#### Ryerson University Digital Commons @ Ryerson

Theses and dissertations

1-1-2007

# Computational fluid dynamics (CFD) analysis of mixing in styrene polymerization

Haresh Patel Ryerson University

Follow this and additional works at: http://digitalcommons.ryerson.ca/dissertations Part of the <u>Chemical Engineering Commons</u>

#### **Recommended** Citation

Patel, Haresh, "Computational fluid dynamics (CFD) analysis of mixing in styrene polymerization" (2007). *Theses and dissertations*. Paper 143.

This Thesis is brought to you for free and open access by Digital Commons @ Ryerson. It has been accepted for inclusion in Theses and dissertations by an authorized administrator of Digital Commons @ Ryerson. For more information, please contact bcameron@ryerson.ca.

## COMPUTATIONAL FLUID DYNAMICS (CFD) ANALYSIS OF MIXING IN STYRENE POLYMERIZATION

by

Haresh Patel

Bachelor of Engineering, National Institutes of India, Rourkela, India, 1996

A thesis

presented to Ryerson University

in partial fulfillment of the

requirements for the degree of

Master of Applied Science

in the Program of

**Chemical Engineering** 

Toronto, Ontario, Canada, 2007

©(Haresh Patel) 2007

PROPERTY OF RYERSON UNIVERSITY LIBRARY

## **Author's Declaration**

I hereby declare that I am the sole author of this thesis.

I authorize Ryerson University to lend this thesis to other institutions or individuals for the purpose of scholarly research.

Haresh Patel

I further authorize Ryerson University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

Haresh Patel

## Computational Fluid Dynamics (CFD) Analysis of Mixing in Styrene Polymerization

Haresh Patel, M.A.Sc., Chemical Engineering, Ryerson University, Toronto, 2007

#### Abstract

A styrene polymerization in a lab-scale CSTR equipped with a pitched blade turbine impeller was simulated using the computational fluid dynamics (CFD) approach. The impeller motion was integrated in the geometry using the multiple reference frame (MRF) technique. The presence of non-linear source term and the highly coupled nature of transport equations of the polymerization, made the convergence difficult to achieve. The effects of the impeller speed, the input-output locations and the residence time on the polymerization in the CSTR were investigated. The CFD simulation shows that good mixing remained limited to the impeller region. Regions far from the impeller remained unmixed due to high viscosity of the polymer mass. The path lines of the particles, released at the inlet, were also generated to analyze the reaction progress as the chemicals travel throughout the reactor. The monomer conversion computed using the CFD model was compared to data reported in the literature. Conversion predicted using the CFD model is in good agreement with that obtained from the CSTR model at low residence time. However, the CFD predicted conversions were higher than those calculated from the CSTR model, at high residence time. It was also found that the input-output locations had significant effect on the conversion and the homogeneity in the CSTR.

## Acknowledgements

I would like to convey my sincere sense of gratefulness to my supervisors, Dr. Ramdhane Dhib and Dr. Farhad Ein-Mozaffari, for their incredible guidance, encouragement, support and for their kindness at all time. This research would not be possible without their help.

I am grateful and thankful to Dr. Mehrab Mehrvar for giving me the opportunity to learn the fundamentals necessary for this research. I am also thankful to Dr. Philip Chan for their timely help.

I would like to extend a special thanks to my dear wife, children and parents whose support and encouragement enabled me to complete this research.

Finally, I also recognize that this research would not have been completed without the financial support of NSERC, Ontario Graduate Scholarship, HPCVL scholarship, Ryerson Graduate Scholarship, the chemical engineering department (Teaching Assistantships), and stipends from my supervisors and express my gratitude to them.

## **Table of Content**

.

