$

$$\dot{m}_{input,y} = [(\rho v) - \frac{\partial(\rho v)}{\partial y} \frac{\partial y}{2}] \partial x \partial z, \quad (3.32)$$

for z-direction, it will be

$$\dot{m}_{output,z} = [(\rho w) + \frac{\partial(\rho w)}{\partial z} \frac{\partial z}{2}] \partial x \partial y, \quad (3.33)$$

$$\dot{m}_{input,z} = [(\rho w) - \frac{\partial(\rho w)}{\partial z} \frac{\partial z}{2}] \partial x \partial y, \quad (3.34)$$

now to satisfy the mass balance for the differential volume, the accumulation of mass for the differential volume will be equal to the difference of the mass flow rate between input and output plus the contribution from any source for unit volume. In mathematical term it can be written as

$$\frac{\partial \rho}{\partial t} (\partial x \partial y \partial z) = \dot{m}_{input,total} - \dot{m}_{output,total} + S_{mass} (\partial x \partial y \partial z). \quad (3.35)$$

By putting the values from eqs. (3.23) to (3.28) in eq. (3.29) one can get

$$\frac{\partial \rho}{\partial t} (\partial x \partial y \partial z) = -[\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z}] (\partial x \partial y \partial z) + S_{mass} (\partial x \partial y \partial z), \quad (3.36)$$

after rearranging eq. (3.30) one can obtain

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z} = S_{mass}, \quad (3.37)$$

mass source term in eq. (3.31) is for unit volume and unit time for a reactive absorption process. In a vector form eq. (3.31) can be written as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = S_{mass}. \quad (3.38)$$

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from eq. (3.32) divergence of mass flux can be further developed as

$$\nabla \cdot (\rho \vec{V}) = \rho \frac{\partial u}{\partial x} + u \frac{\partial \rho}{\partial x} + \rho \frac{\partial v}{\partial y} + v \frac{\partial \rho}{\partial y} + \rho \frac{\partial w}{\partial z} + w \frac{\partial \rho}{\partial z}, \quad (3.39)$$

from eq. (3.32) and eq. (3.33), one can write

$$\frac{\partial \rho}{\partial t} + \rho \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) + \left(u \frac{\partial \rho}{\partial x} + v \frac{\partial \rho}{\partial y} + w \frac{\partial \rho}{\partial z} \right) = S_{mass}, \quad (3.40)$$

by using material derivate the mass conservation eq. (3.34) can be written as

$$\frac{D\rho}{Dt} + \rho \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) = S_{mass}, \quad (3.41)$$

in a vector term eq. (3.35) can be written as

$$\frac{D\rho}{Dt} + \rho (\nabla \cdot \vec{V}) = S_{mass}, \quad (3.42)$$

from eq. (3.28) and eq. (3.42) one can get

$$\frac{D(\rho \vec{V})}{Dt} = \vec{V} \cdot S_{mass} - \vec{V} \rho (\nabla \cdot \vec{V}) + \rho \frac{D\vec{V}}{Dt}, \quad (3.43)$$

from eq. (3.42) and eq. (3.43) both momentum conservation and mass conservation equations can be combined as

$$-\nabla P + \rho \vec{g} + \mu \nabla^2 \vec{V} = \vec{V} \cdot S_{mass} - \vec{V} \rho (\nabla \cdot \vec{V}) + \rho \frac{D\vec{V}}{Dt}, \quad (3.44)$$

from eq. (3.44) one can obtain

$$-\nabla P + \rho \vec{g} + \mu \nabla^2 \vec{V} = \vec{V} \cdot S_{mass} + \rho \frac{\partial \vec{V}}{\partial t}. \quad (3.45)$$

3.3 Energy conservation equation

According to the law of conservation of energy, it can neither be created nor destroyed. Energy only converts from one form to another form. Transfer of energy into a system or out of a system occurs due to heat transfer and work done. Figure 3.5 shows all the heat transfer and work done on the moving fluid element with volume dV .

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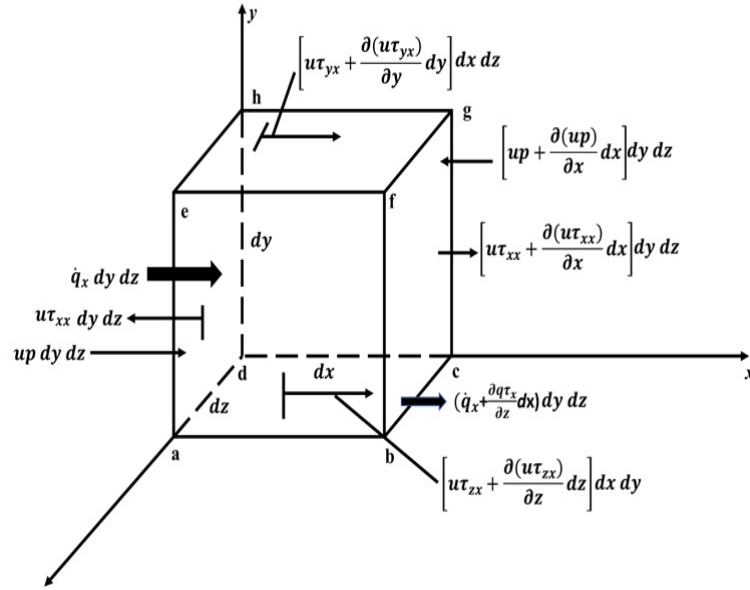


Figure 3.5: Energy fluxes in moving fluid element.

Let us consider a fluid element with volume $(dxdydz)$ and density ρ with velocity $\vec{V}$ as in figure 3.5. The rate of work done by a force is equal to the product of the force and the velocity component along with the force. So, if the fluid element is moving at a velocity $\vec{V}$ the work done on it will be $\rho \vec{f} \cdot \vec{V} dxdydz$. Hence on face abcd the work done will be $u\tau_{yx}dxdz$. The net work done by pressure in the x-direction is given as,

$$[up - (up + \frac{\partial(up)}{\partial x}dx)]dydz = -\frac{\partial(up)}{\partial x}dxdydz, \quad (3.46)$$

the net work done by shear stress in the x-direction is

$$[(u\tau_{yx} + \frac{\partial\tau_{yx}}{\partial y}dy) - u\tau_{yx}]dxdz = \frac{\partial\tau_{yx}}{\partial y}dxdydz, \quad (3.47)$$

now, from figure 3.5, if one takes account into all the forces, the net work done on the moving fluid is given by

$$[-\frac{\partial(up)}{\partial x} + \frac{\partial(u\tau_{xx})}{\partial x} + \frac{\partial\tau_{yx}}{\partial y} + \frac{\partial(u\tau_{zx})}{\partial z}]dxdydz, \quad (3.48)$$

now, considering all the x, y, and z -directions, the net work done will be

$$[-(\frac{\partial(up)}{\partial x} + \frac{\partial(vp)}{\partial y} + \frac{\partial(wp)}{\partial z}) + \frac{\partial(u\tau_{xx})}{\partial x} + \frac{\partial(u\tau_{yx})}{\partial y} + \frac{\partial(u\tau_{zx})}{\partial z}]$$

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$$\begin{aligned} & \frac{\partial(v\tau_{xy})}{\partial x} + \frac{\partial(v\tau_{yy})}{\partial y} + \frac{\partial(v\tau_{zy})}{\partial z} + \frac{\partial(w\tau_{xz})}{\partial x} + \frac{\partial(w\tau_{yz})}{\partial y} + \frac{\partial(w\tau_{zz})}{\partial z}] dx dy dz + \\ & + \rho \vec{f} \cdot \vec{V} (dx dy dz). \end{aligned} \quad (3.49)$$

The heat flux is due to a) volumetric heating such as absorption or radiation b) heat transfer across the surface due to temperature gradients which is thermal conduction. Let us consider the rate of volumetric heat addition for per unit mass is $\dot{q}$. Now, volumetric heating of the element will be equal to $\dot{q} dx dy dz$. The net heat transferred in the x-direction by thermal conduction is

$$[\dot{q}_x - (\dot{q}_x + \frac{\partial \dot{q}_x}{\partial x}) dx] dy dz = - \frac{\partial \dot{q}_x}{\partial x} dx dy dz, \quad (3.50)$$

by taking into account all the directions, one can get the heating of the fluid by thermal conduction as

$$- (\frac{\partial \dot{q}_x}{\partial x} + \frac{\partial \dot{q}_y}{\partial y} + \frac{\partial \dot{q}_z}{\partial z}) dx dy dz, \quad (3.51)$$

hence, the net flux of heat inside the fluid element

$$[\rho \dot{q} - (\frac{\partial \dot{q}_x}{\partial x} + \frac{\partial \dot{q}_y}{\partial y} + \frac{\partial \dot{q}_z}{\partial z})] dx dy dz. \quad (3.52)$$

Now the heat transfer by thermal conduction is proportional to the local temperature gradient. Hence, one can obtain

$$\dot{q}_x = -k \frac{\partial T}{\partial x}, \quad (3.53)$$

$$\dot{q}_y = -k \frac{\partial T}{\partial y}, \quad (3.54)$$

$$\dot{q}_z = -k \frac{\partial T}{\partial z}, \quad (3.55)$$

putting values from eq. (3.53) to eq. (3.55) into eq. (3.52) net flux of heat inside the fluid element become as

$$[\rho \dot{q} + \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y} (k \frac{\partial T}{\partial y}) + \frac{\partial}{\partial z} (k \frac{\partial T}{\partial z})] dx dy dz. \quad (3.56)$$

For per unit mass, the total energy is the sum of internal energy, e , and kinetic energy,

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$\frac{V^2}{2}$. So the total energy is $e + \frac{V^2}{2}$, and the rate of change of energy inside the fluid element becomes as

$$\rho \frac{D}{Dt} \left(e + \frac{V^2}{2} \right) dx dy dz. \quad (3.57)$$

Applying the first law of thermodynamics on it, one can write rate of change of energy inside the fluid element = net flux of heat inside the fluid element + rate of work done on the element due to body and surface forces. Hence, from eq. (3.49), eq. (3.56) and (3.57) one can write

$$\begin{aligned} \rho \frac{D}{Dt} \left(e + \frac{V^2}{2} \right) &= \rho \dot{q} + \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) - \frac{\partial (up)}{\partial x} - \frac{\partial (vp)}{\partial y} - \frac{\partial (wp)}{\partial z} + \\ &+ \frac{\partial (u\tau_{xx})}{\partial x} + \frac{\partial (u\tau_{yx})}{\partial y} + \frac{\partial (u\tau_{zx})}{\partial z} + \frac{\partial (v\tau_{xy})}{\partial x} + \frac{\partial (v\tau_{yy})}{\partial y} + \frac{\partial (v\tau_{zy})}{\partial z} + \\ &+ \frac{\partial (w\tau_{xz})}{\partial x} + \frac{\partial (w\tau_{yz})}{\partial y} + \frac{\partial (w\tau_{zz})}{\partial z} \end{aligned} \quad (3.58)$$

Eq. (3.58) is the energy equation in non-conservation form.

3.4 Derivation of mass source term

In eq. (3.45), the mass source term (S_{mass}) is calculated based on Higbie's theory. The concept of exposure time (τ) is used in this theory. This concept explains that a mass differential element is exposed in gas phase for a certain time (exposure time), and after this time, it returns to the bulk liquid. During this exposure time, the mass transfer at the gas-liquid interface takes place. This approach makes absorption an unsteady process.

In this section, a hypothesis is derived for the mass transfer rate between the liquid and gas phases, which can be carried out using the diffusion equation. For the sake of simplicity, let us consider the scalar form of the one-dimensional diffusion equation as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (3.59)$$

where D is the diffusion coefficient, C is the concentration of liquid, which is a function of space and time. x is the distance from the interface. If $x=0$, then it is interface, and on the other hand, if the distance, $x = \infty$, it will be in liquid bulk. Eq. (3.59) has the following

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initial condition as explained in eq. (3.60)

$$C = 0, \quad \begin{matrix} t = 0 \\ x \geq 0 \end{matrix}, \quad (3.60)$$

eq. (3.59) has the following boundary conditions as explained in eq. (3.61) and eq. (3.62)

$$C = C_{liq,interface}, \quad \begin{matrix} t > 0 \\ x = 0 \end{matrix}, \quad (3.61)$$

$$C = 0, \quad \begin{matrix} t > 0 \\ x = \infty \end{matrix}, \quad (3.62)$$

from eq. (3.59) one can obtain

$$\frac{\partial C}{\partial \zeta} \frac{\partial \zeta}{\partial t} = D \frac{\partial^2 C}{\partial x^2}. \quad (3.63)$$

Let us consider a function which solves eq. (3.63) as

$$\zeta = \frac{x}{\sqrt{4Dt}}, \quad (3.64)$$

thus

$$\begin{aligned} \frac{\partial \zeta}{\partial t} &= -\frac{x}{\sqrt{4D}} \frac{1}{2} t^{-\frac{3}{2}} = -\frac{x}{\sqrt{4D}} \frac{1}{2} t^{-1} t^{-\frac{1}{2}} = \\ &= -\frac{x}{\sqrt{4D}} \frac{1}{2t\sqrt{t}} = -\frac{x}{\sqrt{4Dt}} \frac{1}{2t} = -\frac{\zeta}{2t}, \end{aligned} \quad (3.65)$$

and

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \zeta} \cdot \frac{\partial \zeta}{\partial t}. \quad (3.66)$$

From eq. (3.65) and eq. (3.66), one can express the temporal and spatial derivatives in eq. (3.59) as

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \zeta} \cdot -\frac{\zeta}{2t} = -\frac{\partial C}{\partial \zeta} \cdot \frac{\zeta}{2t}, \quad (3.67)$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{\partial}{\partial \zeta} \cdot \frac{\partial \zeta}{\partial x} \left(\frac{\partial C}{\partial \zeta} \cdot \frac{\partial \zeta}{\partial x} \right) = \frac{\partial}{\partial \zeta} \cdot \frac{1}{\sqrt{4Dt}} \left(\frac{\partial C}{\partial \zeta} \cdot \frac{1}{\sqrt{4Dt}} \right) = \frac{\partial^2 C}{\partial \zeta^2} \cdot \left(\frac{1}{4Dt} \right). \quad (3.68)$$

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Applying Fick's second law from eq. (3.67) and eq. (3.68) one can obtain

$$-\frac{\partial C}{\partial \zeta} \cdot \frac{\zeta}{2t} = D \frac{\partial^2 C}{\partial \zeta^2} \cdot \left(\frac{1}{4Dt}\right), \quad (3.69)$$

and from eq. (3.69), one can write

$$\frac{\partial^2 C}{\partial \zeta^2} + 2\zeta \frac{\partial C}{\partial \zeta} = 0. \quad (3.70)$$

By introducing the notation

$$\frac{\partial C}{\partial \zeta} = Z,$$

thus eq. (3.70) can be re-written as

$$\frac{\partial Z}{\partial \zeta} + 2\zeta Z = 0, \quad (3.71)$$

which is an ordinary differential equation; therefore, one can also write

$$\frac{dZ}{d\zeta} + 2\zeta Z = 0. \quad (3.72)$$

From eq. (3.72), the following detailed derivation can be given by

$$\int \frac{dZ}{Z} + 2 \int \zeta d\zeta = 0, \quad (3.73)$$

$$\ln Z + 2 \frac{\zeta^2}{2} = \ln c_1, \quad (3.74)$$

$$\ln \frac{Z}{c_1} = -\zeta^2, \quad (3.75)$$

$$\frac{Z}{c_1} = e^{-\zeta^2}, \quad (3.76)$$

$$Z = c_1 e^{-\zeta^2}, \quad (3.77)$$

$$\frac{\partial C}{\partial \zeta} = c_1 e^{-\zeta^2}, \quad (3.78)$$

$$\frac{dC}{d\zeta} = c_1 e^{-\zeta^2}, \quad (3.79)$$

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from eq. (3.79) one can obtain

$$C = c_1 \operatorname{erf}(\zeta) + c_2. \quad (3.80)$$

Using the boundary conditions described above, one can write

$$C = C_{liq,interface} = c_2,$$

and

$$0 = c_2 + c_1,$$

thus

$$\begin{aligned} C &= -C_{liq,interface} \operatorname{erf}(\zeta) + C_{liq,interface} = C_{liq,interface}(1 - \operatorname{erf}(\zeta)) = \\ &= C_{liq,interface} \operatorname{erfc}(\zeta), \end{aligned} \quad (3.81)$$

which is the solution of Fick's second law for the concentration C . According to Fick's first law, the mass flux can be calculated as

$$J = -D \frac{\partial C}{\partial x} \Big|_{x=0} = -D \left(\frac{\partial C}{\partial \zeta} \frac{\partial \zeta}{\partial x} \right) \Big|_{x=0} \quad (3.82)$$

and from eq. (3.64) and eq. (3.81) one can obtain

$$J = DC_{liq,interface} \frac{1}{\sqrt{4Dt}} = C_{liq,interface} \sqrt{\frac{D}{4t}}, \quad (3.83)$$

higbie's theory was used later in eq. (3.83) to calculate liquid side mass transfer coefficient k_l .

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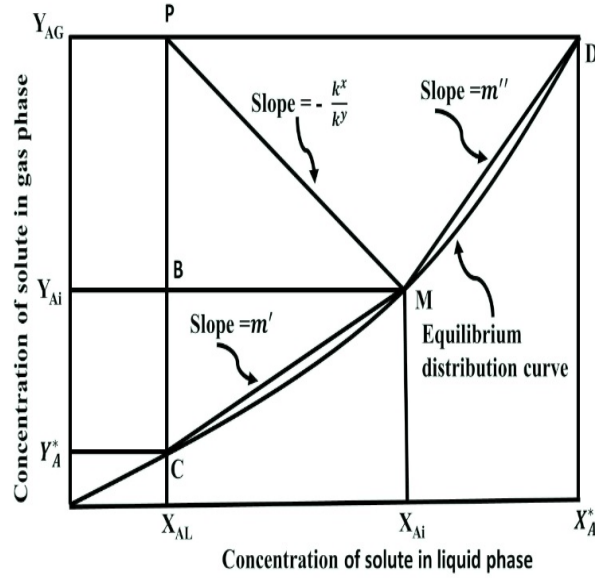


Figure 3.6: Overall concentration differences
[122]

Figure 3.6 is for the overall concentration differences for both gas and liquid phases. Point P is the bulk phase concentration for both gas and liquid phases. Point M is the phase concentration for both gas and liquid phases at the interface. The mass flux J can be expressed in terms of the overall mass transfer coefficient K_l and the difference between the concentration of liquid phase at equilibrium and the concentration of liquid phase in bulk. Hence, from figure 3.6, mass flux can be expressed as

$$J = K_l(X_A^* - X_{AL}), \quad (3.84)$$

if k_l is the local applicable mass transfer coefficient for the liquid phase and k_g is the local applicable mass transfer coefficient for gas phase, the mass flux J can be expressed as below

$$J = k_g(Y_{AG} - Y_{Ai}), \quad (3.85)$$

$$J = k_l(X_{Ai} - X_{AL}), \quad (3.86)$$

from figure 3.6 m' is the slope of chord CM and can be expressed as

$$m' = \frac{(Y_{Ai} - Y_A^*)}{(X_{Ai} - X_{AL})}, \quad (3.87)$$

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similarly m'' is the slope of chord MD and can be expressed as

$$m'' = \frac{(Y_{AG} - Y_{Ai})}{(X_A^* - X_{Ai})}, \quad (3.88)$$

eq. (3.84) can be rearranged as

$$\frac{1}{K_l} = \frac{(X_A^* - X_{AL})}{J} = \frac{(X_A^* - X_{Ai})}{J} + \frac{(X_{Ai} - X_{AL})}{J}, \quad (3.89)$$

from eq. (3.87) and eq. (3.88) if m' and m'' are rearranged eq. (3.89) can be expressed as

$$\frac{1}{K_l} = \frac{(Y_{AG} - Y_{Ai})}{Jm''} + \frac{(X_{Ai} - X_{AL})}{J}, \quad (3.90)$$

by putting the mass flux J from eq. (3.85) and eq. (3.86) into eq. (3.90) the overall mass transfer coefficient becomes as below

$$\frac{1}{K_l} = \frac{(Y_{AG} - Y_{Ai})}{k_g(Y_{AG} - Y_{Ai})m''} + \frac{(X_{Ai} - X_{AL})}{k_l(X_{Ai} - X_{AL})} = \frac{1}{k_g m''} + \frac{1}{k_l}. \quad (3.91)$$

From eq. (3.91), it can be concluded that mass flow will have two resistances one is from gas side $\frac{1}{k_g m''}$ and the other one is from liquid side $\frac{1}{k_l}$. In eq. (3.91) if m'' is too large, the term $\frac{1}{k_g m''}$ becomes very low and can be neglected. In this case liquid phase controls the whole system and the liquid phase is responsible for the mass transfer resistance and $K_l = k_l$, which means under this condition liquid side overall mass transfer coefficient becomes equal to local applicable mass transfer coefficient for liquid phase. Hence, eq. (3.84) can be written as

$$J = k_l(X_A^* - X_{AL}), \quad (3.92)$$

due to the fast chemical kinetics of MEA- CO_2 , term X_{AL} which represents the concentration of bulk liquid phase, can be neglected and eq. (3.92) becomes as below

$$J = k_l X_A^*, \quad (3.93)$$

in eq. (3.93) the term X_A^* represents the liquid phase concentration at the interface and can be written as

$$J = k_l C_{liq, interface}, \quad (3.94)$$

based on eq. (3.83) and eq. (3.94) time dependent liquid side mass transfer coefficient

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can be written as

$$k_l(t) = \sqrt{\frac{D}{\pi t}}. \quad (3.95)$$

If eq. (3.95) is averaged over the exposure time τ , it becomes as below

$$\bar{k}_l = \frac{1}{\tau} \int_0^{\tau} k_l(t) dt = 2\sqrt{\frac{D}{\pi \tau}}. \quad (3.96)$$