Chapter 1 : In	troduction	1
Chapter 2 : Li	iterature Review	6
2.1 Mix	ing in polymerization	6
2.1.1	Mathematical approach	7
2.1.2	Experimental approach	9
2.1.3	CFD approach	14
2.2 Obje	ective	20
2.3 Mot	ivation	20
Chapter 3 : C	FD Theory	22
3.1 Com	nputational domain	
3.2 Che	mical and physical phenomena	
3.3 Tran	nsport equations	
3.3.1	Equations in the stationary reference frame	
3.3.1.1	Continuity	
3.3.1.2	2 Momentum	
3.3.1.3	Energy	
3.3.1.4	Species	
3.3.2	Equations in the rotating reference frame	
3.4 Trar	nsport properties	
3.5 Bou	ndary conditions	29
3.5.1	Inlet boundary	30
3.5.2	Outlet boundary	31
3.5.3	Wall boundary	31
3.5.4	Symmetry boundary	32
3.6 Nun	nerical solution technique	33
3.6.1	The Finite Volume Method (FVM)	34
3.7 Disc	cretization Schemes	35
3.7.1	Upwind schemes	36

3.7.1.1	First order upwind scheme	. 36
3.7.1.2	Power law Scheme	. 36
3.7.1.3	Second order upwind scheme	. 37
3.7.1.4	QUICK scheme	. 37
3.7.2	Pressure interpolation	. 37
3.8 Pres	sure-Velocity Coupling	. 39
3.8.1	The SIMPLE algorithm	. 39
3.8.2	The SIMPLEC	. 41
3.9 Solv	ing the algebraic equations	. 42
3.9.1	Solver	. 42
3.9.1.1	Segregated solver	. 42
3.9.1.2	Coupled solver	. 44
3.9.2	Iterative method	. 45
3.10 Che	cking the convergence	. 45
3.11 Res	ults analysis and Validation	. 47
Chapter 4 : C	FD Model and Simulation	. 48
4.1 Read	ctor Geometry	. 48
4.2 Form	nulation of reactive source term	. 53
4.2.1	Thermal polymerization source term	. 55
4.2.2	BPO initiated polymerization	. 56
4.3 Esti	mation of physical properties	. 58
4.4 Sim	ulation Method	. 60
Chapter 5 : R	esults and Discussion	. 64
5.1 Grid	I Independency Check	. 64
5.2 Con	vergence Criteria	. 69
5.3 Con	putational Time	. 74
5.4 Rea	ctor Simulations	. 76
5.4.1	Thermal polymerization	. 76
5.4.1.1	The effect of the impeller speed	77
5.4.1.2	Reactive flow and non reactive flow	. 87

5.4.1.3	Conversion analysis and validation
5.4.1.4	Effect of input/output location
5.4.2 E	PO initiated polymerization 105
5.4.2.1	Effect of the impeller speed 107
5.4.2.2	Effect of the residence time 119
Chapter 6 : Cor	clusion and Future Recommendations124
6.1 Concl	usion 124
6.2 Future	e Recommendations 126
Nomenclature	
References	
Appendices	
Appendix A:	UDF for the thermal polymerization
Appendix B: UDF for the BPO initiated polymerization14	

.

## **List of Tables**

Table 4.1: Reactor specification	49
Table 4.2: Process parameters for styrene polymerization simulations	53
Table 4.3: Values of kinetic parameters	57
Table 4.4: Constant physical properties	60

## **List of Figures**

Figure 3.1:	Segregated solver loop	3
Figure 3.2:	Coupled solver loop	4
Figure 4.1:	Reactor grid for the side inlet (near liquid level) and outlet 49	9
Figure 4.2:	Reactor grid for the bottom inlet	1
Figure 5.1:	Axial-velocities below impeller on GRID1 and GRID 2	7
Figure 5.2:	Plot of the residual versus the iterations	9
Figure 5.3:	Sum of velocity magnitudes on the top liquid surface versus iteration	2
Figure 5.4:	Convergence history of the styrene transport equation	3
Figure 5.5:	Contour for styrene mass fraction at 100rpm impeller speed and 144min	
	residence time	9
Figure 5.6:	Path lines of the particles released at the inlet (coloured by styrene mass	
	fraction)	1
Figure 5.7:	Styrene mass fraction contour at 500rpm impeller speed and 144min	
	residence time	5
Figure 5.8:	Styrene mass fraction contour at 1000rpm impeller speed and 144min	
	residence time	5
Figure 5.9:	: Contour of viscosity (kg/m s) of the reactive mass at 1000rpm impeller speed	
	144min residence time	7
Figure 5.10	0: Contour of velocity magnitudes (m/s) for the non-reactive mass at 1000rpm	
	impeller speed and 144min residence time	9

Figure 5.11: Contour of velocity magnitudes (m/s) for the reactive mass at 1000rpm
impeller speed and 144min residence time
Figure 5.12: Conversion versus Impeller speed for the residence time of 144min
Figure 5.13: Conversion versus residence time for the impeller speed of 500 rpm
Figure 5.14: Contour of styrene mass fraction at 100rpm impeller speed and 144min
residence time 101
Figure 5.15: Contour of styrene mass fraction for 500rpm and 144min residence time . 103
Figure 5.16: Conversion versus Impeller speed for the residence time of 144min 105
Figure 5.17: Contour of styrene mass fraction for 100rpm impeller speed, 200min
residence time, temp 120°C, BPO conc. 0.01mol/L at the inlet 107
Figure 5.18: Contour of the percentage conversion for 100rpm impeller speed, 200min
residence time, temp 120°C, BPO conc. 0.01mol/L at the inlet 109
Figure 5.19: Contour of initiator mass fraction for 100rpm impeller speed, 200min
residence time, temp 120°C, BPO conc. 0.01mol/L at the inlet 111
Figure 5.20: Contour of propagation rate (kg/m3 s) for impeller speed 100rpm, 200min
residence time, temp 120°C, BPO initiator conc. 0.01mol/L at the inlet 113
Figure 5.21: Contour of propagation rate (kg/m3 s) for impeller speed 500rpm, 200min
residence time, temp 120°C, BPO initiator conc. 0.01mol/L at the inlet 115
Figure 5.22: Conversion versus impeller speed for 200min residence time, temp 120°C,
BPO initiator conc. 0.01mol/L at the inlet 117
Figure 5.23: Contour of styrene mass fraction for 1000rpm, 200min residence time, temp
120°C, BPO initiator conc. 0.01mol/L at the inlet 119

Figure 5.24: Conversion versus residence time for 100rpm impeller speed, temp 120°C,	
BPO initiator conc. 0.01mol/L at the inlet12	1

## **Chapter 1 : Introduction**

Polymer industry has been undergoing a major change in various standards over the past few decades. Now, efforts are more focused on product quality and performance, along with better productivity. Mixing is an important operation in chemical engineering. Mixing in any process is used to reduce the variability of concentration, temperature and many other properties of the mixture. Mixing of fluids is frequently performed in stirred tanks. It is also one of the basic unit operations, in the chemical industry for applications like liquid-liquid contactors, particle and droplet suspensions, polymer reactors, etc. In the reacting systems, mixing improves the chemical reactions, as it can strongly affect their rates and the final product quality. Harada et al. (1968), Tosun (1992), Kemmere et al. (2001), Heidarian et al. (2004), etc. have studied the mixing in polymerization. They concluded that, there exists strong relationship between the polymerization rate, the final polymer properties and the nature of mixing in a polymerization process. However, no solid framework exists at this time to relate mixing to polymerization rate or final polymer properties. Industrial polymerization processes are classified as bulk polymerization, solution polymerization, emulsion polymerization and suspension polymerization. Bulk polymerization processes are difficult to mix, due to the high viscosity of the reaction mass (Moritz, 1989). In solution polymerization, solvent is added to overcome this problem and also to get better heat transfer during the polymerization. Whereas, suspension and emulsion polymerization processes have low dispersion viscosity in comparison to bulk polymerization, hence they are relatively easy to mix.