In eq. (3.96), the exposure time τ was calculated by dividing the length of the liquid film with the velocity at the interface as proposed by Haroun et al. [123]. If the mass flux in eq. (3.94) is multiplied by the effective area A_{eff} ; one will get mass source term. According to Xu et al. [82] the effective area can be calculated by the module of the gradient of the volume fraction in each cell as, $A_{eff} = |\alpha|$. Furthermore, the enhancement factor can be expressed as

$$E = \frac{S_{reac}}{S_{mass}} = \frac{S_{reac}}{JA_{eff}} = \frac{S_{reac}}{k_l C_{liq,interface} A_{eff}}, \quad (3.97)$$

which expresses the ratio between the mass absorption with chemical reaction and without chemical reaction, where

$$S_{reac} = Ek_l C_{liq,interface} A_{eff}. \quad (3.98)$$

enhancement factor was calculated according to Krevelen et al. [124] as

$$E = \frac{\sqrt{M((E_i - E)/(E_i - 1))}}{\tanh(\sqrt{M((E_i - E)/(E_i - 1))})}, \quad (3.99)$$

in eq. (3.99) M is the value for Hatta number squared, E_i is the theoretical enhancement factor and given as

$$E_i = \sqrt{\frac{D_{CO_2}}{D_{MEA}}} \left(1 + \frac{D_{MEA} C_{MEA}}{2D_{CO_2} C_{liq,interface}}\right). \quad (3.100)$$

In the present context, the Hatta number can be introduced based on the Hitikia et al. [125], which is calculated as

$$Ha = \frac{\sqrt{(2/(m+n)) K_{m,n} [A]^{m-1} [B]^n D}}{k_l}. \quad (3.101)$$

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For CO_2 -MEA system it is $m=n=1$. Hence, from eq. (3.101),

$$Ha = \frac{\sqrt{K_f[MEA]D_{CO_2}}}{k_l}, \quad (3.102)$$

thus one can write,

$$E = \sqrt{Ha^2 + 1}. \quad (3.103)$$

The enhancement factor (3.103) for a first-order equation can be approximated as

$$E \approx Ha,$$

and from eq. (3.95) and eq. (3.98), one can obtain

$$S_{reac} = \left(\frac{\sqrt{K_f[MEA]D_{CO_2}}}{k_l} \right) \left(2\sqrt{\frac{D_{CO_2}}{\pi\tau}} \right) A_{eff} C_{liq,interface}, \quad (3.104)$$

and the reaction rate can be calculated as

$$r = K_f[MEA][CO_2]. \quad (3.105)$$

The source terms for each chemical reaction component can be calculated by multiplying the molecular weight of each component by the reaction rate. Hence, one can obtain

$$Mass_Source_{MEA} = -MW_{t_{MEA}}r, \quad (3.106)$$

$$Mass_Source_{CO_2} = -MW_{t_{CO_2}}r, \quad (3.107)$$

$$Mass_Source_{H_2O} = -MW_{t_{H_2O}}r, \quad (3.108)$$

$$Mass_Source_{MEACOO^+} = -MW_{t_{MEACOO^+}}r, \quad (3.109)$$

$$Mass_Source_{H_3O^+} = -MW_{t_{H_3O^+}}r. \quad (3.110)$$

Section 3.1 to section 3.3 are standard CFD equations, but section 3.4 is unique and is developed for this work. This section was developed by using Fick's laws for concentration within a boundary condition, and finally, mass transfer source term for each component of the chemical reaction was calculated based on the molecular weight of the component. This development is novel as it is now possible to track all the components of the chemical reactions individually inside the packed bed at any height.

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3.5 Methodology

CFD process is commonly divided into three stages; Pre-processing, Solver, and Post-processing. So, to achieve a CFD result, the steps below is to be followed accordingly.

3.5.1 Problem Statement (pre-processing)

This is the first approach to all CFD simulations. It gives the details of the task that must be solved. The procedures, as seen below outlines the questions that must be answered in order to tackle any CFD problem. In this problem, a 3D unsteady multiphase flow is considered for a domain of 0.76 m in length and 0.4 m in diameter. Gas and liquid are counter currents. The diameter of the liquid inlet is 0.1 m. The problem has three parts. Firstly, hydrodynamics study, secondly reactive mass transfer and chemical reactions study, and lastly, heat transfer study. For the hydrodynamic study, it was considered that no mass transfer and chemical reactions occur between the phases. For the chemical reactions study, it was considered that no heat transfer occurs between the phases. In table 4.2 to table 4.6, details of solution set-up, boundary conditions, fluid properties, initial values, residual convergence are discussed. The aim of the CFD study is to validate hydrodynamics study, to validate chemical reactions, and to study the effect of heat transfer in carbon removal.

3.5.2 Mathematical Model (pre-processing + solver)

The forces which cause and affect the fluid flow are gravitational force, porous resistance force, dispersion forces, and gas-liquid momentum exchange force inside the structured packed bed column. The computational domain was 0.76 m, and conservation laws for the mass, momentum, and energy were solved. Porous resistance force was implemented by eq. (4.5) to eq. (4.6), gas-liquid momentum exchange force was implemented by eq. (4.8) moreover, dispersion forces were implemented by eq. (4.10) to eq. (4.11). Mass source terms were developed to include chemical reactions. Eqs. (3.106) to (3.110) are source terms that were implemented by UDF.

3.5.3 Discretization process (solver)

The entire domain is divided into meshes by using ICEM-CFD. The details of the mesh are in table 3.1-table 3.3. It is done so to solve the Navier-Stokes equations on each of the cells.

For the spatial discretization, the following schemes were used:

3. Governing Equations and Solution Method

- Green-Gauss node based for gradient
- Second order upwind for momentum
- QUICK for VOF

For the time discretization, second-order implicit scheme was used.

3.5.4 Iterative Solution Strategy (solver)

The fourth step would be to set up the convergence Principles. It is given in table 4.6, and it was made sure that the iterations are converged.

3.5.5 Post-processing and Analysis

This part of the methodology is carried out to extract the needed information from the simulated flow field. For post-processing, Ansys CFD post was used. The CFD model was validated against experimental results.

3.5.6 Details of the mesh

Three different types of mesh were used, namely coarse, medium, and fine mesh. For coarse mesh, total number of elements was 11,456 and nodes were 10366. Details of the mesh are below:

Part name	Number of elements	Number of nodes
Cylinder wall	144	160
Gas inlet	944	960
GEOM	48	48
Outlet	960	969
Solid	9280	10366
Water inlet	80	89

Table 3.1: Details of corase mesh.

For medium mesh, a total number of elements was 210235, and the number of nodes was 204603. Details of the medium mesh are below:

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Part name	Number of elements	Number of nodes
Cylinder wall	7020	7096
Gas inlet	1444	1320
GEOM	227	227
Outlet	1780	1618
Solid	199124	193663
Water inlet	640	679

Table 3.2: Details of medium mesh.

For fine mesh, a total number of elements was 313841, and the number of nodes was 307776. Details of the medium mesh are below:

Part name	Number of elements	Number of nodes
Cylinder wall	8344	8400
Gas inlet	1624	1680
GEOM	168	168
Outlet	1795	1824
Solid	301515	307776
Water inlet	395	424

Table 3.3: Details of fine mesh

All the meshes were made structured by using ICEM-CFD. Later the meshes were transferred to Ansys Fluent to run the simulations.

3.5.7 Details of initial guess

Details of initial values to run the simulation are given below:

Variable	Values
Gas X velocity	0 m.sec^{-1}
Gas Y velocity	0 m.sec^{-1}
Gas Z velocity	0 m.sec^{-1}
Liquid X velocity	0 m.sec^{-1}
Liquid Y velocity	0 m.sec^{-1}
Liquid Z velocity	0 m.sec^{-1}
Liquid volume fraction	0.00001

Table 3.4: Initial values

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3.5.8 Conditions of simulation cases

<i>Cases</i>	<i>Conditions</i>
<i>Hydrodynamic studies</i>	<i>No reaction takes place</i>
<i>Chemical reaction studies</i>	<i>No heat is present in the process.</i>
<i>Heat transfer studies.</i>	<i>Liquid temperature is constant.</i>

Table 3.5: Different cases with simulation conditions

3.5.9 Simulation cases with studied parameters

<i>Cases</i>	<i>Studied parameters</i>
<i>Hydrodynamic studies</i>	<i>Liquid volume fraction</i>
	<i>Liquid hold – up</i>
	<i>Pressure drop</i>
<i>Chemical reaction studies</i>	<i>Concentration of CO₂</i>
	<i>Enhancement factor</i> .
	<i>Mass trasfer coef ficient</i>
<i>Heat transfer studies.</i>	<i>Concentration of CO₂</i>

Table 3.6: Different cases with studied parameters

3.5.10 Details of solution method

Variable	Solution method
Pressure	SIMPLE
Velocity	SIMPLE
Momentum	Second order upwind
Volume fraction	QUICK

Table 3.7: Solution method for simulation

The UDF was developed in such a way that for a particular initial guess, multiple solutions are possible without changing the initial guess. For example, the model will run for any liquid or gas loading without changing the initial guess.

Chapter 4

Validation of the Multi-Phase Liquid Dispersion Model

4.1 Introduction

The two centuries of fossil fuel combustion to address the growing energy demand has significantly increased the level of atmospheric CO_2 and contributed to global warming and climate changes MacDowell et al. [126]. The atmospheric concentration of CO_2 has increased from 280 ppm in the mid-1800s to almost 404 ppm in 2016 and resulted in a nearly increase of 1 °C in global mean surface temperature from pre-industrial levels [127, 128]. The increase in the surface temperature only over the period of 1901-2010 has led to a 20 cm rise in global mean sea level. It is believed that the temperature rise should be limited to a maximum of 2 °C by 2100 (2DS) by adapting short-to-long term strategies to reduce CO_2 emissions Met Office [129] in order to prevent severe climate change events. Accordingly, the UK government has targeted to reduce the GHGs emissions, including CO_2 , by at least 80%, from 1990 baseline, by 2050 [130]. The Power sector has been recognized as one of the major CO_2 emitter and accounts for almost 60% of global CO_2 emissions, thus requires immediate attention. Carbon capture and storage (CCS) is considered as the key mitigation approach for decarbonization of the power sector [131, 132].

Carbon capture is the primary and yet the most expensive step in CCS. The main CO_2 capture technologies are oxy-combustion, pre-combustion and post-combustion capture. In oxy-fuel combustion, the fuel is combusted in oxygen instead of air; thus, the composition of the flue gas is mainly CO_2 , H_2O , SO_2 and particulate matter. Upon separation of H_2O , SO_2 and particulate matter through condensation, desulfurization, and electrostatic precipitator processes, respectively, a relatively pure stream of CO_2 can be

4. Validation of the Multi-Phase Liquid Dispersion Model

achieved. However, the O_2 supply is expensive and can increase the capital cost of the capture system [133, 134]. In pre-combustion capture, the fuel is converted to CO and H_2 through a gasification or gas reforming process. CO is then converted to CO_2 through gas shift reactions. Further CO_2 is captured from the stream and H_2 is combusted in the air. This approach benefits from high CO_2 partial pressure that drastically facilitates the CO_2 capture process [135]. In post-combustion capture (PCC) CO_2 is captured from flue gases prior to release into the atmosphere. Although in PCC, the partial pressure of CO_2 is relatively low (less than 0.15 bar), which can cause extra cost. It can retrofit to existing power stations without any extensive modification. Thus, PCC is considered as the most short-to-medium term viable approach [136, 134].

The chemical solvent scrubbing using mainly monoethanolamide (MEA) in packed columns is a form of PCC and considered as the most commercially proven approach [137]. Although MEA is inexpensive and has a high CO_2 capture capacity, it is energy-intensive and causes a significant plant energy penalty. In addition, due to the low surface area to volume ratio of MEA solution in the packed column, a large reactor is required that can increase the efficiency penalty and correspondingly increase the capital cost [136, 138, 139]. Decreasing the efficiency penalty of the MEA scrubbing is one of the proposed strategies to reduce the large energy requirements of the plant. CO_2 uptake in MEA scrubbing is a mass transfer process with chemical reaction. Therefore, a reduction in the efficiency penalty can be achieved by the intensification of the MEA scrubbing process by increasing the mass and heat transfer so that a smaller reactor can be utilized [140]. So far, a few intensification strategies, such as utilizing a rotating reactor was proposed by Kang et al. [141] and Visscher et al. [142]. On the other hand, structured packings have been proposed and applied by Razi et al. [15].

Structured packing has been widely used in industrial applications for distillation, scrubbing, and stripping and due to several advantages, such as low-pressure drop, good wettability, and high capacity and efficiency, been considered for MEA scrubbing [15]. The initial and key factor in understanding the mass transfer and chemical reaction in structured packing and proposing further structural optimization is an accurate predication of hydrodynamics.

Computation fluid dynamics (CFD) is a powerful tool for field-based quantification of measures that is hard to achieve through experiments and has already been used to study CO_2 -MEA scrubbing within structured packing in different scales [143]. The investigation on the liquid scrubbing within the structure packing has been performed in three distinct but complementary scales: micro, meso, and macro scale [144]. Micro-scale studies have been performed in millimeter-sized domains and mainly focused on the prediction of liquid-gas interface profile, liquid hold-up, and reactive mass transfer [145, 146, 147]. Meso-scale researches have studied gas-liquid flow behavior, mainly pressure drop, liquid

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hold-up and interfacial area, and mass transfer over a set of representative elementary units (REUs) of structured packing (centimetre-sized domains) [148, 143]. On the other hand, macro-scale investigations have been focused on the hydrodynamic and chemical reactions within the entire column (meter-sized domains), and have been mainly used to study the liquid dispersion and design optimisation [14, 149, 65, 13].

In the macro-scale, bulk parameters such as porosity and permeability appear due to volumetric averaging of micro-scale properties such as pore size and pore space geometry. The averaging is done on a scale that is larger than the pore sizes and results in the formation of dispersion for both gas and liquid phases. In addition, due to the presence of the porous zone, required resistance terms need to be considered, which can be implemented by relevant closure laws [150]. The liquid spreading profile within the structured packing are affected by four mechanisms: namely capillary and mechanical dispersion, gas-liquid momentum transfer, and porous resistance. Capillary dispersion is associated with pressure gradient at the liquid-gas interface and might be neglected in the macro-scale modeling (Fourati et al. [14]). Mechanical dispersion is a macro-scale based mechanism, and occurs due to advection of momentum by phases, in which induces a stochastic velocity field through the porous media [151]. Gas-liquid momentum exchange is attributed to the induced shear stress at the interface of the countercurrent gas-liquid flow mode [24]. Porous resistance is associated with viscous and inertia resistances through the porous media that result in the loss of viscous and kinetic energies [152].

It is necessary and complementary to obtain an in-depth understanding of the gas-liquid flow through the structure packing in all three scales. However, only the macro-scale modeling can realistically reveal the spreading profile of liquid within the entire column [153]. Ali et al. [154] developed a single-phase model to explore the gas distribution within the packing column during the initiation step. A 3D turbulent single (gas) phase was deployed by Owens et al. [153] to evaluate the pressure drop within a real geometry of Sulzer's Mellapak N250Y structure packing. Solomenko et al. [63] made a series of 2D axisymmetric and 3D Eulerian-Eulerian CFD models and validated them with γ -ray tomography experimental data. The models were used to simulate the spreading of liquid in a gas-liquid co-current trickle-bed reactor. Fourati et al. [14] developed a 2D axisymmetric Eulerian-Eulerian CFD model and implement porous resistance, gas-liquid momentum exchange, and dispersion forces. The structured packing was considered as a porous zone, and the model was validated with their experiments. A relatively acceptable agreement between the experiment and the numerical model implied that porous zone could be successfully considered as structured packing. Further, Kim et al. [149] and Pham et al. [13] extended the Fourati et al. [14] model by incorporating the mass transfer and chemical reaction to investigate the CO_2 removal from the natural gas in an absorber reactor with structure packing. The accurate prediction of CO_2 -MEA hydrodynamics in

4. Validation of the Multi-Phase Liquid Dispersion Model

structured packing is the crucial step for realistic modeling of mass transfer and chemical reaction, and further optimization of the absorber reactor design. Despite those CFD models developed to predict and/or improve the hydrodynamics of CO_2 -MEA scrubbing in structured packing, there remains a considerable discrepancy between the numerical models and experimental data.

In this work, 3D transient multiphase Eulerian-Eulerian numerical models were implemented to predict and explore the hydrodynamics of MEA scrubbing within a structured packed bed. For the prediction of the liquid dispersion in a counter-current gas-liquid flow, two different models of mechanical dispersion were implemented and assessed. In addition, the model was compared with the 2D models presented in the literature to determine the anisotropic behavior of the fluid flow. Moreover, the validated model was further used to study the effect of liquid nozzles on the flow behavior within the column.

4.2 Governing Equations

The hydrodynamics of gas-liquid flow through the structured packing was studied using a 3D multiphase Eulerian-Eulerian approach (two-fluid model). In this modeling the following assumption is considered: (i) both gas and liquid phases are incompressible and Newtonian; and (ii) The capillary dispersion is negligible due to the large size of the reactor (Fourati et al.[14]). In the two-fluid model, a set of continuity and momentum equations are solved for each individual phase. The continuity equation for phase k (k can be liquid, l, or gas, g) is

$$\frac{\partial}{\partial t}(\alpha_k \rho_k) + \vec{\nabla} \cdot (\alpha_k \rho_k \vec{u}_k) = 0, \quad (4.1)$$

The momentum equation for phase k is

$$\begin{aligned} \frac{\partial}{\partial t}(\alpha_k \rho_k \vec{u}_k) + \vec{\nabla} \cdot (\alpha_k \rho_k \vec{u}_k \vec{u}_k) = & -\alpha_k \vec{\nabla} p + \vec{\nabla} \cdot (\alpha_k \vec{\tau}_k) + \\ & + \alpha_k \rho_k \vec{g} + \frac{\alpha_k}{\varepsilon} \vec{S}_{Porous,k} + \varepsilon \vec{R}_{l,k} + \vec{F}_{disp,k}. \end{aligned} \quad (4.2)$$

The volume fraction of phase k , α_k , can be calculated as $\alpha_k = \frac{V_k}{V}$, in which V_k is the volume of the phase k in a given occupied volume of V . Since both liquid and gas phases are mathematically considered as interpenetrating continua, there is no overlapping of the phases and $\sum \alpha_k = 1$. The porosity, ε , can be calculated as $\varepsilon = \frac{(V_g + V_l)}{V}$. Now, $\vec{S}_{Porous,k}$ (Porous resistance force), $\vec{R}_{l,k}$ (gas-liquid momentum exchange force), and $\vec{F}_{disp,k}$ (gas-liquid dispersion force) are source terms and will be discussed in detail in the following

4. Validation of the Multi-Phase Liquid Dispersion Model

sections. Three different models, case 1-3, based on different proposed mechanical dispersion and gas-liquid momentum transfer models, were developed (the same porous resistance model was used in all models). The summary of the models is tabulated in table 4.1.

	Mechanical dispersion	Porous resistance	Gas-liquid momentum transfer
Case 1	No dispersion)	(Iliuta et al.)[24]	(Iliuta and Larachi)[25]
Case 2	(Lappalainen et al.)[65]	(Iliuta et al.)[24]	(Iliuta and Larachi)[25]
Case 3	(Mewes et al.) [155]	(Iliuta et al.)[24]	(Iliuta and Larachi)[25]

Table 4.1: Summary of the implemented models in this work.

4.2.1 Porous resistance force

The liquid-solid and gas-solid interaction forces are quantified based on the proposed approach by Iliuta et al. [24] and Iliuta and Larachi [25]

$$\vec{S}_{Porous,g} = (1 - f_e)K_{gs} |\vec{u}_g|, \quad (4.3)$$

$$\vec{S}_{Porous,g} = f_e K_{ls} |\vec{u}_l|, \quad (4.4)$$

where K_{gs} and K_{ls} are gas-solid and liquid-solid drag coefficients and calculated by Eq. (4.5) and (4.6), respectively

$$K_{ls} = \frac{a.E_1}{36} \cdot \frac{\varepsilon a_s^2}{\alpha_l^2} \mu_l + \frac{b.E_2}{6} \frac{\varepsilon a_s}{\alpha_l} \rho_l |\vec{u}_l|, \quad (4.5)$$

$$K_{gs} = \frac{a.E_1}{36} \cdot \frac{a_s^2}{\varepsilon} \mu_g + \frac{b.E_2}{6} \frac{a_s}{\varepsilon} \rho_g \alpha_g |\vec{u}_g|. \quad (4.6)$$

E_1 and E_2 are Ergun coefficients, and for Mellapak 250X are 160 and 0.16, respectively [25]. a and b are the modification factors for the Ergun coefficients and considered as 1 in this study (Fourati et al. [14]). $a_s(m^2.m^{-3})$ is the specific surface area of the structured packing, f_e is the fraction of wetting area and is defined as the ratio of the effective contact area between the gas and liquid phases. a_e to a_s , μ_g and μ_l are the dynamic viscosity of gas and liquid respectively, and ρ_g and ρ_l are the density of gas and liquid, respectively.

4.2.2 Gas-liquid momentum exchange

The gas-liquid momentum exchange force can be express by eq. (4.7)

$$\vec{R}_{exc,gl} = f_e K_{lg} (\vec{u}_g - \vec{u}_l), \quad (4.7)$$

4. Validation of the Multi-Phase Liquid Dispersion Model

where K_{lg} is the coefficient of momentum exchange. For case 1 and 3, the proposed K_{lg} by Iliuta and Larachi [25] was implemented, eq. (4.8)

$$K_{lg} = \frac{c.E_1}{36} \frac{a_s^2}{\varepsilon \alpha_g} + \frac{d.E_2}{6} \frac{a_s}{\varepsilon} \rho_g |\vec{u}_g - \vec{u}_l|, \quad (4.8)$$

c and d are the modification factors for the Ergun coefficients and were considered as 1 (Fourati et al. [14]). The special case should be taken when the model is being implemented. For very small α_g (in the absence of gas) K_{lg} tends to be to infinity and results in unphysical $\vec{R}_{exc,gl}$ and poor hydrodynamic prediction. To avoid the aforementioned issue, the following algorithm was implemented.

$$\begin{cases} K_{lg} = Eq.(4.8) & \alpha_g > 0.0001 \\ K_{lg} \approx 0 & \alpha_g \leq 0.0001 \end{cases}. \quad (4.9)$$

4.2.3 Dispersion forces

For case 1 and 2, the gas and liquid mechanical dispersion forces in the structure packing were calculated by eq. (4.17) and (4.18) respectively [65]. Dispersion force for gas and liquid is given by Lappalainen et al. [65] for structured packing as below:

$$\vec{F}_{disp,g} = \alpha_g K_{gs} \vec{u}_{d,g} + \varepsilon K_{lg} (\vec{u}_{d,g} - \vec{u}_{d,l}), \quad (4.10)$$

$$\vec{F}_{disp,l} = \alpha_l K_{ls} \vec{u}_{d,l} - \varepsilon K_{lg} (\vec{u}_{d,g} - \vec{u}_{d,l}), \quad (4.11)$$

where $\vec{u}_{d,g}$ and $\vec{u}_{d,l}$ are the gas and liquid drift velocities and can be calculated by eq. (4.12) and (4.13) respectively.

$$\vec{u}_{d,g} = -\frac{f_{spread} |\frac{|\vec{u}_g|}{\alpha_g}|}{\alpha_g} \vec{\nabla} \alpha_g, \quad (4.12)$$

$$\vec{u}_{d,l} = -\frac{f_{spread} |\frac{|\vec{u}_l|}{\alpha_l}|}{\alpha_l} \vec{\nabla} \alpha_l, \quad (4.13)$$

f_{spread} is the spread factor, and in this study was considered as 3.7 mm (Fourati et al. [156]). For case 3, the mechanical dispersion model proposed by Mewes et al. [155] was implemented, Eq. (4.21) .

$$\vec{F}_{disp,l} = \bar{\xi} \cdot (\bar{S} \times (\alpha_l \vec{u}_l)), \quad (4.14)$$

4. Validation of the Multi-Phase Liquid Dispersion Model

where $\bar{\bar{S}}$ is liquid spreading tensor. No closure law was found for approximation of $\bar{\bar{S}}$ thus, in this study, it is considered as a constant value of 3.7 mm, as it was proposed and experimentally determined by Fourati et al. [156]. $\bar{\bar{\zeta}}$ is a resistance tensor arisen from the wall shear stress, and can be calculated by Eq. (4.22) as proposed by Fourati et al. [14].

$$\bar{\bar{\zeta}} = -\frac{K_{lg}}{\varepsilon} (\bar{\bar{S}} \cdot \vec{\nabla} | \vec{j}_l |). \quad (4.15)$$

Where j_l is the local liquid flow rate and was calculated as $j_l = \alpha_l \vec{\nabla} \cdot \vec{u}_l$ and K_{ls} was calculated by Eq. (4.5).

Numerical method The governing equations were solved by utilizing an unsteady pressure-based segregated algorithm established in a finite-volume based commercial software Ansys® Fluent v. 14.5. The discretized momentum equation was approximated using both second order upwind and QUICK schemes. Since the discrepancy between the obtained solutions by the two schemes was negligible, the second-order upwind scheme was used to carry out the simulations. The pressure-velocity coupling was achieved by the SIMPLE scheme. A series of Hexahedral-based meshes were constructed using ICEM CFD Meshing Software. Preliminary runs showed that for single and multiple inlet geometries, meshes consisted of 210235 and 284544 cells, respectively, can assure high accuracy and acceptable computational cost. The simulations were performed using Astral supercomputing facility at Cranfield University using 48 CPU cores. A summary of boundary condition used for the simulations are provided in table 4.2. The fluid properties of phases are provided in table 4.3. The Reynolds no of MEA was calculated as 1.18×10^4 and air as 5.48×10^4

General	Solver : Pressure based Time : Transient
Models	Multiphase -Eulerian. Viscous-Laminar.
Materials	Water -liquid. Carbon-di-oxide.
Phases	Primary phase: Carbon-di-oxide. Secondary phase : Water-liquid.
Solution controls	Pressure =0.3 , Density =1.0 Momentum =0.7 , Volume fraction=0.5
Run calculation	Time step size=1e-05 Number of time steps=1e+07

Table 4.2: Solution set up

4. Validation of the Multi-Phase Liquid Dispersion Model

Boundaries	Type
Liquid / Gas inlet	Velocity inlet
Cylinder wall	No-slip wall
Outlets	Pressure outlet
Cylinder body	Porous zone

Table 4.3: Summary of boundary conditions in this work

		ρ ($Kg.m^{-3}$)	μ (m .Pa-s)
Liquid phase	Water	997	0.001
Gas phase	Air	1.105	1.0×10^{-5}
Liquid phase	30 wt% MEA	1012	2.48
Gas phase	Carbon dioxide	1.79	1.37×10^{-2}

Table 4.4: Fluid properties of liquid and gas phases

Residual	Convergence criteria
Continuity	0.001
U-gas	0.001
V-gas	0.001
W-gas	0.001
U-liquid	0.001
V-liquid	0.001
W-liquid	0.001
VF-liquid	0.001

Table 4.5: Residual convergence

Liquid velocity	1.2 m.sec^{-1}
Gas velocity	1.05 m.sec^{-1}
Diameter of liquid inlet	24 mm

Table 4.6: Conditions for simulations

4. Validation of the Multi-Phase Liquid Dispersion Model

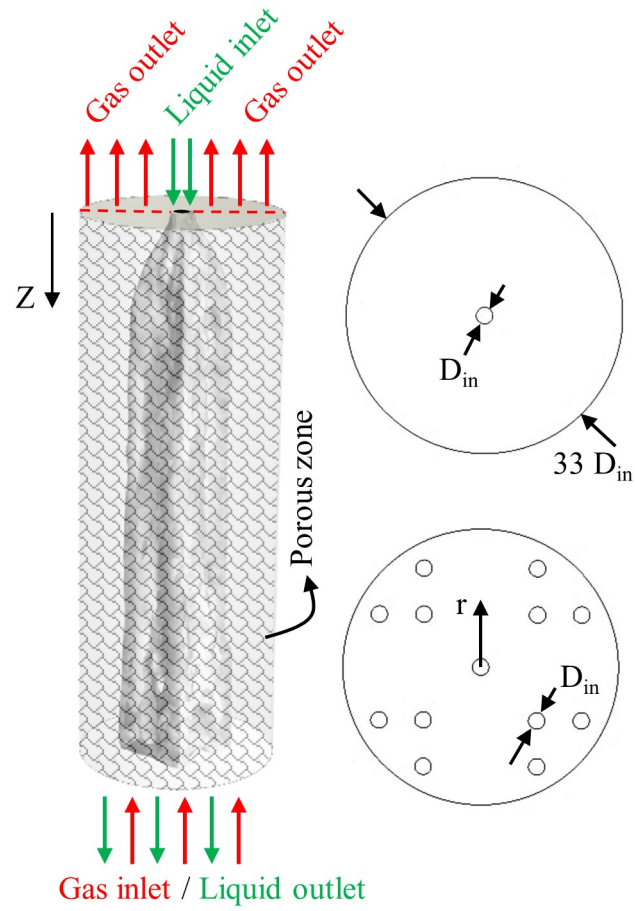


Figure 4.1: Schematic of simulated geometry with single and multiple inlets, along with and boundary conditions. The height of reactor was 660 mm, the diameter of the reactor was 400 mm, and $D_{in} = 24$ mm

4. Validation of the Multi-Phase Liquid Dispersion Model

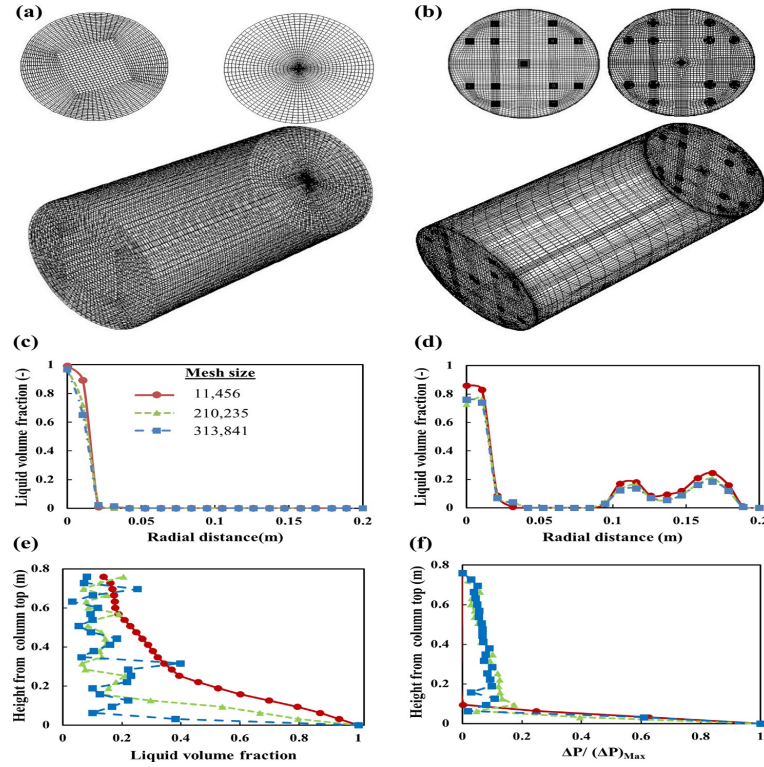


Figure 4.2: An example of Hexahedral mesh used in this study

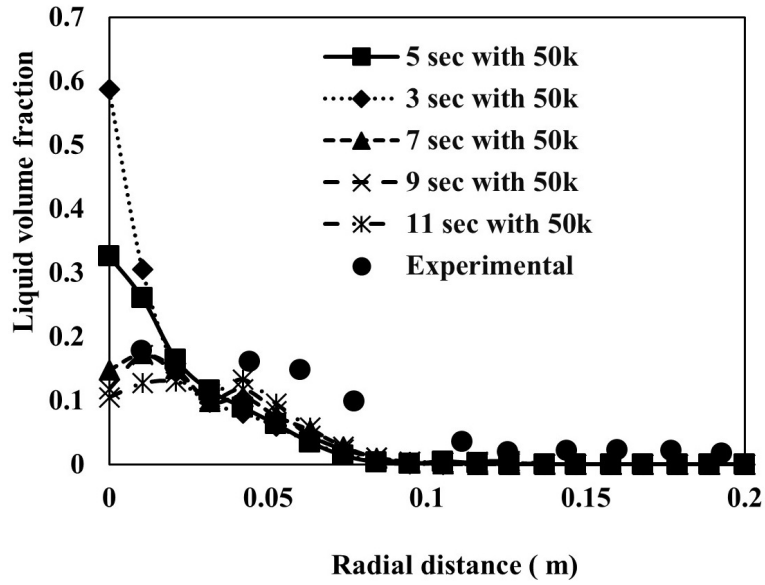


Figure 4.3: Effect of different simulation times with conditions in table 4.6.

4. Validation of the Multi-Phase Liquid Dispersion Model

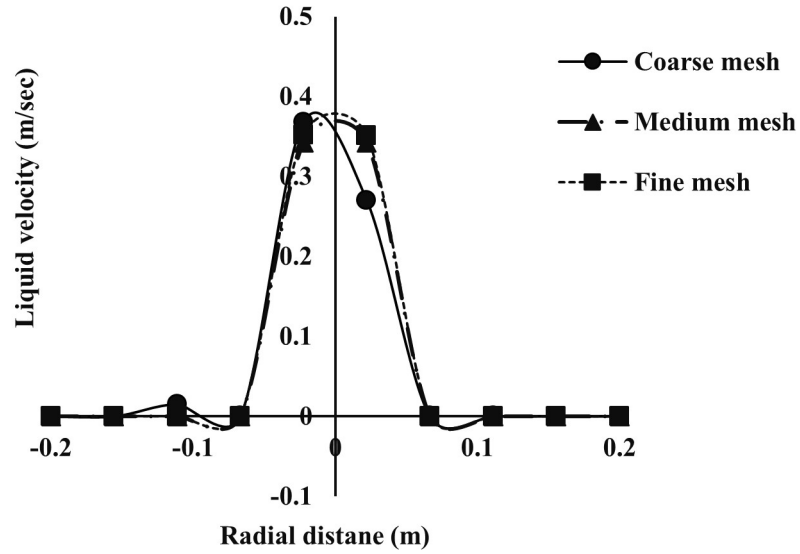


Figure 4.4: Velocity profile for different mesh with conditions in table 4.6.

The simulation was stopped after 11 seconds for a 50 k mesh. The total simulation time was studied for 3 sec, 5 sec, 7 sec, 9 sec, 11 sec, respectively (figure 4.3) and R^2 values were also calculated (table 4.7). The models were compared with the experimental values for a height of 0.32 m inside the packed bed column. It was found that after 5-sec result does not change that much; the reason is after this time, the model becomes a steady state.

Figure 4.4 is to represents the velocity profile for coarse, medium, and fine mesh. Based on figure 4.2 and figure 4.4, it can be concluded that very coarse mesh can lead to significant error in solution but, at the same time, medium mesh is capable of capturing the flow physics for this problem.

4. Validation of the Multi-Phase Liquid Dispersion Model

Simulation time (Sec)	R ² value
3	0.6018
5	0.6235
7	0.6243
9	0.6315
11	0.6521

Table 4.7: Effect of simulation time for 50 K meshes with conditions in table 4.6.

Now, although the solution with 50 k mesh helps to understand the simulation time, there is still a considerable difference between the experimental and simulation values. This problem was solved by increasing the number of mesh to 250 k with a 5 sec simulation time. The R² value, in this case, was calculated as 0.8534, and the simulation matches much well with the experimental values. Hence the optimum mesh number was 250 k for the rest of the remaining work.

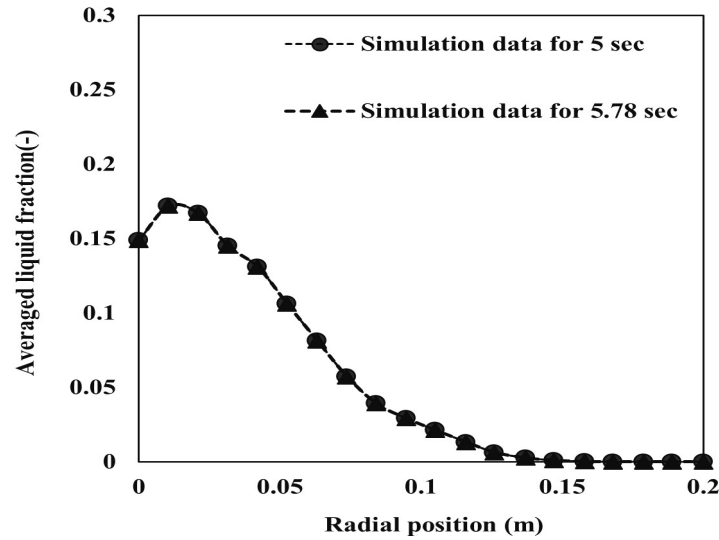


Figure 4.5: 5 sec and 5.78 sec simulation time for 250 k meshes with conditions in table 4.6.

With 250 k mesh, the total simulation time the model could run was 5.78 sec, and after that, it crashed. It was found that the result does not change at all between 5 sec and 5.78 sec, as presented in figure 4.5. For this reason, simulation time was kept for 5 sec for this work.

4. Validation of the Multi-Phase Liquid Dispersion Model

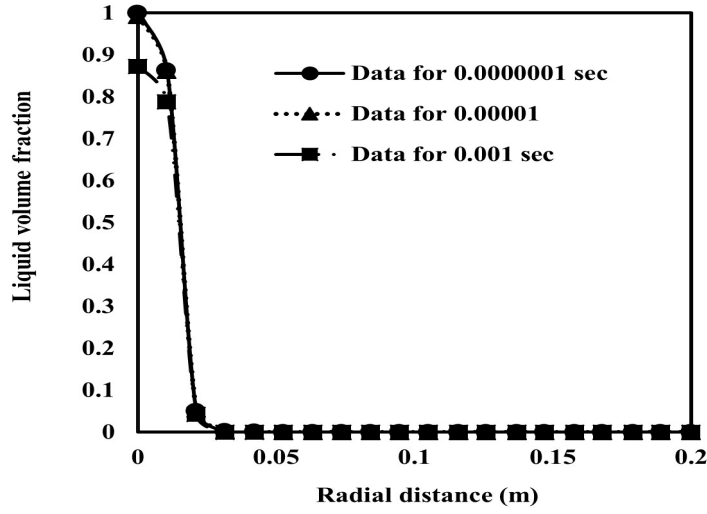


Figure 4.6: Time step selection with conditions in table 4.6.

In selecting the time step at first, the concept of courant number was used. Courant number is defined as $C = \frac{u \Delta t}{\Delta x}$, where C is the courant number, u is the velocity of the fluid, Δt is the time step in a sec, Δx is the spacing distance of mesh. Courant number determines the rate of information traverses across a cell in the computational domain. It is recommended to keep below 1. In this case, it was taken 0.5. For medium mesh for a single case, the time step is calculated as 0.0018 sec, and for multi-case it is calculated as 0.0012 sec. But this approach is not suitable for this case. Due to the nature of this case, the time step must be very small. As the simulation has to deal with very low liquid volume fraction and very fast chemical reactions, in this case it was taken 10^{-5} sec. The courant number approach was not used in literature as well. Fourti et al. [14] and Pham et al. [13] used 10^{-4} sec and 10^{-3} sec. Figure 4.6 is added in this case to explain the effect of time step in the solution. Based on figure 4.6, it can be concluded that results improve a lot with lower time steps.

With the single inlet, it was found a large area of the packed bed is dry. To overcome this problem, multi inlets were used, and as a result, more areas got wetted, and the more mass transfer happens. This type of design has an advantage in choosing the liquid distributor. For this problem, a separate phase tray was considered [156]. Shower head or spray nozzle is not helpful in this case as the spread of liquid was studied by gamma-ray tomography it was needed to have better control over the orifice meter.

Figure 4.7 is to presents the residuals plots. It shows the residual values have reached the specified tolerance. For unsteady simulations, each spike represents a new timestep. Successive spikes show each peak at the same height. Simulation has no change on all

4. Validation of the Multi-Phase Liquid Dispersion Model

the convergence criteria after certain iterations or time steps, and hence we can consider that the solution has reached a steady-state, i.e, converged.

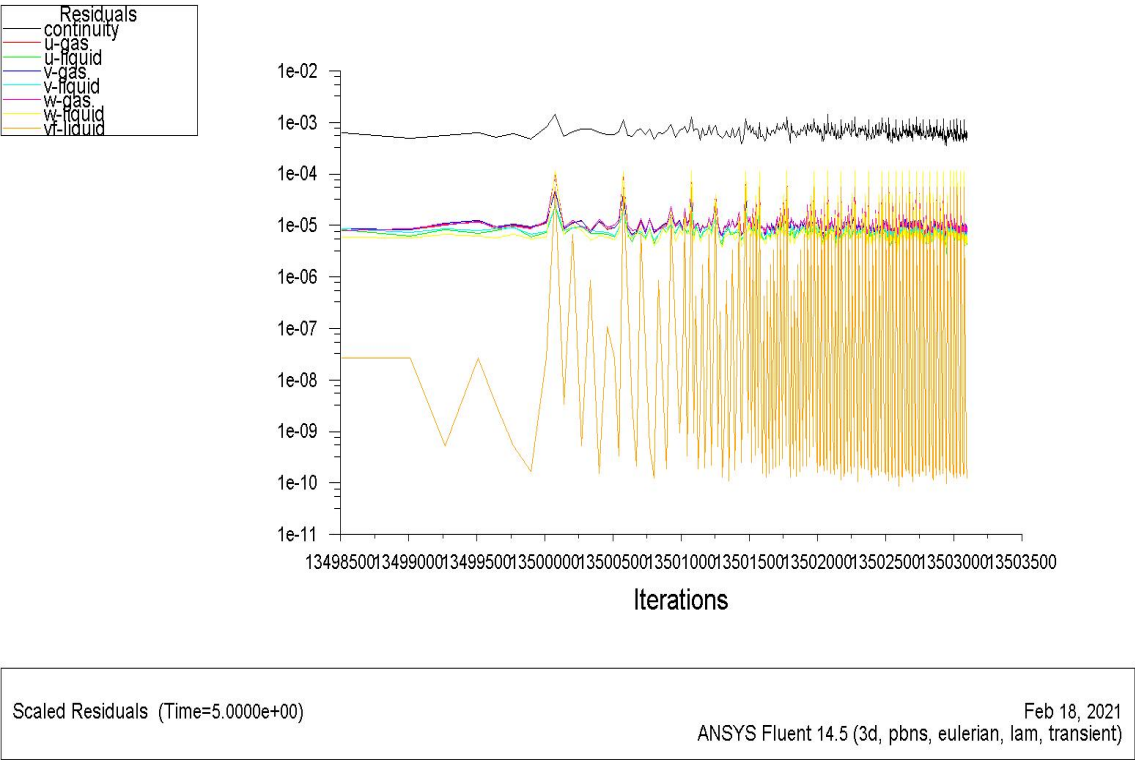


Figure 4.7: Residuals after 5 sec simulation time with conditions in table 4.6.

4.3 Simplified models to validate the methodology

As there was no manufactured solution available for this case, the methodology was validated by using several simplified models. The details of these models are given below in table 4.8.

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Different cases	Details of cases
Case 1	Entire domain is fluid region. No porosity. No dispersion forces.
Case 2	Entire domain is porous region. No dispersion forces.
Case 3	Entire domain is porous region. With dispersion forces.