Mixing deserves unique attention in a highly viscous media such as a polymerization process. Unlike several other products in chemical industry, polymeric materials must be produced with the required specifications, at the reactor stage itself (Brooks, 1997). Insufficient mixing leads to formation of dissimilar concentration pockets, which in turn influences the polymer properties like particle size distribution, number averaged molecular weight ( $\overline{M}_n$ ) and weight averaged molecular weight ( $\overline{M}_w$ ) (Tosun, 1992). When the reaction mixture is not well mixed, some regions in the reactor may have hot spots or may become dead zones in which the flow and reaction differs from the rest of the reactor. The formation of hot spots, in the polymerization accelerates the reaction in local regions and may end up in charcoal formation, which eventually results in deteriorated polymer quality. Most polymerization reactions are exothermic so the heat of reaction must be removed. Mixing plays an important role in heat removing. Conversion in polymerization reaction is also affected by mixing.

In order to get enhanced control of polymerization process for operation and product quality, it is necessary to have better understanding of the mixing process. Also an understanding of the flow behaviours, within the stirred tank reactor is essential, from equipment design and process scale-up point of view. Local and overall mixing characteristics of the reactor are related to stirrer construction and impeller speed selected (Wilkens et al., 2003).

Mixing takes place on micro as well as macro scale (Harada et al., 1968). Micro-mixing is governed by diffusion process whereas macro-mixing is governed by convective

process (Middleton et al., 1984). For very fast reactions, intense stirring cannot ensure that the process will occur under isothermal conditions. Chemical reactions of this type commence the moment, the reactants enter the reaction zone, and hence there is insufficient time for reactants to get well mixed. Such fast chemical reactions occur in the diffusion region and are determined by the process of micro-mixing of reactants. Micromixing concept has been applied to find out the effect of feed point on product selectivity and conversion. It has been shown by a number of researchers that feeding in the impeller region (in highly turbulent region) reduces by-product formation in competitiveconsecutive types of reaction and increases yield (Randick, 2000). Similarly, feeding at the surface of the reaction medium increases by-product formation, if the reactions are fast enough. In this case, the mixing time of reactants is generally longer than the characteristic reaction time and mixing dominates the reactions. Alternatively, it seems that mixing may not govern slow reactions because required degree of homogeneity is achieved before the reaction can even take place. However, this is true only for the chemical system having low viscosity. However, degree of homogeneity strongly depends on macro mixing, which in turn depends on the reaction mass viscosity. All Polymerization processes take place in highly viscous media. Therefore, in addition to micro-mixing, macro-mixing plays an important role in polymerization.

Earlier studies for mixing were based on the development of mathematical models of mixing. Problems encountered in these models, of batch or continuous stirred tank polymerization was that, the viscosity rise in polymerization quickly changed the initial assumptions about the homogeneity, which governs major aspects of the mixing process.

Another problem for stirred tank reactors, in general, is the difficulty of combining the complex mathematical polymerization kinetics with mixing models. These problems can be partly overcome with the use of Computational Fluid Dynamics (CFD) (Paul et al., 2004). CFD is emerging as a design tool for the development of new processes and optimization of existing ones at a fraction of the cost and time of traditional experimental and pilot-plant approaches. The development of Computational Fluid Dynamics (CFD) has opened the gates to visualize mixing processes without conducting real-time experiments, which may not be feasible in some cases. Recent development in computer capability has made CFD an attractive tool to design, optimize and visualize various processes. Unfortunately, it has not been exploited well enough in polymerization processes. Mixing patterns evaluated by CFD, and its effect on polymerization has very wide scope of application in polymer industries, as it is very helpful in scaling up from laboratory scale to pilot plant or to commercial production. CFD also provides information about turbulence zone and hence feeding in regions with intense turbulence can help us to improve the yield. In parallel, experimental approaches to understand the flow behaviours in reactor vessels are valuable, but the uneven nature of reactive fluids and the complex impeller blade geometry, can make quantitative measurements and flow visualization, more expensive and time consuming. Additionally, experimental methods can neither cover all relevant parameters involved in the mixing process, nor achieve the desired degree of spatial resolution within the stirred tank vessel. For these reasons, Computational Fluid Dynamics (CFD) has been rapidly developed into a useful tool that can provide real time simulation of mixing with relatively short time and provide an opportunity to look into the details of complex mixing flows.

The present work explores efficient ways to control the product quality, by ensuring good mixing in a continuous stirred tank styrene polymerization reactor, using the Computational Fluid Dynamics package (FLUENT 6.3.26). Literature review presented in Chapter Two explores various approaches adopted to study the effect of mixing on polymerization. The advantages of the CFD approach are also discussed. The CFD theory is briefly presented in Chapter Three. The CFD model development for styrene polymerization in a CSTR reactor and simulation methods are thoroughly discussed in Chapter Four. The results of the present research are discussed in Chapter Five. Conclusion and future recommendations are given in Chapter Six and Seven, respectively.

## **Chapter 2 : Literature Review**

### 2.1 Mixing in polymerization

Chain polymerization reaction consists of three main steps, namely initiation, propagation and termination. Sometimes due to viscosity rise during the polymerization, termination reactions becomes diffusion controlled and freezes in extreme conditions, leading to the well-known Gel effect. This effect may be due to poor micro mixing on molecular level and may end up in reactor instability. Micro-mixing affects both propagation and termination reaction rates. These effects are usually considered in the formulation of the two reaction rate constants in which diffusion control takes over and auto-acceleration polymerization become function of conversion. However, macro-mixing cannot be treated the same way and need different approach. In order to understand this behaviour, it is necessary to analyze the mixing in the polymerization reactor. Despite the significant importance of mixing in a polymerization, very few attempts were made to find out the effect of mixing on polymerization. The literature review related to mixing in polymerization can be classified in three categories:

- 1. Mathematical approach
- 2. Experimental approach
- 3. CFD approach.

#### 2.1.1 Mathematical approach

Most of the studies done on mixing were limited to modeling. Prochukhan et al. (1988) attempted to study the effect of mixing on ultra fast cationic polymerization of isobutylene in a tubular reactor. They found that the way of feeding monomer and catalyst into the reactor had significant effect on the polydispersity index and the molecular weight of the polymer formed. However, they considered only co-axial feeding of the monomer and the catalyst, moreover, both fed at the same velocity into the reactor. They also ignored the spatial variation of flow field velocities along the radial direction. However, for ultra-fast polymerization, polymer may start forming right at the inlet, and viscosity can quickly rise. Hence, the velocity gradient starts at the inlet zone and cannot be neglected.

Tosun (1992) developed a mathematical model to find out the effect of mixing on chain polymerization in a semi batch stirred tank reactor. He considered two distinct mixing volumes, completely homogenous volume and a completely segregated volume. He used Villermaux model (1989) for mixing, combined with the lumped kinetic model to study the mixing effect. His results showed that the number averaged degree of polymerization  $DP_n$  was not sensitive to mixing, whereas the weight averaged degree of polymerization  $DP_w$  was. However, no model validation was done. Moreover, time constants for erosion of the segregated volume by bulk flow were taken from empirical correlations derived under different conditions. It was also assumed that the time scales were constant for all species, including dead polymers, and not depending on molecular chain length. This assumption limits the applicability of the model to relatively low viscosity processes like solution polymerization.

Tefera et al. (1997) compared different mixing models for their ability to predict the free radical polymerization up to high conversion. Good methodology was presented for the model selection for the diffusion-controlled processes. However, these diffusion-controlled processes are of more interest in high conversion. They concluded that the models, which incorporated the change in initiator efficiency, were able to predict the experimental data very closely.