Table 4.8: Different cases for simplified models

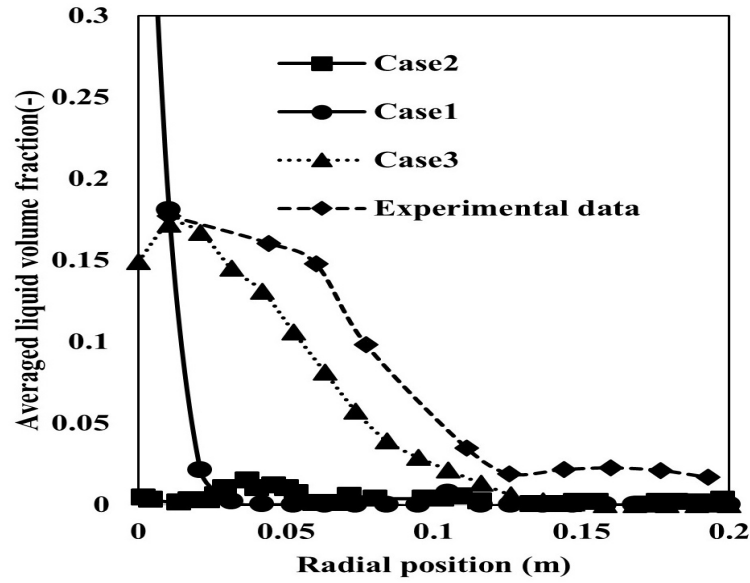


Figure 4.8: Effect of methodology on the solution with conditions in table 4.6.

Figure 4.8 is to justify the solution method. It was found that if the entire domain is taken as a porous region, and if the dispersion forces for both gas and liquid are taken into account, then the results become close to the experimental result. Based on this finding, for the entire study in this work, the whole domain was taken as a porous zone with porosity 0.98, dispersion forces for both gas and liquid, and gravitational force were taken into account.

4. Validation of the Multi-Phase Liquid Dispersion Model

4.4 Results and Discussions

In this section, the simulation results were compared with experimental results for different heights inside the packed bed column. Two variables were taken for this purpose. The first one was liquid volume fraction and the second one was the pressure drop. Finally, the effect of inlets was also studied in this section.

Validation and assessment of numerical model Figure 4.3 shows the quantitative comparison of the radial distribution of average liquid volume fraction of various Cases (1–3) with the experimental (Fourati et al. [156]) and numerical data [14] at $Z = 13.7$ Din and $Z = 20.0$ Din, with a liquid loading, q_L of $16 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$ and inlet velocity of gas of $1.05 \text{ m}.\text{sec}^{-1}$ (corresponding to a gas capacity factor of $1.16 \text{ Pa}^{0.5}$). The details of the experimental setup can be found in the work of Fourati et al. [156]. Amongst the developed CFD models in this study, Case 2, showed very good agreement with experimental data. The poor prediction of Case 1 is due to the fact that liquid dispersion is not considered in the model. Case 3 resulted in a slight under-prediction of the average liquid volume fraction compared to the experimental data of Fourati et al. [156]. The liquid saturation profile predicted by Case 3 shows a lesser spread in the radial position. This implies that the models of mechanical dispersion proposed by Mewes et al. [155] with the specified liquid spreading tensor based on the advection–diffusion model of flow resistance tensor may not be capable of accurately predicting the mechanical dispersion in structured packing. The Mewes model was originally developed and tested for trickle-bed, and monolithic reactors, and the model was extended to apply in the structural packed bed column. However, its validation with the experimental data was not reported quantitatively [157]. The proposed dispersion model is based on both the flow resistance tensor and liquid spreading tensor. The flow resistance tensor depends on velocity as well as the volume fraction. One of the limitations of this model when considered to be extended to the structured packing is modeling approach of the flow resistance and liquid spreading tensor values.

In this work, the anisotropic spreading tensor of liquid was replaced by an isotropic scalar factor for model simplification, i.e., a constant value of liquid spreading tensor of 3.7 mm, proposed by Fourati et al. [14], was used. An advection–diffusion-based model equation was used for the resistance tensor. Thus, further modification needs to be considered in the exact method of liquid spreading and the flow resistance tensor predictions for the Eulerian simulation of structured packing. It should be highlighted that the liquid dispersion within the packed bed column can be modeled based on mechanical dispersion, spread tensor, and tortuosity. The current simulations were developed based on mechanical dispersion (Lappalainen et al. [65]) and the spread tensor approach (Mewes et al.

4. Validation of the Multi-Phase Liquid Dispersion Model

[155]). Also, the advection–diffusion model used for the spread factor calculation needs to be developed in a more conservative form. A comparison of liquid spreading profiles reproduced by cases 1–3 (table 4.1) is presented in figure 4.4. A narrow distribution of liquid along the column in case 1 was observed. It is evident that cases 2 and 3 showed a wider liquid spatial distribution. Moreover, case 2 resulted in a noticeably more accurate reproduction of experimental data compared with the 2D axisymmetric CFD model developed by Fourati et al. [14], specifically in the lower range of radial distance (r) of 0–0.05 m. This can be attributed to the 3D nature of multiphase flow through structured packing and the distribution of flow anomalies, highlighting the necessity of 3D models for accurate prediction of hydrodynamics.

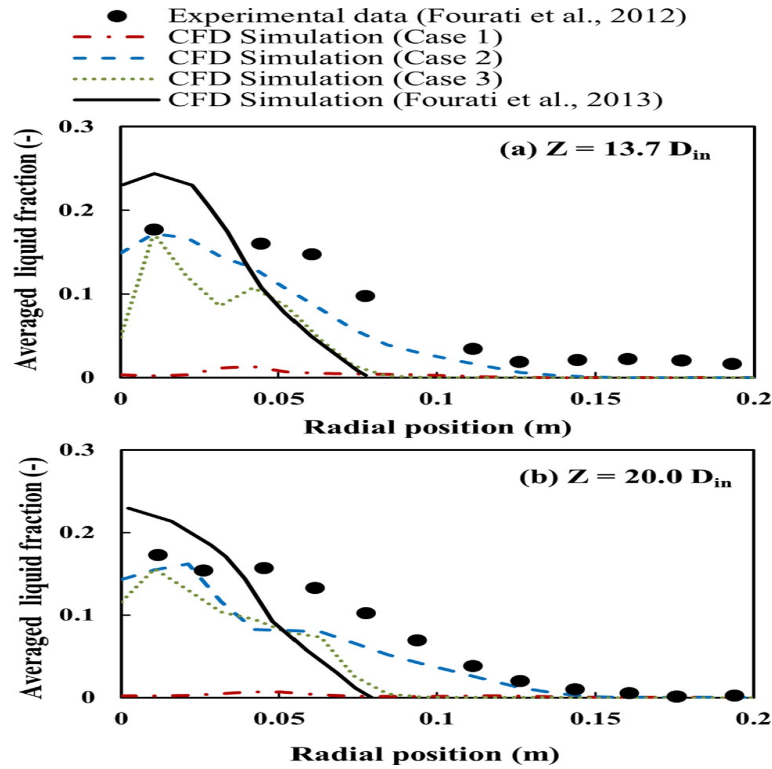


Figure 4.9: Validation of developed CFD models with existing experimental and numerical data: radial distribution of average liquid volume fraction at (a) $Z = 26.7 D_{in}$; and (b) $Z = 40.0 D_{in}$ $D_{in} = 24$ mm, $V_{in,l} = 1.2$ m.sec⁻¹, $V_{in,g} = 1.05$ m.sec⁻¹ as presented in table 4.1.

4. Validation of the Multi-Phase Liquid Dispersion Model

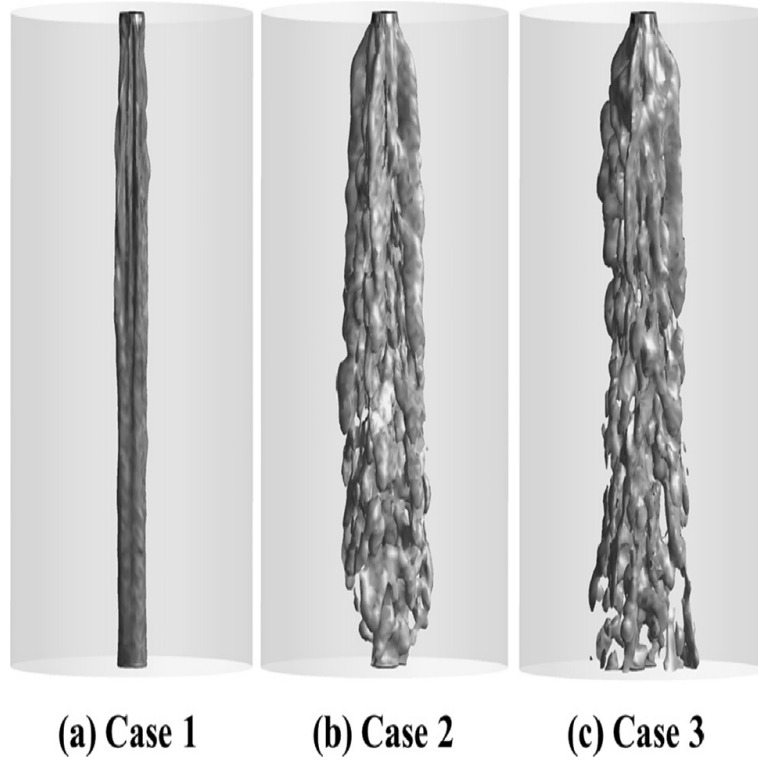


Figure 4.10: Simulated 30 wt% MEA/CO₂ flow behavior within a structured packed bed using the developed CFD models [with boundary conditions in table 4.3 and fluid properties in table 4.4 in this study](#). $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$, $D_{in} = 24 \text{ mm}$.

4.4.1 Effect of geometry on flow behavior

Since case 2 showed the best agreement with experimental data, the proposed approach by Lappalainen et al. [65] for mechanical dispersion was used in further investigation of the flow behavior in the packed column. The effect of liquid loading on the liquid hold-up in a packed column with a single inlet for liquid is presented in figure 4.6 (a). In the same plot, the empirical relation between liquid hold-up and liquid loading reported by Billet [158] and Fourati et al. [156] is also considered to verify the present model for the prediction of liquid hold-up quantitatively. The liquid hold-up (h_L) is calculated using eq. (4.16) Pham et al. [13]

$$h_L = \frac{\sum_i \alpha_{l,i} \Delta V_i}{\sum_i \Delta V_i}, \quad (4.16)$$

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where ΔV_i is the cell volume. An increase in liquid loading from 15.5 to 80.3 $m^3.m^{-2}.h^{-1}$ caused the liquid hold-up to rise from 0.02 to 0.05. This is mainly attributed to the dynamic hold-up and accumulation of larger amounts of liquid along the packed column at higher liquid loading. The liquid hold-up predicted by the present model based on the experimental data of Fourati et al. [156] and Tsai et al. [159] matches the empirical correlation presented by eq. (4.17), which was proposed by Billet [158],

$$h_L = 0.555(u_l^2 \frac{a_s}{g\epsilon^{4.65}}), \quad (4.17)$$

where u_l is the liquid velocity. However, the correlation reported by Fourati et al. [156] as presented by eq. (4.18), over-predicts liquid hold-up

$$h_L = 0.0209(\frac{\mu_L}{\mu_w})^{1/3} q_l^{0.4}, \quad (4.18)$$

in eq. (4.18) μ_w is the dynamic viscosity of water. A similar observation is reported by Fourati et al. [156] experimentally measured and developed a correlation for the liquid hold-up in a packed column with a single inlet for liquid. They found that the averaged liquid hold-up is almost two times higher than that presented in the literature. Figure 4.6(b) shows the effect of liquid load on wet pressure drop obtained in this study as well as a correlation reported by Stikkelman et al. [16], eq. (4.19). From source point or distributed points $\Delta P_w/L = q_l^{0.37}$. [Pressure drop for per unit length will be as,](#)

$$\frac{\nabla P}{l} = \frac{3}{4f_0' \left[\frac{1-\epsilon'}{\epsilon'^{4.65}} \right] \rho_g u_g^2 d_p'}. \quad (4.19)$$

where

$$f_0' = f_0 \left\{ \left[1 - \epsilon \left(1 - \frac{h_L}{\epsilon} \right) \right] / (1 - \epsilon) \right\}^{c/3}, \quad (4.20)$$

$$f_0 = \frac{5}{Re_g} + \frac{3}{Re_g^{0.5}} + 0.45, \quad (4.21)$$

$$\epsilon' = \epsilon \left(1 - \frac{h_L}{\epsilon} \right), \quad (4.22)$$

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$$c = \frac{\left[-\frac{5}{Re_g} - \frac{3}{2Re_g^{0.5}} \right]}{f_0}, \quad (4.23)$$

$$d'_p = d_p \left\{ \frac{\left[1 - \varepsilon \left(1 - \frac{h_L}{\varepsilon} \right) \right]}{(1 - \varepsilon)} \right\}^{1/3}, \quad (4.24)$$

$$d_p = 6(1 - \varepsilon)/a_s. \quad (4.25)$$

The condition used for wet pressure drop prediction is the same as that used in liquid hold-up prediction. It was found that the wet pressure drop increased when the liquid loading was raised from 15.5 to 80.3 $m^3.m^{-2}.h^{-1}$. At a constant gas velocity, increasing liquid loading leads to an increase in liquid volume fraction and reduces the available cross-sectional area for gas flow, consequently resulting in a higher pressure drop. In addition, pressure drop occurs due to friction at the gas-liquid interface and the induced drag when in contact with the reactor wall. Therefore, a rise in liquid loading causes an increase in the liquid velocity at the gas-liquid and wall-liquid interfaces, which elevates the shear stress and, consequently, the pressure drop. It was also found that the wet pressure drop obtained from the present model matches with the eq. (4.19) for the lower liquid loading but underpredicts for the higher liquid loading.

The wet pressure drop along the column in the multiple liquid inlets case was validated with the experimental data of Tsai et al. [159], who studied CO_2 absorption within several structured packings including, M250X. At a liquid loading of $\sim 24.4 m^3.m^{-2}.h^{-1}$ and gas capacity factor of $1.16 Pa^{0.5}$, the predicted pressure drop by the model was $0.24 mbar.m^{-1}$, which was in very good agreement with the measured experimental pressure drop of $0.22 mbar.m^{-1}$. The radial distribution of the liquid volume fraction along the column, as a function of the inlet velocity of liquid ($V_{in,l}$), is presented in figure. 4.5. It can be clearly seen that an increase in the inlet velocity of liquid from 1.2 to $6.2 m.sec^{-1}$ resulted in wider radial distribution of liquid. However, the variations in the radial distribution of liquid reduced when the inlet velocity of liquid exceeded $2.9 m.sec^{-1}$. It was also noticed that at a constant Z, the liquid volume fraction was relatively low at the center of the column and overconcentrated at its border. This behavior was intensified with an inlet velocity of the liquid, and the largest liquid volume fraction at its border was observed at $V_{in,l}$ of $6.2 m.sec^{-1}$ for $Z = 0.1 - 0.5$ m. Moreover, the radial distribution of liquid in all cases was anisotropic, implying the necessity of 3D models for exploring the liquid-gas

4. Validation of the Multi-Phase Liquid Dispersion Model

interaction within packed columns. The anisotropic fluid flow behavior was confirmed experimentally by Fourati et al. [156]. From a modeling perspective, the reason for the anisotropic behavior of the liquid inside the structured packing can be associated with the dispersion term in the momentum equation, i.e., eq. (4.11) for the Lappalainen et al. [65] model and eq. (4.14) for the Mewes et al. [155] model. To demonstrate that the observed dispersion pattern does not stem from any numerical instability, the radial distribution of the liquid volume fraction along the column for the case without a dispersion term (case 1) is also provided in figure 4.7. It can be seen that the same anisotropic pattern, similar to case 2 (figure 4.5), associated with liquid dispersion in structured packing, is captured.

Number of liquid nozzles	1	13
Liquid hold-up (–)	0.018	0.062
Wet pressure drop (Pa/m)	1	13

Table 4.9: Effect of the number of liquid nozzles on the liquid hold-up and wet pressure drop based on Case 2. For single liquid inlet $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, and for multiple liquid inlets $V_{in,l} = 0.09 \text{ m.sec}^{-1}$. In both cases, liquid mass flow rate is constant at 0.54 Kg.sec^{-1} . $V_{in,g} = 1.05 \text{ m.sec}^{-1}$ and $D_{in} = 24 \text{ mm}$.

Table 4.8 presents the comparison of liquid hold-up and wet pressure drop for the packed column with single and multiple liquid inlets (13 nozzles) of the same diameter ($D_{in} = 24 \text{ mm}$, figure 4.1) and liquid mass flow rate of 0.54 kg.sec^{-1} . It was found that increasing the number of liquid inlets from 1 to 13 resulted in almost three times larger liquid hold-up and raised the wet pressure drop from 98 to 310 Pa.m^{-1} . A comparison between the radial distribution of volume fraction along the reactor with single and multiple liquid inlets is presented in figure 4.8. The packed column with a single liquid inlet was characterized with relatively low volume fraction, but a wider radial distribution of the liquid, which is associated with significantly larger inlet velocity (1.2 m.sec^{-1}) compared to that of multiple inlets (0.09 m.sec^{-1}). On the other hand, the column with multiple liquid inlets featured a narrow radial distribution of liquid and relatively overconcentrated liquid fraction at the center of the trajectory for each inlet. Therefore, the increased liquid hold-up and pressure drop along the column with multiple inlets can be attributed to multiple regions with a narrow liquid spreading and overconcentrated liquid regions at the center.

It should be noted that during CO_2 capture, a larger liquid volume fraction can potentially enhance CO_2 uptake. However, a narrow region of liquid with a high volume fraction at the center of the trajectory for each inlet, in the case of multiple inlets, may reduce the mass transfer rate of CO_2 into the amine solution due to the maldistribution of liquid. Thus, for future work, physical and reactive mass transfer need to be implemented in this model to provide a better understanding of such behavior.

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4.4.2 Effect of finer mesh

The hydrodynamic model was tested for three different finer meshes 1million, 5 million, and 10 million cells to reduce truncation error. But the simulation crashed due to SIGSEGV error. This error in Ansys Fluent is associated with memory. The model was tested for 256 cores but still was not enough. So, for a finer mesh, a much higher core is needed, and hence it is recommended for future work.

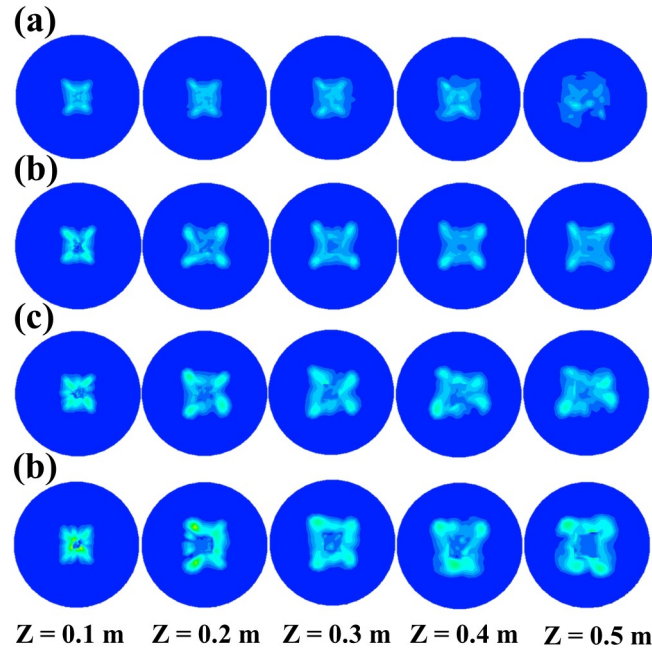


Figure 4.11: Evolution of cross-sectional liquid volume fraction counters along the reactor at liquid inlet velocity $V_{in,l}$ of (a) 1.2 m.sec^{-1} ; (b) 2.9 m.sec^{-1} ; (c) 4.3 m.sec^{-1} ; (d) 6.2 m.sec^{-1} . $V_{in,g} = 1.05 \text{ m.sec}^{-1}$, $D_{in} = 24 \text{ mm}$.

4. Validation of the Multi-Phase Liquid Dispersion Model

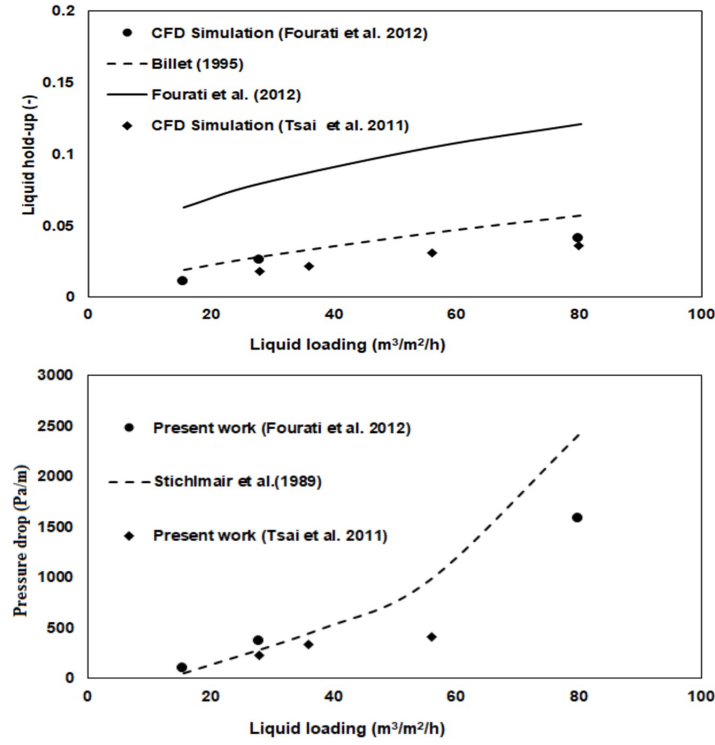


Figure 4.12: Variation of liquid hold-up and wet pressure drop as a function of liquid loading with medium mesh. $V_{in,l} = 1.2 - 6.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$, $D_{in} = 24 \text{ mm}$

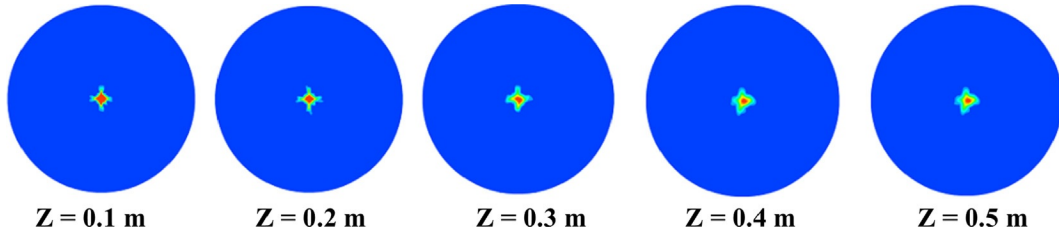


Figure 4.13: Liquid volume fraction contours for case1 (without dispersion) for different height

4. Validation of the Multi-Phase Liquid Dispersion Model

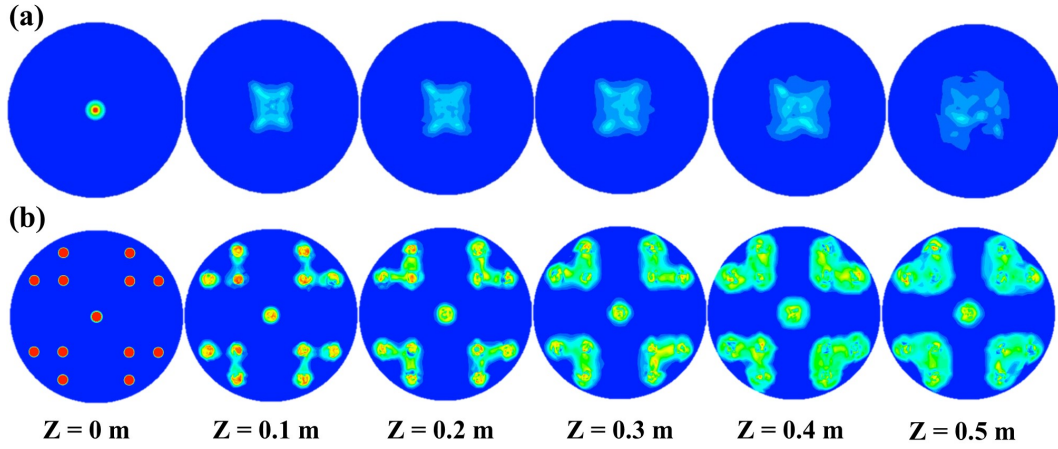


Figure 4.14: Effect of number of liquid inlet (N) on cross-sectional counters of liquid volume fraction along the reactor: (a) $N = 1$, $V_{in,l} = 1.2 \text{ m.sec}^{-1}$; (b) $N = 13$, $V_{in,l} = 0.09 \text{ m.sec}^{-1}$. In both cases liquid flow rate is constant and $0.11184 \text{ kg.sec}^{-1}$. $V_{in,g} = 1.05 \text{ m.sec}^{-1}$, $D_{in} = 24 \text{ mm}$

4.5 Conclusion

3D transient Eulerian-Eulerian two-fluid models were developed by implementing different models for mechanical dispersion in order to further improve the predictability of liquid dispersion within a structured packing. The results showed that the model proposed by Lappalainen et al. [65] provided a better prediction of the liquid dispersion when compared with the model developed by Mewes et al. [155] based on the spread tensor approach. In addition, the liquid dispersion was shown to be highly anisotropic, which implied the necessity of utilizing 3D models. Thus, much better agreement with experimental data was achieved compared to previously developed 2D models. It was found that increasing the liquid velocity from 1.2 to 2.9 m.sec^{-1} considerably widened the radial distribution of the liquid. Further, increase in velocity to 6.2 m.sec^{-1} did not have a significant effect on the liquid distribution profile but led to a shift in liquid hold-up from the center of the column to its border. Moreover, the average liquid hold-up and wet pressure drop predicted by the present model were compared with the empirical correlations available in the literature. An increase in the number of liquid inlets from 1 to 13, at constant liquid mass flow rate, increased liquid hold-up, but formed several narrow overconcentrated liquid regions, which increased pressure drop from 98 to 310 Pa.m^{-1} . Although an increase in liquid hold-up in the column can be beneficial, the presence of overconcentrated narrow regions, observed when multiple liquid nozzles were used, may reduce mass transfer due to the maldistribution of liquid. Therefore, in future work, physical and reactive mass transfer should be implemented in such models.

Chapter 5

A Hypothesis on the Multiphase Mass Transfer and Chemical Reactions

5.1 Introduction

According to IPCC 2018 report, due to human activities, global warming of 1 °C occurred above the pre-industrial level. If this continues at this scale, global warming would have occurred to 1.5 °C between the years 2030 and 2052. It will rise to the seawater level. Moreover, CO_2 emissions from fossil fuel will also contribute to the acidification of the oceans, and the nitrogen cycle in the atmosphere will be affected [7] Three options proposed to reduce the carbon emissions: a) use of energy has to be reduced by improving efficiency b) use of other energy sources like renewables to replace fossil fuel c) carbon capture and storage (CCS). The best option to reduce carbon is to go for renewable energy sources. But, at present renewable energy sources are not a good option compared to fossil fuel due to the cost of production and technological challenges. Therefore, the only option is to consider CCS to reduce CO_2 emission [9].

In post-combustion carbon capture, scrubbing is a very effective technology to remove CO_2 from the flue gas before it is released to the atmosphere. It is a chemical absorption technology where the gas enriched with CO_2 reacts with a solvent. Chemical absorptions involve the reaction of CO_2 with a chemical solvent to form a weakly bonded intermediate compound which is regenerated with the use of heat-producing the original solvent. Two main phenomena are involved. Mass transfer of CO_2 from the bulk gas phase to the liquid solvent phase and the chemical reaction between CO_2 and the solvent. Reactive absorption is a separation process in which the absorption of gaseous species and a chemical reaction occurs simultaneously in the absorption column. Compared to physical absorption, reactive absorption does not need elevated pressure. Chemical absorption can

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be modeled by two approaches, equilibrium-based and rate-based approaches [71]. The equilibrium stage assumes the liquid and vapour phases at equilibrium. These models may assume the reactions at the equilibrium or may consider the reaction kinetics. In the rate-based approach, actual rates of multi-component mass transfer and chemical reactions are considered. A more rigorous approach involves the inclusion of an enhancement factor to estimate actual absorption rates [71].

In the past, researcher had worked in the post-combustion carbon capture both experimentally and numerical modeling. Haunling et al. [160] used ammonia scrubbing for CO_2 removal. They concluded that with ammonia scrubbing, the CO_2 removal efficiency could be as high as 98%. But, due to the nature of the high corrosion of ammonia, this approach is not very cost-effective. To overcome this problem, aqueous solutions of ethanolamine, particularly monoethanolamine (MEA), are used for CO_2 removal because of its low volatility, thermal stability, and high reactivity. Post-combustion capture with MEA is a reactive absorption process. For the rational design of absorption equipment, the knowledge of chemical kinetics between CO_2 and MEA is very important. Although many studies reported on it, there is a considerable discrepancy between previous results [160]. The discrepancy between experimental and CFD modeling happens due to the inability to handle a large number of input parameters like gas solubility, and liquid diffusivity has not been able to address all chemical reactions involved in the process. Since all these reactions are very fast and instantaneous, previous CFD studies did not give proper insight inside the reactor to explain all those instantiations reactions.

In reactive absorption, reliable and accurate models are needed for mass transfer of gaseous CO_2 from the gas bulk into the gas boundary layer, across the gas-liquid interface, from the interface through the reaction boundary layer of the liquid phase, and at last into the liquid bulk. Based on the assumption, several mass transfer models are available in the literature, namely the film model, higbie's penetration model, surface renewal model, and interfacial turbulence model. According to the penetration model, due to the random motion of the solute molecules, the diffusion of gas into the film is an unsteady process. The advantage of higbie's penetration model is that it takes mass transfer as a transient process and is most accepted in multiphase CFD modeling. Higbie penetration model is based on the assumptions that i) the mass transfer coefficient is proportional to the square root of the diffusion ii) from the bulk fluid eddies go to the interface, remain at the interface for a certain time (exposure time), and then return to the bulk uniformly [73].

Liquid side mass transfer coefficient predicted based on higbie's model (Bravo et al. [17]) depends on liquid flow rate, exposure time but does not depend on the gas flow rate. This model assumes that the packing surface is fully wetted. Based on penetration theory, Xu et al. [74] predicted gas mass transfer by taking into account the effect of liquid hold-up, and they showed that with the increase of superficial gas velocity, the gas mass

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transfer coefficient increases, but the height of the mass transfer unit for gas phases is decreased. Faramarzi et al. [95] developed a model based on two-film theory for mass transfer and a rate-based model for chemical reactions by using Boundary Value Problem solver (BVP). One of the big problems of it is due to guessing it is obvious to bring a significant amount of errors in the model. FORTRAN programming was used by Aboudheir et al. [96] to study reaction kinetics in CO_2 capture. The reaction kinetics between CO_2 and MEA was investigated for a wide temperature range by using both the zwitterion mechanism and the termolecular mechanism. They developed a new termolecular mechanism to explain chemical reactions between CO_2 and MEA for a better prediction of reaction kinetics. Lawal et al. [97] developed a process model for CO_2 capture using two different approaches of equilibrium and rate-based to understand the dynamic behavior of the absorber using Aspen Plus. They concluded that the rate-based approach shows a better prediction compared to the equilibrium-based approach, but, the main problem of this type of study is due to too many input parameters and adjustable parameters, this approach is not quite robust and reliable. These types of problems can be easily overcome by CFD modeling as it is quick, less expensive, and can work on any geometry with minimum input parameters. Several researchers used this for CO_2 capture modeling.

For CFD modeling of multi-phase flow problems, two approaches are available. One is the Eulerian-Eulerian approach and the other one is the Eulerian-Lagrangian approach. In the Eulerian-Eulerian approach, the volume fraction of each phase is considered, and as a result, the interphase between the fluids can be tracked. In space and time, these volume fractions exist as scalar values. On the other hand, in the Eulerian-Lagrangian approach, Navier-Stokes equations are solved for continuous phase, and the number of particles of the dispersed phase is tracked by exchanging mass, momentum and energy with the continuous phase using the Lagrangian approach. This approach is not suitable for any case where the volume fraction of the secondary phase cannot be dropped. This work used the Eulerian-Eulerian approach to model multiphase flows in a post-combustion absorption reactor. Three different scales, namely micro, meso, and macro scales, can be used to model CFD multiphase flow within post-combustion absorption reactors. In a micro-scale case, the computational domain is limited to few centimeters to calculate gas-liquid interface. In this case, liquid wetting on the plate or packing surface can be studied. The magnitude of the liquid wetting is dependent on the ratio of inertia and surface tension forces. In meso-scale the computational domains are limited to several representative elementary units (REUs). These are repeating geometrical units and form the structured packing bed. In this scale, the simulations are done only with the gas phase. As a result, only dry pressure drop characteristics are available on this scale. The pressure loss per unit length in this scale for a set of REUs is the same as the whole absorber but the results need to be corrected with the experimental correlations to calcu-

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late the wet pressure drop of the packing by taking account of the liquid hold-up. On the macro scale, the whole reactor is taken as a porous medium. In this scale, geometrical features are studied. In this model, the advection-diffusion equation can be used to study the spreading of the liquid. Asendrych et al. [84] reported a 2D axisymmetric CFD model for CO_2 capture. They used amine solvent with counter-current two-phase flow. For hydrodynamics, a two-fluid Eulerian model was applied, and they also included chemical reactions. They concluded that CO_2 capture efficiency is mostly influenced by the ratio of the liquid to the gas mass fluxes. They validated the model with their experiments. The accurate prediction of CO_2 -MEA hydrodynamics in a structured packing is the key step for realistic modeling of mass transfer and chemical reaction and further optimization of the absorber reactor.

An effort to fill this gap was made by Sebastia et al. [98]. They developed a 3D model for small scale. They used the VOF model by taking into account hydrodynamics, physical mass transfer and reaction kinetics for micro-scale in a structured packed bed. They used Higbie's penetration theory to describe physical mass transfer. They concluded that as the concentration of MEA increases the enhancement factor also increases and the model can describe reactive enhancement factor successfully. From their work, it was understood that the CFD model is a very good tool to understand reaction kinetics and associated parameters for the 3D case. But their work was done for a micro-scale. There is still a gap in knowledge for chemical kinetics in meso and macro-scales by taking account of the whole reactor. Large-scale 3D CFD modeling was done by Pham et al. [13]. They used the 3D Eulerian-Eulerian CFD model to investigate hydrodynamics, mass transfer and chemical reaction for MEA with multiple inlets in the structured packed bed. They concluded that a higher mass transfer coefficient leads to higher CO_2 removal. Although by their work, we understand the reaction kinetics and CO_2 removal rate in the whole reactor, there is still a knowledge gap in 3D large scale CFD modeling. For chemical reaction modeling they used a simplified model based on molar concentration. Probably it was done to reduce the complexity in the CFD modeling. This simple model is made by considering the chemical reaction rate a fixed one. Secondly, they used a constant mass transfer coefficient for liquid, but which is not correct as the mass transfer coefficient varies across the column height.

In this work, a 3D transient multiphase Eulerian-Eulerian numerical model was developed to predict CO_2 capture by MEA scrubbing within a structured packing bed. The results were validated with the experimental literature result and were found in very good agreement with the experimental data. With this model, it can be possible to explain reaction kinetics inside the packed bed much better, which is needed for optimization. Moreover, the influence of single and multi-inlets of liquid on CO_2 absorption and the effect of pressure and concentration of MEA are established in CO_2 removal.

5. A Hypothesis on the Multiphase Mass Transfer and Chemical Reactions

5.2 Model development

The model was developed in three parts. The first one is hydrodynamics, and the second one is the mass transfer, and the third one is chemical reactions.

5.2.1 Hydrodynamics

The hydrodynamics part of the model was the same as the previous work. All the governing equations were the same as previous chapter.

5.2.2 Mass transfer

For the gas phase,

$$\frac{\partial(\alpha_g \rho_g y_g)}{\partial t} + \nabla \cdot (\alpha_g \rho_g \vec{v} y_g) + \nabla \cdot [D_g \nabla (\alpha_g \rho_g y_g)] - S_{lg} = 0, \quad (5.1)$$

For the liquid phase,

$$\frac{\partial(\alpha_l \rho_l y_l)}{\partial t} + \nabla \cdot (\alpha_l \rho_l \vec{v} y_l) + \nabla \cdot [D_l \nabla (\alpha_l \rho_l y_l)] + S_{lg} = 0, \quad (5.2)$$

hence

$$S_{lg} = k_l a_e c_l (y_i^* - y_l) = k_g a_e c_g (y_g - y_g^*). \quad (5.3)$$

where k_l and k_g are the liquid side and gas side mass transfer coefficients, respectively. As the mass transfer occurs from the gas to liquid phase at the gas-liquid interface, the mass fraction of the gas phase is equal to the solubility of the gas phase in the liquid phase. Henry's law can be used to calculate this solubility. Two film theory was used to calculate the mass transfer source term.

$$k_l = 2 \sqrt{\frac{D_l}{\pi \tau}}, \quad (5.4)$$

where D_l is CO_2 diffusion coefficient, τ is the exposure time. According to film theory, a stagnant film of both gas and liquid is assumed on the two sides of the liquid-gas interface. In this layer, resistance to the mass transfer is concentrated, and mass transfer occurs by molecular diffusion. For each computational cell, the gradient of the volume fraction was used to calculate the effective area a_e as:

$$a_e = |\nabla \alpha_g| = |\nabla \alpha_l|, \quad (5.5)$$

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the overall mass transfer coefficient as derived from two film theory is given by

$$\frac{1}{K_L} = \frac{1}{Ek_l} + \frac{1}{Hk_g}, \quad (5.6)$$

where K_L is the overall liquid mass transfer coefficient, H is the Henry's constant, and E is the enhancement factor. As the most overall mass transfer resistance comes from the liquid side resistance, the overall mass transfer coefficient can be assumed as:

$$K = Ek_l. \quad (5.7)$$

Hatta number is a relative parameter to compare the rate of reaction in a liquid film to the rate of diffusion. A higher Hatta number will indicate a higher reaction rate compared to diffusion. As a result, the reaction will take place mostly in the film:

$$E = \sqrt{1 + Ha^2}. \quad (5.8)$$

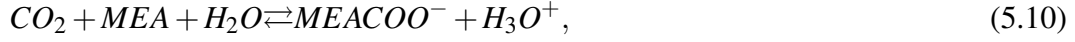
Two factors govern the absorption process between the liquid phase and the gas phase. a) mass transfer between the phases and b) chemical kinetics. Chemical kinetics depend on the solution that contains the dissolved reactive absorbent, but the mass transfer depends on the type of reactive absorbent and the equipment. Diffusivities, fluid mixing, geometries determine the mass transfer. So, faster mass transfer and faster kinetics are important for better performance.

5.2.3 Chemical reactions

In choosing the reaction scheme, two mechanisms are proposed firstly, zwitterion mechanism and secondly termolecular mechanism. Zwitterion mechanism is a two steps mechanism, and it is about the formation of zwitterion when CO_2 reacts with MEA. Then this zwitterion forms carbamate. The overall reaction rate can be presented as a function of the concentration of CO_2 , MEA, and H_2O . According to the termolecular mechanism as CO_2 reacts with MEA it forms a loosely bound product rather than zwitterion, and it is a single-step mechanism. The concentration of water in MEA is larger than the other species and as a result, transport property model is required to determine various physical and thermal properties like pressure drop, liquid hold-up, mass transfer coefficient, thermal conductivity. In this work, the zwitterion mechanism is used, and the following chemical reactions were taken into account



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As per eq. (5.9), bicarbonate is formed due to the reaction between CO_2 and hydroxide OH^- and carbamate is formed from eq. (5.10). Both of these reactions are finite rate and were implemented to the FLUENT by UDF as a source term. Eqs. (5.11-5.14) are instantaneous reactions.

Phase	$\rho(Kg.m^{-3})$	$\mu(m. Pa-s)$	Solubility($g.l^{-1}$)	Diffusivity($c.m^2.sec^{-1}$)
20 wt.% MEA	1012	2.48	1.06	0.41×10^{-5}
30 wt.% MEA	1020	5.51	1.14	0.26×10^{-5}
50 wt.% MEA	1026	12.46	1.20	0.19×10^{-5}
Carbon dioxide	1.79	1.37×10^{-2}	1.064×10^{-3}	0.405×10^{-9}

Table 5.1: Properties of MEA

5.3 Results and discussions

Apart from the validation, all the work is done considering 100% CO_2 , with 30% MEA solution. CO_2 reacts with the amine to form a molecule called a zwitterion. This zwitterion then turns into carbamate. All the reactions were implemented by UDF. Liquid speed was $1.19 m.sec^{-1}$ and gas speed was $1.052 m.sec^{-1}$. The porosity was 0.98. Although it is bit a higher, for Mellapac 250X the porosity was reported as 0.98 by Pham et al. [13]. This value of porosity was also used by Fourati et.al [156]. Porosity can be between 0.7 to 0.98 but in line with other researchers, the porosity in this study was taken as 0.98.

5.3.1 Effect of MEA concentration:

Concentration was varied from 30 % to 50 % to see this effect on CO_2 removal for a single inlet of liquid. Figure 5.1 (a) shows the averaged molar concentration of CO_2 in the liquid phase along with the height of the column. It can be seen that higher MEA concentration removes higher CO_2 . This behavior is due to the fact that the increase of the MEA concentration reaction rate increased. The reason can also be explained with the help of the kinetic theory. According to the kinetic theory, as the concentration is increased, the probability of reactants molecules to trigger the reaction becomes higher.

5. A Hypothesis on the Multiphase Mass Transfer and Chemical Reactions

Figure 5.1 (b) shows the variation of enhancement factor along with the height of the column. A higher concentration of MEA leads to higher enhancement factors. This is due to the fact that enhancement directly relates to the Hatta number, which is proportional to the squared root of amine concentrations in the aqueous solution. The radial variation of enhancement factor at different height of column for different amine concentration is shown in figure 5.2. The enhancement factor at the top of the column is higher compared to the bottom of the column. This is due to more amount of MEA at the top. So, it will be better to improve the enhancement factor in chemical reaction than changing the area of the packed bed.

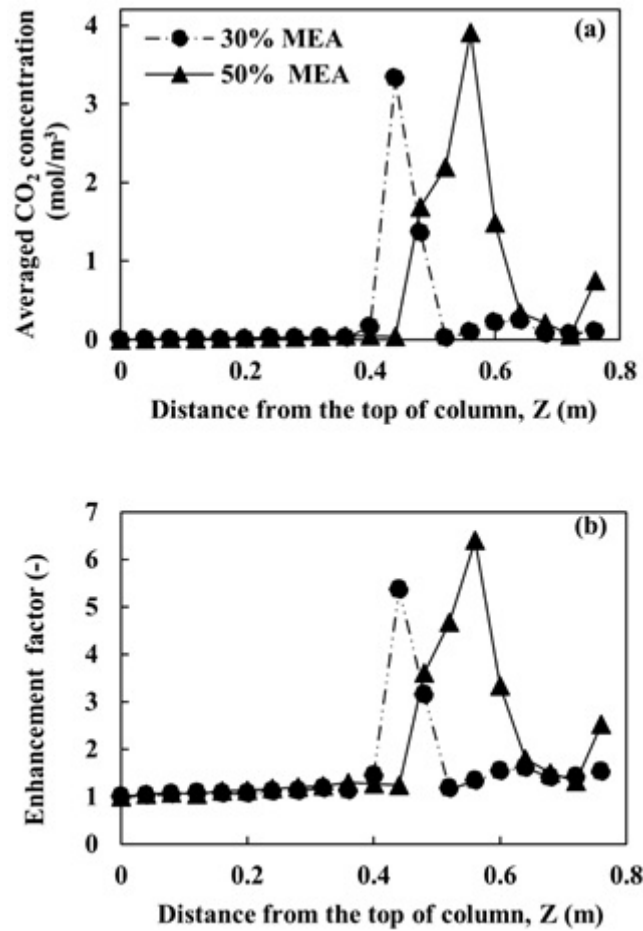


Figure 5.1: (a) Averaged molar concentration of CO_2 in liquid phase (b) Changes of enhancement factor along the column heights for single liquid inlet with $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$.