Kim and Laurence (1998) formulated a mathematical model to study the effect of mixing on free radical Methyl Methacrylate (MMA) solution polymerization. Two different mixing zones, one near impeller and the other the far away, were considered. The regions were assumed exchanging flow with each other. Two parameters, namely the volume ratio and the flow exchange ratio, of two zones, were selected arbitrarily in their bifurcation analysis of the system. Their model considered two extremes mixing conditions similar to those considered by Tosun (1992). However, they were able to incorporate the mixing model in the prediction of reactor dynamics.

Villa et al. (1998) studied the effect of imperfect mixing on low-density polyethylene (LDPE) reactor dynamics using three-compartment model. They found that imperfect mixing increases stability range of the reactor operation and made the reactor operation easier to control, than a perfectly mixed reactor. Their selection of re-circulation

8

parameters was not supported by theory or experimental data, but rather chosen arbitrarily to study the stability. Even after determining the stable region from the analysis, its practical implication was limited to controlling re-circulation. However, their study revealed the importance of mixing in reactor stability. Similarly, Louis (1997) noted that mixing could affect stability of a CSTR styrene polymerization reactor through heat transfer rate.

Chen and Fan (1971), Atiqullah and Nauman (1990), Kaflas (1992), Lee and Lee (1987) Dierendonck (1980) and many more researchers have adopted similar approaches to study the effect of mixing. However, none of the above mentioned approaches were able to give spatial distribution of flow variables to visualize the effect of mixing.

#### 2.1.2 Experimental approach

Most of the practical styrene polymerization processes are either bulk polymerization or suspension polymerization. Solution polymerization process is used occasionally despite the advantage of handling low viscosity mass, as it involves additional cost of solvent separation processes.

Hui (1967) conducted experiments on solution polymerization of styrene in toluene. He used his experimental results, to develop a viscosity correlation. He adjusted termination rate constant and initiator efficiency using the viscosity correlations at each time interval and then devised a polymerization kinetic model, valid for high conversion. However, they did not consider the effect of shear rate on diffusion-controlled reaction.

Harada et al. (1968) studied the effect of mixing on solution polymerization using helical ribbon and paddle impeller. They found that micro-mixing affected conversion rate. But, the effect of the impeller speed on conversion was minor. This might be due to a premixed feed of monomer and initiator, which was introduced at the reactor bottom, near the impeller. Hence, the reaction mass was likely homogenous even at low impeller speed. However, they observed a minor increase in conversion with increased impeller speed, for conversions exceeding 45%.

Cole (1975) experimentally studied the effect of mixing on anionic solution polymerization of butadiene. He observed that the agitator speed had significant effect on the molecular weight distribution and branching factor. Polymer branching increased with the degree of back mixing and the use of a batch reactor. An increase in residence time produced more branched polymer. His work also demonstrated that the tracer technique could be successfully used to model non-ideal mixing under actual operating conditions, of polymerization reactors.

Erdogen et al. (2002) studied a batch polymerization of styrene in toluene. They found that the conversion increased with an increase in impeller speed, up to certain limit beyond which the conversion reversed its direction.

Robertson (1959) carried out experimental study in dilatometers for polymerization of styrene and methyl methyacrylate. Polymerization of methyl methyacrylate was more

10

sensitive to diffusion control compared to polymerization of styrene. He found that, at low conversion, initiator efficiency remained constant. However, he noticed that, initiator efficiency dropped at high conversion for styrene polymerization and onset of diffusion control of the termination reaction led to auto-acceleration at high conversion. Further towards the end of reaction, he explained, the sudden drop in polymerization was due to the onset of diffusion controlled propagation reaction.

Duerksen (1968) carried out a set of experiments for free radical polymerization of styrene in continuous stirred tank reactors. He did not find any effect of the impeller speed on the conversion and the molecular weight distribution. However, he studied a polymerization with up to a viscosity 125 cp and varied the impeller speed 100rpm to 400rpm only. In this low viscosity range, even an impeller speed of 100rpm is sufficient to achieve a homogenous mass.