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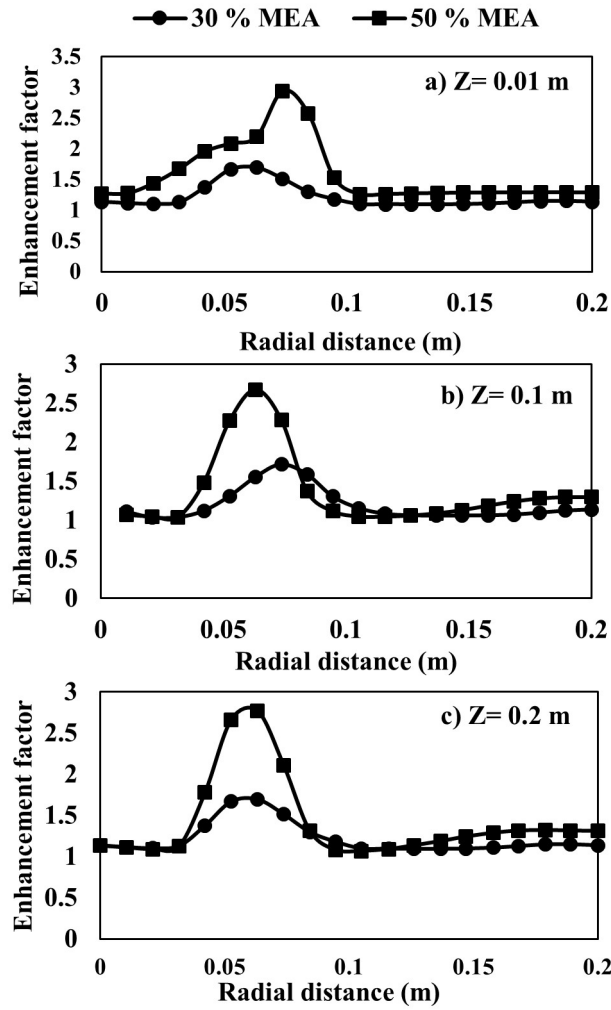


Figure 5.2: Changes of Enhancement factor in CO_2 removal with 100 % CO_2 in gas phase with $V_{in,l} = 1.2 \text{ m}\cdot\text{sec}^{-1}$, $V_{in,g} = 1.05 \text{ m}\cdot\text{sec}^{-1}$ for various column heights with single inlet.

Figure 5.3 (a) shows the total amount of dissolved CO_2 in the packed bed, and dissolved CO_2 increases with increasing MEA concentration. This is due to an enhanced chemical reaction when MEA concentration increased. The increased reaction rate leads to the formation of a high amount of carbamate and hydronium ions, as shown in Figure 5.3 (b). It is found that the concentration of hydronium ion goes down if the concentration of MEA is further increased from 30%. The reason is for higher MEA concentration, hydronium ions become more reactive and got solvated by water. Generally, hydronium ion is very acidic and can exist in water as the most acidic species.

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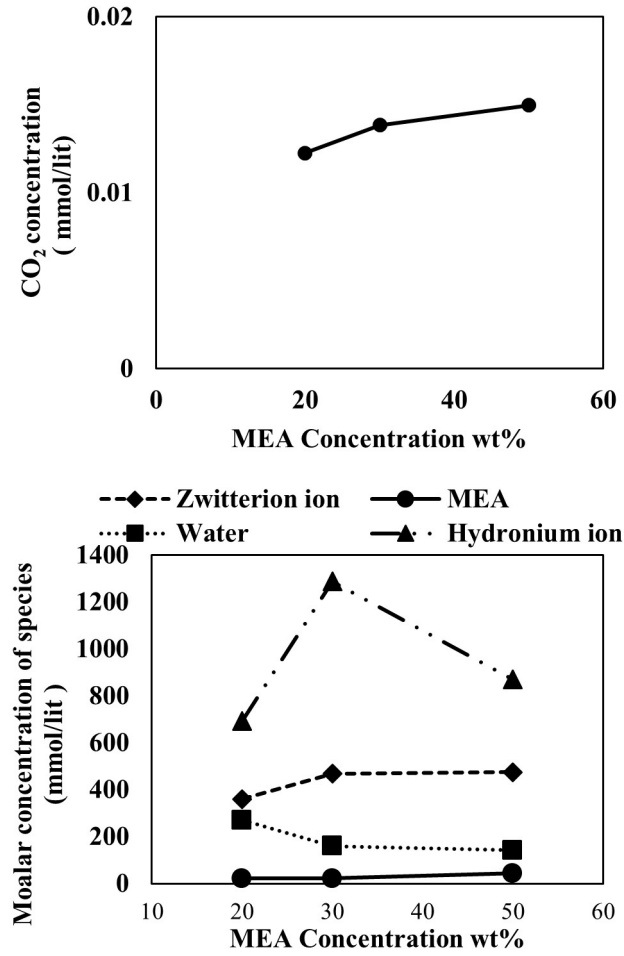


Figure 5.3: Changes of averaged concentration of (a) CO_2 species in liquid phase (b) other species with MEA solution with $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$.

5.3.2 Effect of multiple liquid inlets on the chemical absorption

Simulations were performed to study the effect of multiple liquid inlets on chemical absorption. For this simulation, liquid inlet velocity, $V_{in,l}$ of 1.2 m.sec^{-1} and gas inlet velocity, $V_{in,g}$ of 1.05 m.sec^{-1} were used. Figure 5.4 shows the variation of the molar concentration of CO_2 along the radial direction at different heights of the column for the multi-inlet case. It is shown from figure 5.4 that a non-uniform profile of the molar concentration of CO_2 is observed with the radial distance of the column. With the more inlets, more liquids flow into the packed bed, and as a result, more mass transfer occurs along the radial direction. It is also found that the maximum concentration of CO_2 occurs at the farthest distance from the liquid inlet. For multi-inlets more liquid is available due

5. A Hypothesis on the Multiphase Mass Transfer and Chemical Reactions

to multi-source point to take part in a chemical reaction and as the liquid travels further, due to multi-inlets more liquid enters into the packed bed and the concentration of the liquid gets higher as the liquid travels towards the bottom the column. Hence, more CO_2 is dissolved at the farthest distance from the liquid inlet or in other words towards the bottom of the column. The radial variation of the enhancement factor at different heights of columns for multi-inlets case is shown in figure 5.5. As the liquid travels more, the interfacial area increases, and MEA concentration becomes more dominant in reaction kinetics. The enhancement factor becomes highest at the farthest distance from the liquid inlet. For multi-inlets and 30 wt.% MEA the total CO_2 removal was $84.93 \text{ kmol.m}^{-3}$. According to figure 5.6 it can be concluded that carbon capture can be increased significantly with the increase of more liquid inlets.

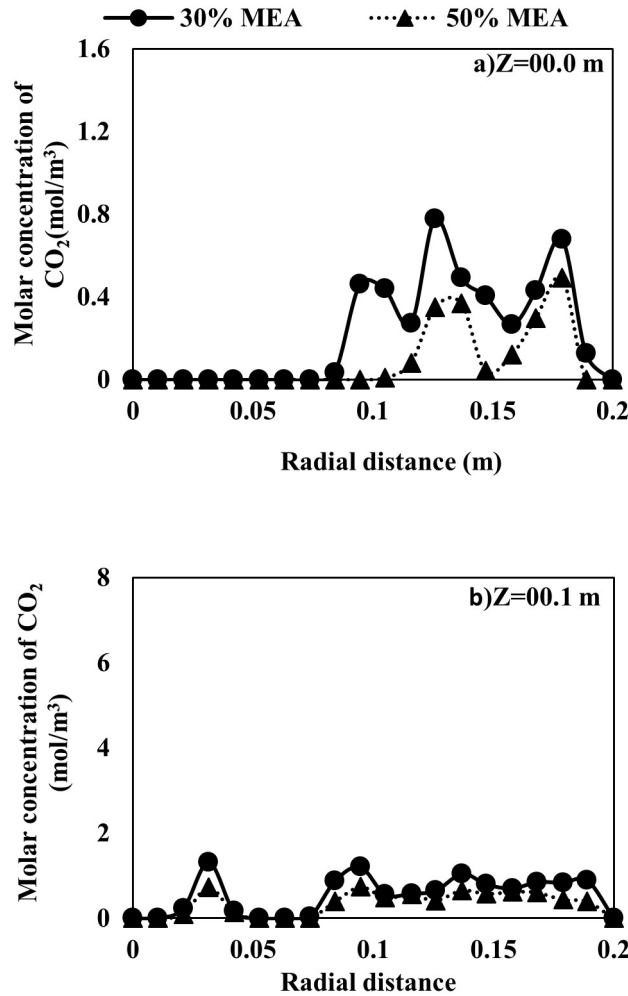


Figure 5.4: Changes of CO_2 concentration in liquid phase at different column heights for multi-inlets with $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$.

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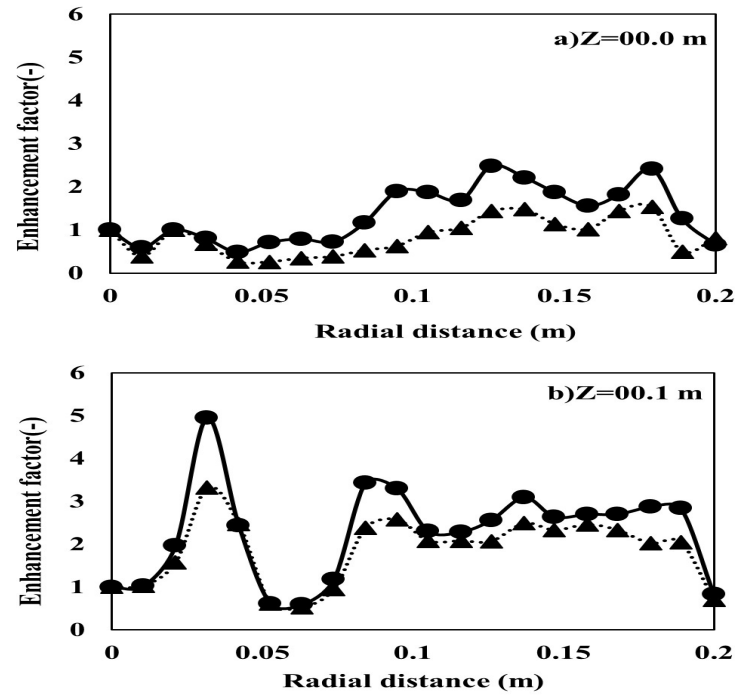


Figure 5.5: Changes of enhancement factor at different column heights for multi-inlets with $V_{in,l} = 1.2 \text{ m}\cdot\text{sec}^{-1}$, $V_{in,g} = 1.05 \text{ m}\cdot\text{sec}^{-1}$.

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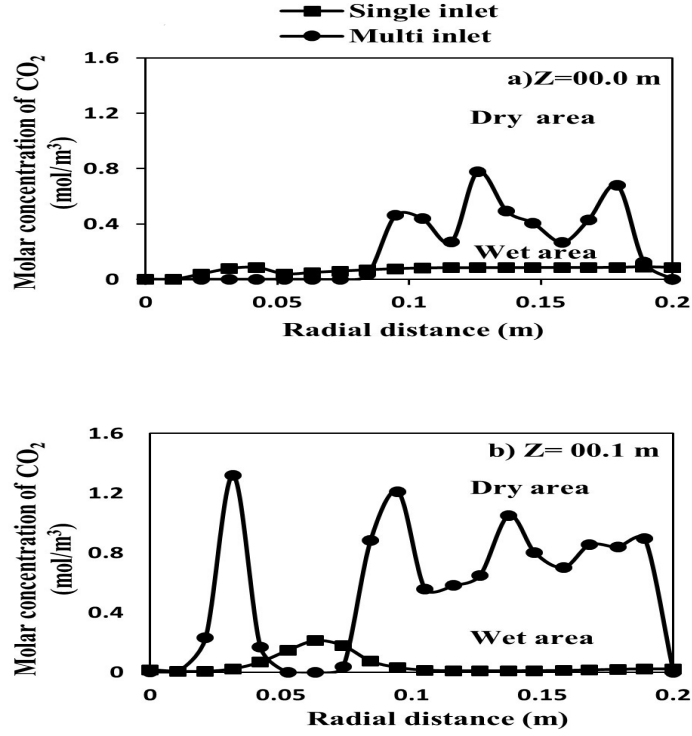


Figure 5.6: Effect of liquid inlets on molar concentration of CO_2 in liquid phase with 100 % CO_2 in gas phase and 30 % MEA in liquid phase for $V_{in,l} = 0.09 \text{ m} \cdot \text{sec}^{-1}$ and $V_{in,g} = 1.05 \text{ m} \cdot \text{sec}^{-1}$.

In figure 5.6, the area under the curve for both single and multi inlets are wet area, and the remaining is the dry area.

5.3.3 Effect of liquid loading

Liquid loading was increased from $28 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $80 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ by keeping the gas loading constant. Figure 5.7 shows the effect of liquid loading on the chemical absorption of CO_2 for the case of a single liquid inlet. It was found that if the liquid loading is increased molar concentration of CO_2 is increased. It happens as the mass transfer occurs from gas to liquid, higher liquid loading increases the interfacial area (figure 5.7 (b)), and an increase of enhancement factor also takes place (figure 5.7 (c)). This result is quite significant in carbon removal. The averaged quantities of the molar concentration of CO_2 , interfacial area, and enhancement factor are calculated in the reactor, which are in table 5.2. It can be seen that averaged values of CO_2 concentration, interfacial area, and enhancement increase with the liquid load. This is due to the fact that the mass transfer rate increases by increasing the available interfacial area when liquid load increases. This trend agrees with the literature (Sebastia-Saez et al. [146]). The increasing absorption

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rate leads to an increase in the reaction rate which results in a higher the enhancement factor.

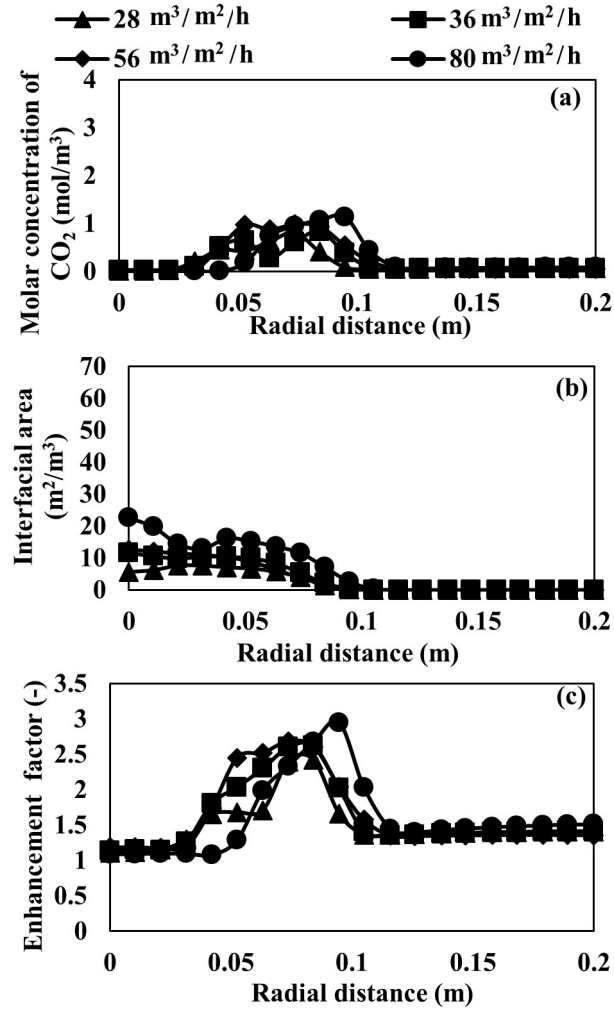


Figure 5.7: Effect of liquid loading on the radial variation of (a) dissolved CO_2 in liquid phase concentration in liquid phase (b) interfacial area (c) enhancement factor at $Z=0.4$ m.

Liquid loading	CO_2 concentration ($mol.m^{-3}$)	Interfacial area ($m^2.m^{-3}$)	Enhancement factor
28	0.2976	2.47	1.63
36	0.3981	3.39	1.84
56	0.4532	3.92	1.85
80	0.4838	6.81	1.93

Table 5.2: CO_2 concentration in liquid phase for different liquid loading

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5.3.4 Effect of pressure

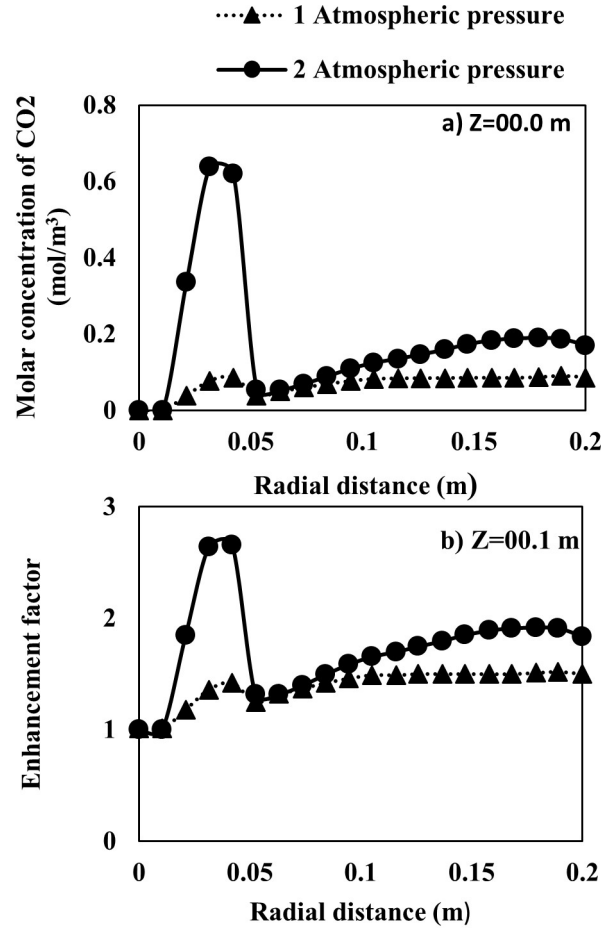


Figure 5.8: Effect of pressure on CO_2 removal with 100 % CO_2 in gas phase and 30 % MEA in liquid phase for $V_{in,l} = 0.09 \text{ m} \cdot \text{sec}^{-1}$ and $V_{in,g} = 1.05 \text{ m} \cdot \text{sec}^{-1}$.

The operating pressure was varied from 1 atmospheric pressure to 2 atmospheric pressure. Figure 5.8 shows the pressure effect on dissolved CO_2 concentration in the liquid phase and enhancement factor for a single inlet case. It was found that carbon removal was increased with the increase of pressure. It happened as the solubility of the gas increased due to an increase of pressure.

5.4 Validation of the Mass Transfer Hypothesis

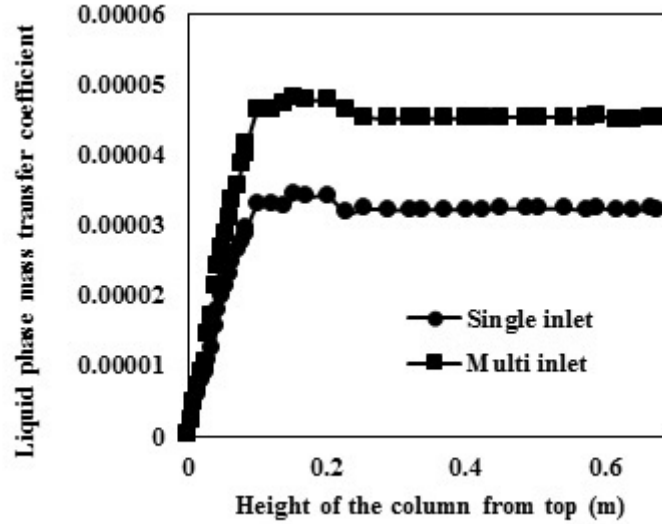


Figure 5.9: Change of mass transfer coefficient along with the column height with 100 % CO_2 in gas phase and 30 % MEA in liquid phase for $V_{in,l} = 0.09 \text{ m}\cdot\text{sec}^{-1}$ and $V_{in,g} = 1.05 \text{ m}\cdot\text{sec}^{-1}$.

The mass transfer for this work was studied by the interfacial area. It was also studied by the change of mass transfer coefficient along with the column height. It was found that the mass transfer coefficient increases along with the column height, and it was also in line with the literature. The higher liquid mass transfer coefficient plays a big role in determining the increasing absorption performance. If the liquid load is increased, the mass transfer coefficient also increases. Mass transfer of CO_2 into the liquid phase is significantly influenced by the chemical reaction. If CO_2 reacts closely to the gas-liquid interface, the reaction will be fast, and the concentration of CO_2 far from the interface is zero.

Figure 5.9 is for the liquid side mass transfer co-efficient along with the column height. The variation of the liquid side mass transfer coefficient is calculated by eq. (5.4) along with the height of the absorber for both single and multi-inlets. The liquid side mass transfer coefficient was calculated in the centreline of the packed bed column for both single and multi-inlets. It was found that for both cases, the mass transfer coefficient increases across the height of the column and then remains constant after traveling some distance from the liquid inlet. [The reason is, the liquid spreads in more area at the bottom of the column compared to the top side of the column.](#) It was also found that the liquid phase mass transfer coefficient is slightly higher for multi-inlets than that in the single

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inlet. The reason is, for multi inlets, more area was wetted compared to the single inlet. The range of liquid phase mass transfer coefficient (1.5×10^{-5} - 2.5×10^{-5}) obtained in this work matches with the literature [146]. The mass transfer process in packed columns is dependent on many factors, such as vapour/liquid rates, physical properties, and vapour-liquid equilibrium value. All these factors change from location to location along the column [74].

Although it was not possible to validate the model at this stage, the flow physics in this chapter follow the literature. For example, the higher concentration of MEA, will remove more CO_2 than the lower concentration of MEA and higher pressure will also remove more CO_2 . It was also found that as the multi inlets provide less dry area and increase mass transfer, it is better to consider multi inlets with separate phases tray for liquid distribution.

5.5 Summary and Conclusions

It was found that the developed 3D multi-phase CFD model is capable of predicting carbon removal with higher accuracy. Depending on the requirements, the model can be used in growing confidence to predict carbon removal. Based on the CFD model, it is also possible to design the structured packed bed with a number of inlets. It was also found that for greater efficiency, liquid loading should be kept as low as possible, and it is always better to increase the enhancement factor rather than packed bed surface area for greater removal efficiency.

Chapter 6

Multiphase Heat Transfer

6.1 Introduction

There are two models for the convection heat transfer in porous media 1) local thermal equilibrium model 2) local thermal non-equilibrium model. For the local thermal equilibrium model, it is assumed that the fluid temperature is equal to the solid phase temperature. It can also be explained as the local thermal equilibrium between the fluid and solid phase at any point of the porous media [102]. If the wall temperature is uniform in the packed bed, heat transfer occurs because of three basic methods. Due to the temperature gradient between the bed and conduit wall, heat is transferred to the bed particles by conduction and convection. Heat is transferred from the bed to the fluid flowing through the bed is by forced convection. This heat transfer is affected by the mechanism of the fluid flow adjacent to the solid surface. Heat transfer takes place only when there is a temperature difference between the conduit wall and the fluid flowing through the conduit [105]. When heat transfer takes place, the temperature of the moving fluid is the same as the temperature of the solid particles that made the bed. At some distance from the bed, fluid temperature is the same as the undisturbed stream known as the thermal boundary region[105]. In a packed bed, the forced convective heat transfer is influenced by many parameters like Reynolds number, Prandlt number, void fraction, the ratio of tube diameter to sphere diameter, local flow conditions, the effect of radiation, natural convection, surface roughness, and the ratio of bed height to sphere diameter [106]. On the other hand, for the non-equilibrium model, two equations (two-temperature) model needs to be solved, and it is more complex [102].

The thermal conductivity of a packed bed depends on the fluid flow and heat transfer conditions and on the size and shape of the particles. Effective conductivity of the stagnant gas is influenced by several heat transfer mechanisms 1) conduction through the gaseous

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phase, 2) conduction through the solid phase, 3) heat radiation through solid-solid and through the void area to the next layer 4) conduction through the contact area and, 5) pressure-dependent conductivity caused by the smoluchowski effect [106].

Few mathematical models are available for predicting the effective heat transfer in a packed bed. The first one is the cell model. It consists of two contacting spheres. It is assumed that heat conduction occurs in two parallel paths. One is the conduction through solid and fluid phases, and the other one is the conduction through the fluid-filled voids. This model was used by Kunii et al. [109]. This model was further developed by Schlunder et al. [110] by considering cylindrical cells. This cylindrical cell contains two contacting particles with deformable shapes. Both two models are based on a representative geometric unit. Due to empirical equations, representative geometric unit needs a large number of parameters determined by experiments. Another drawback is if the thermal conductivity ratio between the solid and fluid is very high (greater than 1000) these models underestimate the effective thermal conductivity [111]. Argento et al. [112] solved this problem by applying the packing structure concept in the model to predict the effective thermal conductivity. Only the heat transfer between the particle contact area was considered, and the effect of liquid was ignored. As a result, this model applies to the compressed packed beds that are filled with particles with large deformation [111].

By using CFD codes, it is possible to solve mass, flow, and energy balances in complicated geometries like the packed bed. In a large number of control volumes, the differential forms of these control volumes are applied. The computational domain is made of the total number of these control volumes. After implementing the boundary conditions, the flow and energy balanced are solved by numerical iterations. The accuracy of the solution largely depends on the number of control volume and the size of the cells [101]. For a non-isothermal bed, the temperature profile is developed along the axial coordinate of the bed, and the temperature field is not periodic. The momentum and energy balances must be decoupled to use the periodic flow boundary conditions. Flow parameters, such as viscosity and density, are assumed independent of temperature for this type of boundary condition [101]. Yaghoub et al. [118] used 2D CFD techniques to investigate hydrodynamic and heat transfer phenomena in a gas–solid fluidized bed reactor by taking few assumptions as 1. Gas-phase is ideal and incompressible. 2. Heat transfer between different solid phases is negligible. 3. Solid particles release constant heat flux. They commented that the Eulerian-Eulerian model is suitable for modeling the industrial fluidized bed. Particles with smaller diameters have a lower volume fraction at the bottom of the bed and a higher volume fraction at the top of the bed [118]. Ahmadi et al. [121] used a Three-dimensional CFD model to study hydrodynamic and heat transfer characteristics of a randomly packed bed with cylindrical particles. They concluded that CFD could be used to confidently discuss the flow and heat transfer behavior[121].

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Tal et al. [114] CFD-DEM models to predict momentum and heat transfer between fluid and solid particles. They examined the influence of particle roughness on heat transfer. Discrete Element Method (DEM) uses Newton's second law to solve the motion of discrete particles, and the fluid flow is solved by locally averaged Navier-Stokes equations known as computational fluid dynamics (CFD). Heat transfer mechanisms like particle-fluid convection, radiation, and direct conduction were examined. They commented that heat transfer predictions are significantly influenced by the average surface roughness slopes, and particles with high roughness cannot be predicted with DEM only. Romkes et al. [113] used CFD modeling to predict particle to fluid heat transfer of a single free sphere for a composite structured packing (CSP). In their modeling, the temperature of the surface of the particle was set to surface temperature, and the fluid at the boundary of the domain was set to a lower bulk temperature. They commented that CFD could predict heat and mass transfer characteristics with an average error of 15%. Michiel et al. [101] performed 3D Computational fluid dynamics (CFD) analysis of simultaneous flow and heat transfer through realistic spherical packings in the wall region of a fixed-bed reactor and concluded that there is no statistical relationship between the local flow features and the wall heat flux and larger-scale flow structures in the bed is related to local patterns of wall heat flux.

From the literature, it can be concluded that the CFD technique could be used to study the heat transfer effect in a packed bed. But, for carbon capture, there is a significant knowledge gap in the area of heat transfer, like the change of carbon capture with the application of heat, change in concentration, and effect of gas and liquid temperature on carbon capture. This work fills this gap.

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6.2 Governing Equations and model development

Enthalpy conservation equation for gas is given by

$$\begin{aligned} \frac{\partial(\alpha_g \rho_g H_g)}{\partial t} + \nabla \cdot (\alpha_g \rho_g \vec{V}_g H_g) = & -\nabla \cdot \alpha_g \cdot q_g + h_{ks}(T_f - T_g) + \\ & + \bar{\tau}_g \cdot \nabla \cdot \vec{V}_g + \alpha_g \left[\frac{\partial}{\partial t} p + \vec{V}_g \nabla p \right] \end{aligned} \quad (6.1)$$

Enthalpy conservation equation for liquid is given by

$$\begin{aligned} \frac{\partial(\alpha_l \rho_l H_l)}{\partial t} + \nabla \cdot (\alpha_l \rho_l \vec{V}_l H_l) = & -\nabla \cdot \alpha_l \cdot q_l + h_{ks}(T_f - T_l) + \\ & + \bar{\tau}_l \cdot \nabla \cdot \vec{V}_l + \alpha_l \left[\frac{\partial}{\partial t} p + \vec{V}_l \nabla p \right] \end{aligned} \quad (6.2)$$

with

$$H_l = \int_0^T C_{pl} \cdot dT, \quad (6.3)$$

$$H_g = \int_0^T C_{pg} \cdot dT, \quad (6.4)$$

$$q_g = -\lambda_g \nabla T, \quad (6.5)$$

$$q_l = -\lambda_l \nabla T. \quad (6.6)$$

The model was the same as before with the liquid dispersion and chemical reactions. Only heat transfer effects were included.

Where T_f is the interphase temperature, T_l is the liquid temperature, T_g is the gas temperature, C_{pg} is the specific heat capacity for the gas phase and C_{pl} is the specific heat capacity for the liquid phase and the value of C_{pg} was taken 1.006 ($KJ.Kg^{-1}.K^{-1}$) from Pianko-Oprych [103] and C_{pl} was taken 0.16772 ($KJ.Kg^{-1}.K^{-1}$) from Shokouhi et al. [161], H_l is the enthalpy of liquid, H_g is the enthalpy of gas, h_{ks} is the heat transfer coefficient and its value was taken as 16.27 ($W.m^{-2}.K^{-1}$) from Pianko-Oprych [103]), λ_l is the thermal conductivity for liquid phase with value 0.239 ($W.m^{-1}.K^{-1}$) from Shokouhi et al. [161]), λ_g is the thermal conductivity for gas phase with a value 0.0242 ($W.m^{-1}.K^{-1}$) from Pianko-Oprych [103].

6.3 Results and Discussions

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Validation of the model was done in this section by comparing the simulation results with experimental results for different heights inside the packed bed column. In this section, the presence of heat in the carbon removal process was studied in detail, and an optimum temperature range was found to maximize the carbon removal.

6.3.1 Validation of the numerical model

Figure 6.1 presents a quantitative comparison of simulated CO_2 concentration in the gas phase along the column with the experiments of (Aroonwilas et al.[78]), in which an acceptable agreement was achieved. The gas and liquid phases at the inlet consisted of 15% CO_2 in CH_4 , and 30 wt% MEA in water, respectively, and Mellapak 500X ($a_s=500\text{ m}^2.\text{m}^{-3}$) was used as structured packing. The inlet liquid velocity ($V_{in,l}$) was $1.77\text{ m}.\text{sec}^{-1}$, and the inlet gas velocity ($V_{in,g}$) was $0.097\text{ m}.\text{sec}^{-1}$. The operating temperature was 304 K, and pressure was kept to 1 atmospheric pressure to comply with the experimental result; others had also done the same(Pham et al. [13]). The CO_2 concentration in the numerical results was calculated by azimuthal averaging in different heights of the column.

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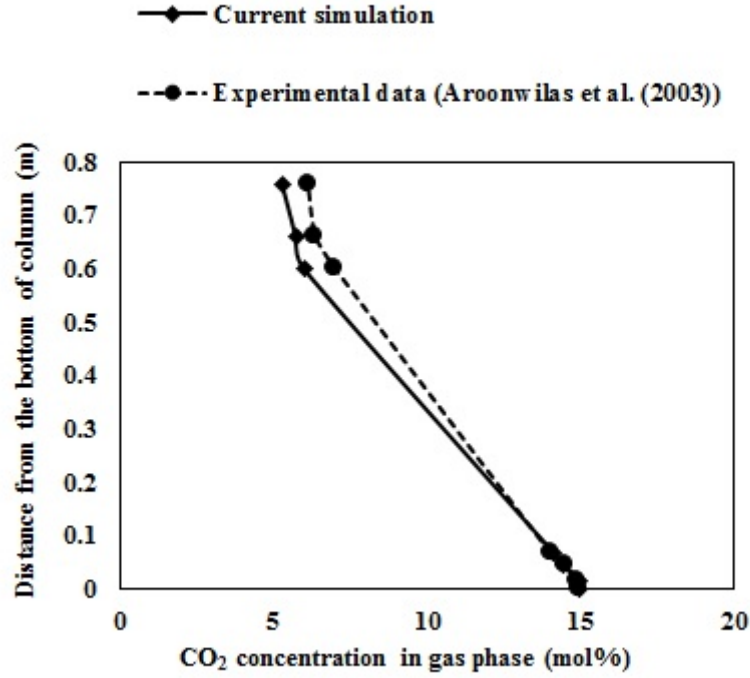


Figure 6.1: Validation of the CFD model with the experiment of (Aroonwilas et al., 2003): CO_2 concentration in the gas phase along the column. $V_{in, l} = 1.77 \text{ m}\cdot\text{sec}^{-1}$, $V_{in, g} = 0.097 \text{ m}\cdot\text{sec}^{-1}$, and $D_{in} = 24 \text{ mm}$.

The following sections discuss the numerical results obtained in this work. In all cases, $V_{in, l} = 1.19 \text{ m}\cdot\text{sec}^{-1}$, $V_{in, g} = 1.05 \text{ m}\cdot\text{sec}^{-1}$, and Mellapak 250X was used as structured packing column with operating isothermal temperature of 304 K. Moreover, the gas phase was considered 100% CO_2 . The value of R^2 is calculated as 0.9687

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6.3.2 Comparison between heat transfer and without heat transfer modeling

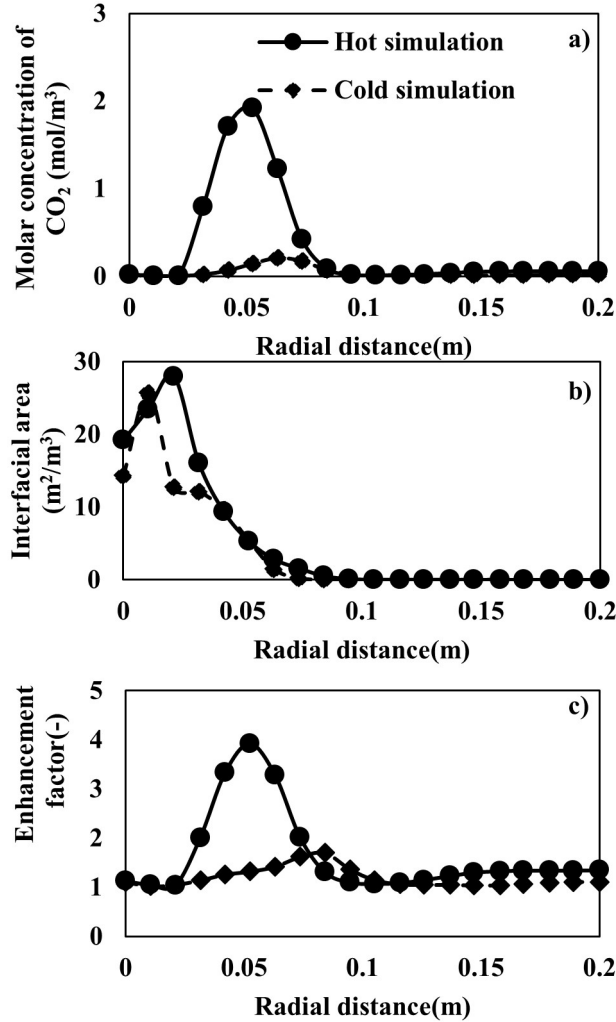


Figure 6.2: Comparison between hot and cold modeling on carbon capture for $z=0.1$ m for single inlet with $V_{in,l} = 1.2 \text{ m}\cdot\text{sec}^{-1}$, $V_{in,g} = 1.05 \text{ m}\cdot\text{sec}^{-1}$.

When we increase the temperature of any system, it increases the average kinetic energy of each of the components. As the kinetic energy increases, it causes the components to move faster and collide with each other more frequently in a given amount of time. This results in the components having greater energy or force on each collision. The increase in activity and energy increases the reaction rate. From figure 6.2, it can be concluded that temperature plays a vital role in increasing interfacial area and enhancement factor, and as a result, more carbon is increased compared to cold modeling. The absorption

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process between gas and liquid is determined by two factors firstly by the mass transfer between the phases and secondly by chemical kinetics. Chemical kinetics depends on the dissolved reactive absorbent in the solution, and on the other hand, mass transfer depends on the dissolved reactive absorbent and the type of equipment, diffusivities, fluid mixing, and geometries. Hence, faster mass transfer and faster kinetics are needed for better performance [69]. Adding heat in the process can achieve this.

For low temperature (< 450 K), the heat transfer effect in structured packed bed column occurs in three mechanisms, firstly conduction through the stagnant fluid between two points or non-contacted particles, secondly, conduction through the stagnant fluid between two areas contacted area and finally conduction through the contact area between two areas contacted particles (Yang et al. [99]). In liquid fluid flow through the packed bed column, kinematic viscosity plays a dominant role in determining film thickness. Film resistance is directly proportional to the film thickness, and film conductivity is inversely proportional to kinematic viscosity. With the effect of temperature, the viscosity of MEA is lowered significantly, and a thinner liquid film is formed. As the liquid film controls the absorption process, the thinner liquid film improves mass transfer and finally increases in chemical reaction rate (Joel et al.[162]).

6.3.3 Effect of MEA concentration on CO₂ removal

Figure 6.3 (a) shows the averaged molar concentration of CO₂ in the liquid phase along the column with the single liquid inlet as a function of MEA concentration. It can be seen that an increase in the MEA concentration from 30 wt% to 50 wt% led to higher CO₂ uptake. Moreover, as expected, the maximum CO₂ uptake occurred in the bottom half of the reactor and slightly away from the gas inlet, $16.7 < Z/D_{in} < 29.2$. This finding is consistent with the distribution of enhancement factor along with the column figure 6.3 (b), in which a larger E was calculated for 50 wt% MEA case within the region with higher CO₂ uptake.

The radial variation of enhancement factor at different height of column for different amine concentration is shown in figure 6.4. The enhancement factor at the top of the column is higher compared to the bottom of the column. This is due to more amount of MEA at the top. So, it will be better to improve the enhancement factor in chemical reaction than changing the area of the packed bed in the presence of heat.

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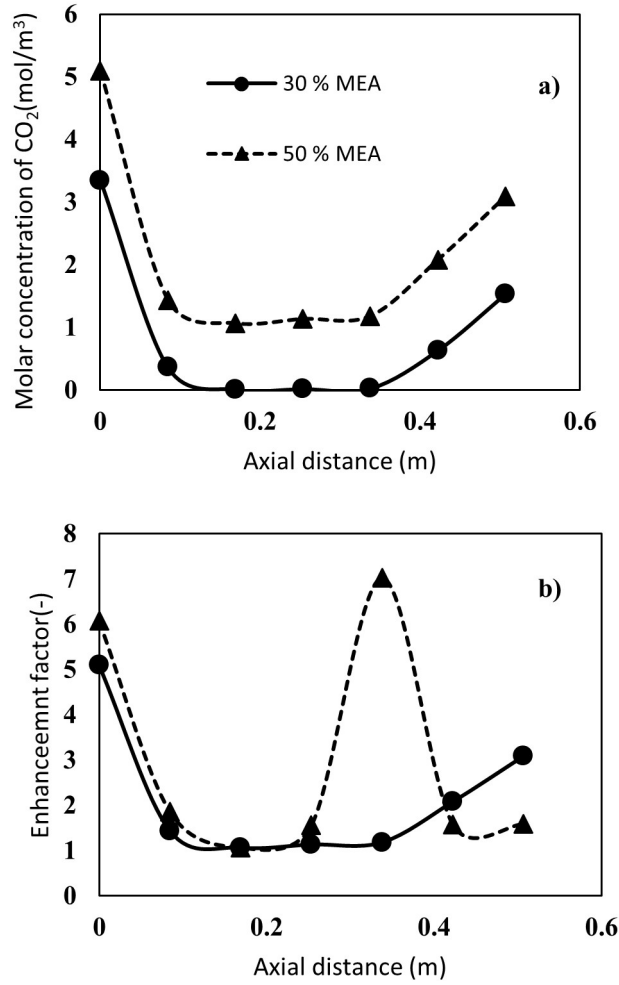


Figure 6.3: : (a) Averaged molar concentration in liquid phase of CO_2 (b) Changes of enhancement factor along the column heights for single liquid inlet with $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$.

The diffusion rate through the gas film is proportional to the difference of solute concentrations inside and outside of the gas film. The thickness of the liquid film is dependent on the liquid concentration at the gas-liquid interface and the concentration of the liquid on another side of the film. As the film surface is very thin, the amount of liquid inside the film surface is very small and can be neglected compared to the diffusion through the film surface. As the solute which passes through one film must also pass through another film (in this case, gas and liquid), two diffusional resistance can be considered in series [81]. Due to the application of heat, this diffusional resistance is lowered, which gives rise to a higher diffusion rate and eventually more CO_2 removal.

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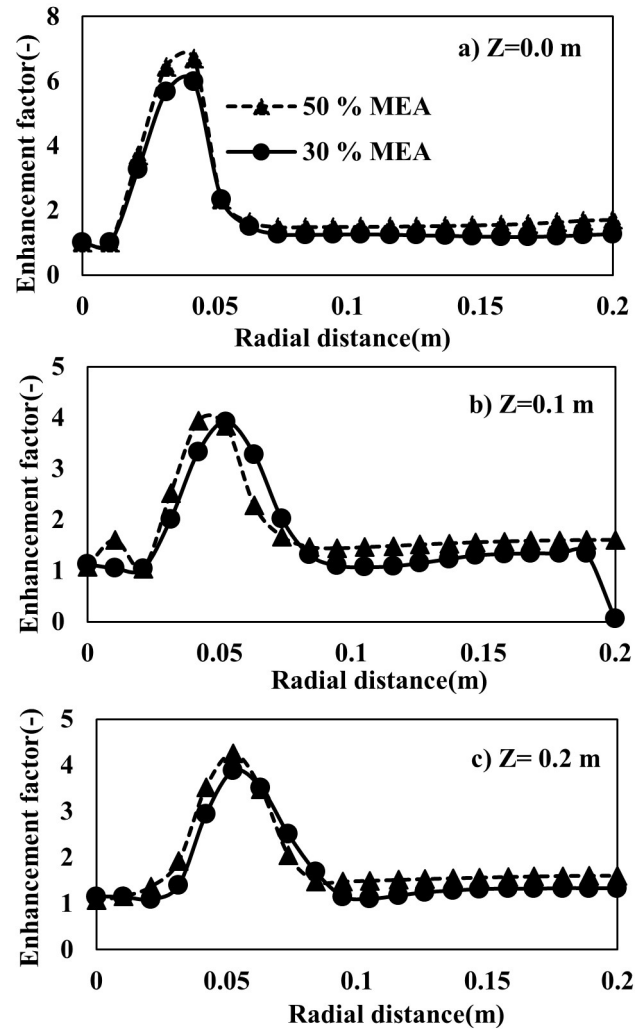


Figure 6.4: Changes of Enhancement factor in CO₂ removal with 100 % CO₂ in the gas phase with $V_{in,l} = 1.2 \text{ m} \cdot \text{sec}^{-1}$, $V_{in,g} = 1.05 \text{ m} \cdot \text{sec}^{-1}$ for various column heights with single inlet.

Figure 6.5 (a) shows the total amount of dissolved CO₂ concentration in the liquid phase with MEA concentration. It is shown that the dissolved CO₂ increases with increasing MEA concentration. This is due to an enhanced chemical reaction when MEA concentration increased. Figure 6.5 (b) shows the change in all the species that are present in the absorption process. It is found that the concentration of hydronium ion goes down if the concentration of MEA is further increased from 30% even the heat is present in the system.

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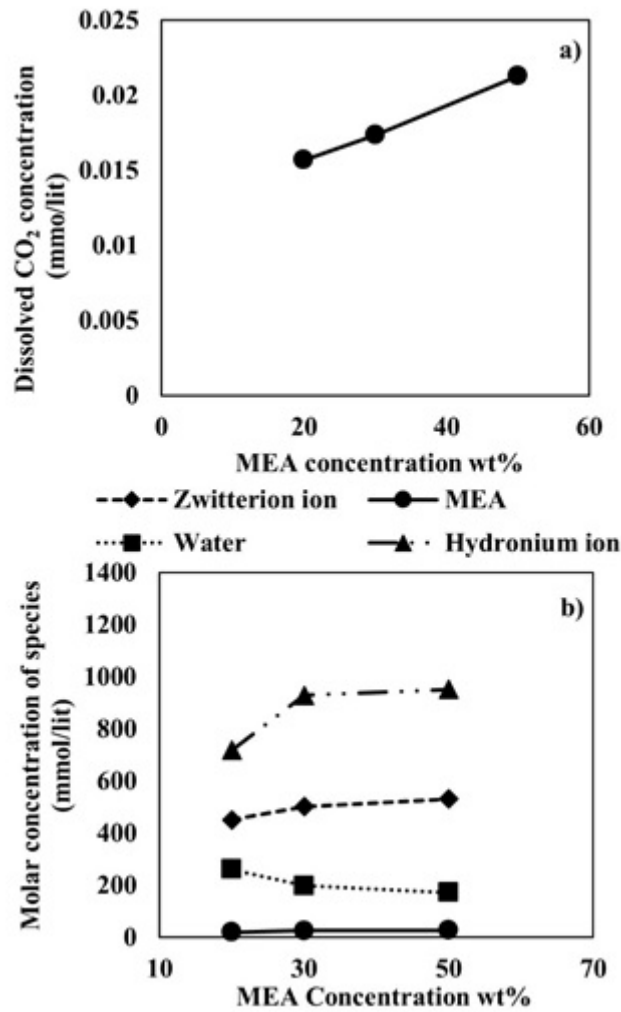


Figure 6.5: Changes of averaged concentration of (a) CO_2 species in liquid phase (b) other species with MEA solution with $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$.

6.3.4 Effect of multiple liquid inlets on the chemical absorption

Simulations were performed to study the effect of multiple liquid inlets on the chemical absorption in the presence of heat.

6. Multiphase Heat Transfer

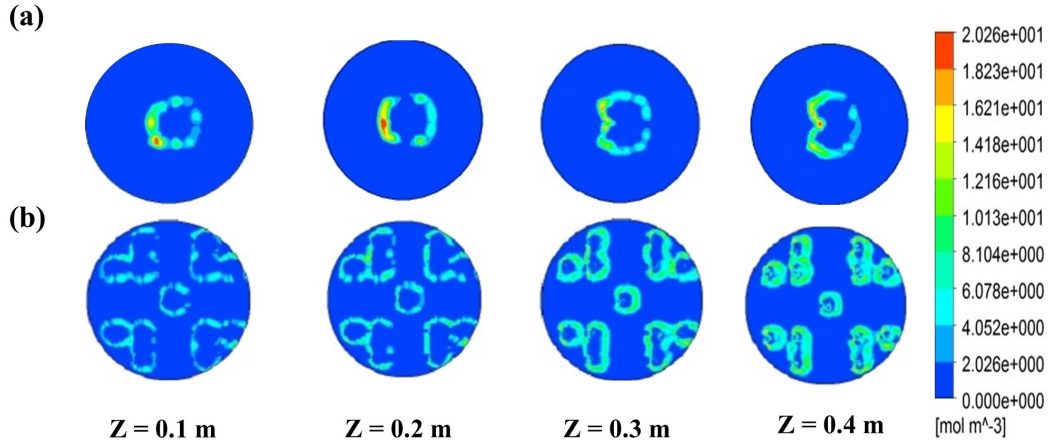


Figure 6.6: Contour plot of liquid phase CO_2 concentration in liquid phase at 30 % MEA in liquid phase with $V_{in,l} = 1.2 \text{ m.sec}^{-1}$, $V_{in,g} = 1.05 \text{ m.sec}^{-1}$ for a) single inlet b) multi-inlets.

Figure 6.6 shows the contours plots of liquid phase CO_2 concentration at different heights of column for both single liquid inlet and multi inlets. The liquid mass flow rate was kept the same for both single and multi-inlet. It can be seen from figure 6.6 that more concentration of dissolved CO_2 is observed for single inlet whereas, in multi inlets, more dispersion of liquid CO_2 with the lower concentration is observed. The reason is, for a single inlet, the concentration of MEA is highest at the liquid inlet. A comparison of the radial variation of the concentration of dissolved CO_2 between single and multi-inlet is shown in figure 6.7. There was a difference in carbon removal rate in both single and multi-inlets for the same gas and liquid velocities. A more dissolved concentration of CO_2 is found for multi-inlets in comparison with the single inlet. For multi inlets and 30 wt.% MEA, the total CO_2 removal was $84.93 \text{ kmol.m}^{-3}$. Carbon capture can be increased significantly with the increase of more liquid inlets. The reason is for multi-inlets, although it has several source points for liquid inlet, due to higher diffusion, more liquid travels inside the packed bed, and as a result, more mass transfer and chemical reaction take place. Eventually, more CO_2 is removed.

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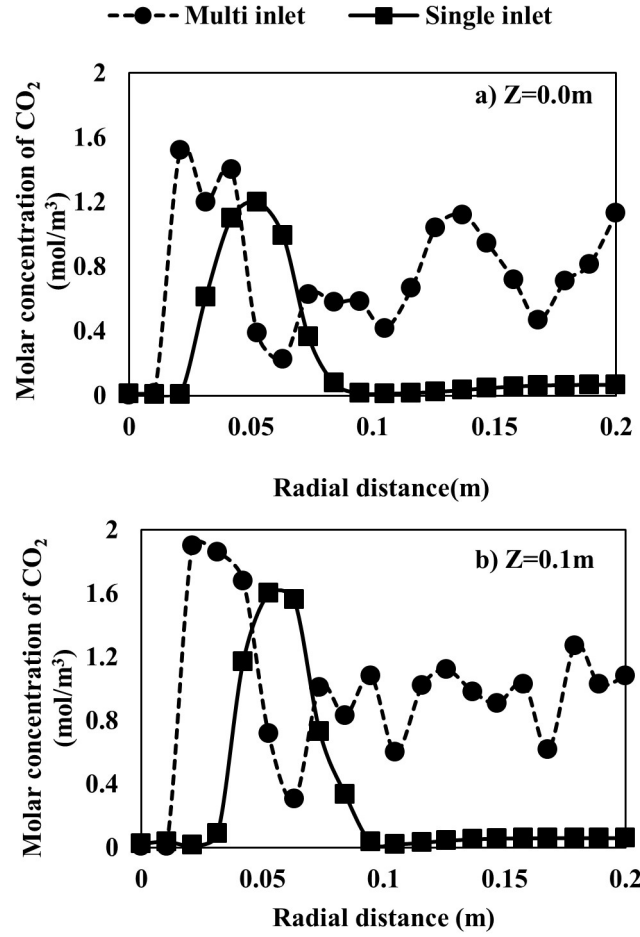


Figure 6.7: Effect of liquid inlets on molar concentration in liquid phase of CO_2 with 100 % CO_2 in the gas phase and 30 % MEA in liquid phase for $V_{in,l} = 0.09 \text{ m} \cdot \text{sec}^{-1}$ and $V_{in,g} = 1.05 \text{ m} \cdot \text{sec}^{-1}$.

6.3.5 Effect of liquid loading:

Liquid loading was increased from $28 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $80 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ by keeping the gas loading constant. Figure 6.8 shows the effect of liquid loading on the chemical absorption of CO_2 for the case of a single liquid inlet. It was found from figure 6.8 (a) that, in the presence of heat, if the liquid loading is increased molar concentration of CO_2 is increased as well. The reason is higher liquid loading increases the interfacial area (figure 6.8 (b)) and enhancement factor (figure 6.8 (c)). The averaged quantities of the molar concentration of CO_2 , interfacial area, and enhancement factor are calculated in the reactor, which is in table 6.1. It can be seen that averaged values of CO_2 concentration, interfa-

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cial area ,and enhancement increases with the liquid load. This is due to the fact that the mass transfer rate increases by increasing the available interfacial area when liquid load increases in the presence of heat. This trend agrees with the literature (Sebastia-Saez et al. [146]). The increasing absorption rate leads to an increase in the reaction rate, which results in a higher enhancement factor. With the increased liquid loading, liquid velocity is also increased, and as a result, thinner liquid films are created. This leads to an enhancement in the gas-liquid interfacial area and a reduction in the mass transfer resistance (Zhao et al. [75]).

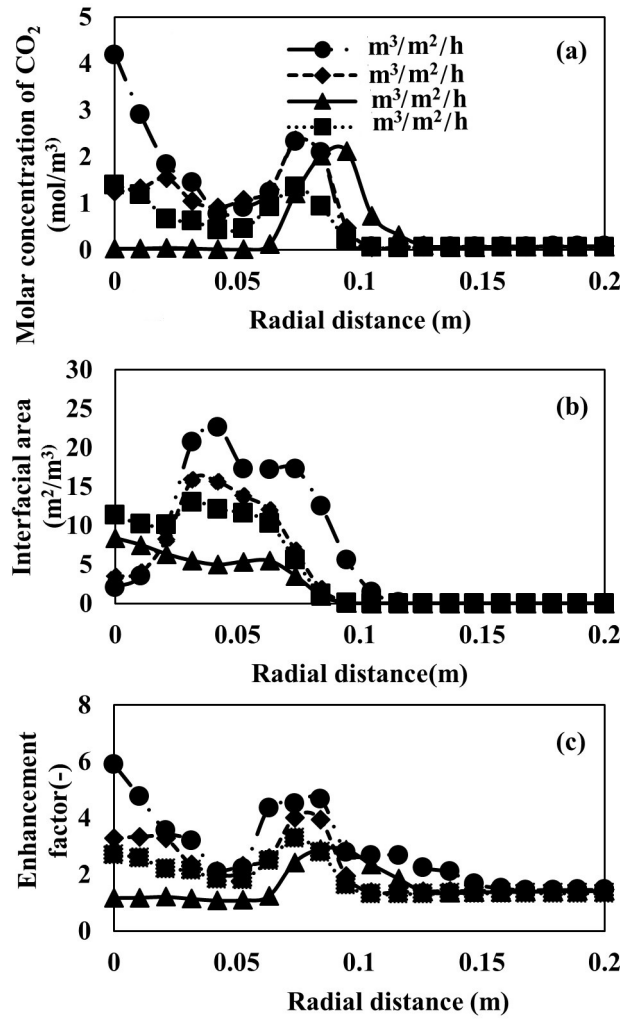


Figure 6.8: Effect of liquid loading on the radial variation of (a) dissolved CO_2 concentration in the liquid phase (b) interfacial area (c) enhancement factor at $Z=0.4$ m.

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Liquid loading	CO_2 concentration ($mol.m^{-3}$)	Interfacial area ($m^2.m^{-3}$)	Enhancement factor
28	0.4827	9.47	1.42
36	0.5149	12.60	1.88
56	0.8235	14.56	2.17
80	1.2426	18.15	2.73

Table 6.1: CO_2 concentration in the liquid phase for different liquid loading

6.3.6 Effect of higher temperature:

Aqueous MEA used in CO_2 removal goes through oxidative and thermal degradation, and this finding was also established experimentally [163]. As a result, several volatile and non-volatile organic compounds like nitramine and nitrosamine compounds are formed and can be released to the environment both in the vapor phase and droplets and causing adverse environmental impact [163]. Moreover, solvent loss, corrosion of plant equipment, hydrodynamic instability occurs due to oxidative and thermal degradation. Finally, this contributes to a higher operational cost. Hence, it is very important to understand both oxidative and thermal degradation. Oxidative degradation happens due to the presence of oxygen dissolved in the solvent. In this work, oxidative degradation is not considered, only thermal degradation was taken into account.

Experimentally it is found that thermal degradation happens at 100 °C or a higher temperatures [163]. Figure 6.9 is for the very high liquid temperature. It is found that if the liquid temperature is very high (100 °C), carbon capture drops quite significantly. From this temperature, if it is increased more, the CO_2 removal drops more. The developed model can predict this.

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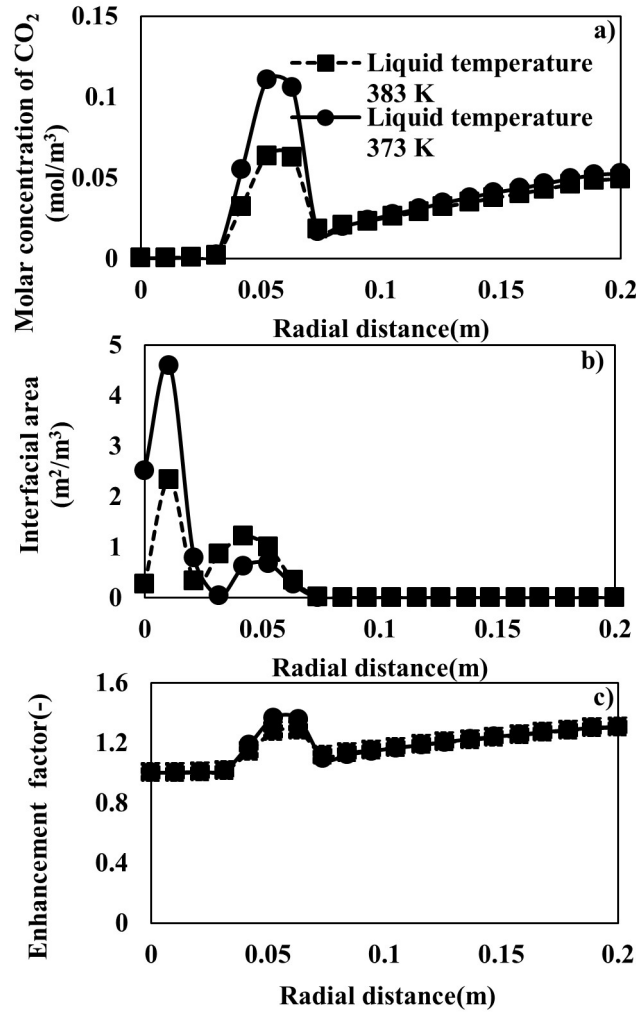


Figure 6.9: Effect of temperature with higher temperature on MEA degradation for $z=0.1$ m for single inlet with $V_{in,l} = 1.2 \text{ m}\cdot\text{sec}^{-1}$, $V_{in,g} = 1.05 \text{ m}\cdot\text{sec}^{-1}$.

The model explains the thermal degradation in a much better way. From figure 6.9 it is seen that with the increased temperature, both interfacial area and enhancement factor are decreased, and as a result, less carbon is removed.

Structured packed bed column made with material with a smaller void fraction experience faster liquid-phase mass-transfer whereas gas phase mass transfer is faster in material with a higher void fraction. The increasing mass transfer performance with the liquid temperature is influenced by the greater mass transfer coefficient. Increasing the temperature from 20-35 °C almost doubles the mass transfer coefficient [164] but for higher temperatures, the liquid film thickness will decrease significantly, and there will not be sufficient MEA at the gas-liquid interface to keep up the chemical reaction and as a result, the system becomes equilibrium-controlled rather than kinetically controlled.

6.4 Summary and Conclusions

In this work, a rate-based CFD chemical reaction model is developed for carbon removal by using a structured packed bed column. The model has taken account of the gas and liquid dispersion inside the packed bed, mass transfer and heat transfer between both gas and liquid, and all the chemical reactions between gas and liquid. The model is then validated with experimental results and was found a very good arrangement. Although all the chemical reactions are very fast and instantaneous, the model is quite capable of predicting all the by-products of the reactions. It was found that with a higher concentration of MEA, more CO_2 will be removed. Again, CO_2 removal can be increased by increasing the pressure. The model is capable of predicting the mass transfer coefficient, the effective area between gas and liquid, and as well as the enhancement factor. The study also showed that CO_2 removal could be increased significantly by using multi inlets, and enhancement factor plays a vital part in removal efficiency. Temperature plays a vital role in removing CO_2 . It was also found that with the increase of temperature, both the enhancement factor and interfacial area increase, and finally, more CO_2 is removed. As higher temperatures cause thermal degradation, for maximum CO_2 removal, the operating temperature should be kept between 30-50 °C.

Chapter 7

Summary and Conclusions

7.1 Summary and Conclusions of the Research Work

Research work in this thesis starts from chapter 4 to chapter 6. A gross summary is discussed below.

Chapter 4 is about hydrodynamics modeling. In this problem, hydrodynamics can be modeled based on dispersion forces, tortuosities, and spread factor. As there is no literature available for tortuosities modeling, hydrodynamics modeling was done based on dispersion forces and spread factor. It was found that hydrodynamics modeling based on spread factor does not provide good results. Hence, it is better to stick to dispersion forces modeling. The hydrodynamic model was validated, and it was found a very good agreement with the experimental results. [Drag force is implemented in the model based on a very low volume fraction of gas, and it improved the result significantly.](#)

Chapter 5 is based on chemical reactions and mass transfer modeling. In chemical reaction modeling, all the reactions were taken into account along with hydrodynamics. So far, it was only available in a reduced-order model. The chemical reactions model was also validated, and it was also found in a good arrangement with the experimental results. In this chapter effect of MEA concentration, the number of inlets was studied. The chemical reaction model can also predict the enhancement factor and the gas-liquid interface area. It was not available before. Due to the present work, it has become much easier to predict the role of all the reaction products in carbon removal.

Chapter 6 is about to include a heat transfer effect in the model. In this chapter, a detailed study of the influence of temperature in carbon capture was studied for different MEA concentrations and liquid temperature. It was found that if the temperature is present in the system, CO_2 removal improves significantly.

7. Summary and Conclusions

7.2 Contribution to the Knowledge

The contribution to the knowledge in the present Ph.D. thesis has been summarized as

1. The drag force **between gas and liquid** is modeled in a much better way by using the concept of very low gas volume fraction (**secondary phase**) for the porous media, and as a result, validation of liquid saturation in hydrodynamics provided very good results. This made a significant improvement in the model.
2. 3D validation of liquid saturation in a packed bed is done. At present, it is available in 2D form. As the real fluid flow is 3D, this validation was needed to keep confidence in the model since this model will be used in chemical reactions later on.
3. Apart from the dispersion forces, hydrodynamics studies were done by using spread tensor. In the present model, the originally anisotropic spreading tensor has been replaced by an isotropic scalar factor which is a model simplification, because the elements of the three-dimensional spreading tensor should be determined relying on experimental data. However, experimental observations also indicate that the magnitude of [eq. \(4.21\)](#) tends to equal to zero far from the inlet, and the model presented in this work underlines these experimental and modeling observations. **Due to this work, it is now possible to conclude that hydrodynamics modeling should be done based on mechanical dispersion forces rather than spread tensor.**
4. The effects of inlets into the packed bed are clear to understand now. It was shown that if the number of liquid inlets is increased, CO_2 removal is also increased. Based on this work, it is now possible to determine how many liquid inlets to be made depending on the gas loading.
5. All the chemical reactions were taken into account along with hydrodynamics. In CO_2 removal, several instantaneous chemical reactions occur. No model was available before by taking considerations of all these chemical reactions. Due to present work, it has made now it possible to see the effects of all the chemical reaction products in carbon capture.
6. The effects of the solvent concentration are clear now. If the MEA concentration is increased CO_2 removal is increased as well due to collision between reactant molecules become higher, which triggers the higher reaction. Depending on the requirements, it is now possible to select the right solvent with the right concentration.

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7. Effects of the gas-liquid interface area are understood more easily due to this work. Mass transfer between gas and liquid is largely determined by the size of the gas-liquid interface area. If the area is larger, more mass transfer will take place, and for the smaller area, it will be small as well. For a large scale, the calculation of this area was not available for different MEA concentration(20%, 30%, 50%). Present work provides this.
8. Effects of chemical enhancement in carbon capture is clear now. For a higher Enhancement factor, the chemical reaction will be much faster and as a result more carbon will be removed. For large scale, the calculation of this enhancement factor was not available for different MEA concentrations (20%, 30%, 50%). Present work provides this.
9. The effect of pressure is clear now in carbon capture. It was found that if the pressure is increased, carbon capture also increases due to the increases in gas solubility. Based on the present work, it will be possible now to select the right pressure for maximum carbon removal.
10. The effect of temperature on MEA concentration is also understood in carbon capture. It is now possible to select the right solvent [for the right operating temperature](#).
11. [Effect of temperature on carbon removal is clearly understood now. It was found that carbon capture can be increased by increasing liquid temperature.](#)
12. [Effect of thermal degradation in carbon capture is also clear now. It was found that if the liquid side temperature is increased, too much thermal degradation of MEA occurs, and as a result, carbon capture is reduced significantly.](#)

7. Summary and Conclusions

7.3 Future Work

1. To use other solvents like aqueous ammonia. This will allow comparing the performance of both MEA and Ammonia in carbon removal.
2. Use a rotating packed bed for CO_2 removal modeling. With a rotating bed, the mass transfer will be increased, and as a result, carbon removal will also be increased. With this work, it will be possible to compare the performance of a fixed bed and a rotating bed in carbon capture.
3. Optimize the packing bed by combining small scale, medium, and large scale. With this work, the size of the packing bed can be optimized to capture carbon.
4. Interface the CFD model with a process model like Aspen to get the complete picture of the power plant.

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