Fields and Ottino (1987) analysed the effect of mixing on a polymerization process of polyurethane by conducting experiments with linear and cross-linked system using the adiabatic temperature rise technique. They found that both urethane systems were sensitive to mixing and the behaviour of the cross-linking system was more influenced by diffusion resistance. As the rotational speed of the impeller was increased, the initial rate of reaction and the ultimate temperature were increased.

Lu and Biesenberger (1997) elaborated the effect of reactor type on polymer quality. They experimentally concluded that modified twin-screw extruder could produce CSTR like back mixing. Their observation was based on the residence time distribution (RTD) comparison of CSTR and twin screw. In comparison with plug flow reactor without any back mixing, they also showed that the molecular weight distribution was broader in back mix reactor for step growth polymerization.

Boodhoo and Jachuck (1999) developed new kind of spinning disk reactor for continuous polymerization. This spin disc technology used centrifugal forces to create very thin films on rotating disc. Formation of microfilm on disc improved mass and heat transfer rate. A significant enhancement in reaction rate was observed even at high viscosity. They were able to produce polystyrene with tight molecular weight distribution.

Heidarian et al. (2004) conducted experiments on the polymerization of polyamides to detect the effect of mixing on foaming. They found that foaming at low temperature requires high mixing rate where as at high temperature it requires low mixing rate. They noticed that at high impeller speed, foaming could not be avoided even at the lowest temperature range of industrial interest. They also observed that at higher mixing rate, foaming last longer even though the rate of reaction was sufficiently low.

Hosogai and Tanaka (1992) analysed the effect of the impeller on mean droplet diameter of a polystyrene dispersed phase, in a circular loop reactor, equipped with a pitch blade impeller. They proposed a correlation relating droplet mean diameter to the operating condition. They found that at low ratio of impeller to tank diameter, brake-up phenomena of droplets was governed by isotropic turbulence, whereas at higher ratio it was governed by the velocity gradient near the wall. Yang and Takahashi (2001) conducted similar experiments to find the effect of impeller speed and direction on coalescence rate of bubbles in suspension polymerization of styrene. They found that an increase in impeller speed increased coalescence rate. They argued that high impeller speed imparted more turbulence, hence allowing droplets to collide more violently.

Ozdeger et al. (1998) studied the effect of impeller speed on polymerization rate of an emulsion co-polymerization of styrene and n-butyl at high concentration of solid. They found that the effect of solid contents was more pronounced than other variables like, impeller type and speed, for the emulsion co-polymerization of styrene and n-butyl acrylate.

Kemmere et al. (2001) conducted a set of experiments on emulsion polymerization of styrene. They reported that the polymerization started only after a critical impeller speed necessary to maintain good emulsification. They concluded that suitable process condition for good emulsification could be determined from a simple experimental visualization.

More work has been reported on suspension polymerization. For instance, Tanaka and Izumi (1985) studied the effect of impeller speed in the suspension polymerization with draft tube enclosing the impeller. Impeller speed affected the particle size. However, no effect of the impeller height was observed on the mean droplet diameter and on the mean final particle size.

Baade et al. (1982) studied the effect of mixing on the kinetics of vinyl acetate suspension polymerization reaction. No significant effect of mixing on polymerization rate was found, as suspension polymerization has low characteristic viscosity compare to bulk polymerization.

Mitchell (1986) conducted an experimental study to find out the effect of agitator geometry and speed on suspension polymerization of styrene. He noticed that the turbulent flow field created, by the turbine agitator used to mix the reactor contents, had a profound effect on the size of the beads formed. He found that, the increase in agitator diameter decreased the mean drop size, due to higher energy dissipation rates. According to him the droplet size was governed by two-mechanism: drop coalescence rate and droplet break-up rate. They showed that the turbulent drop break-up theory predicted accurately the drop size dependency on the agitator speed.

Various experimental studies are reported in open literature to investigate the effect of mixing in suspension and emulsion polymerization. Despite the significant importance of mixing in bulk polymerization in a CSTR (Bhat et al., 2004), very few attempts were made to study the mixing in bulk polymerization. Open literature presents no experimental study to visualize the mixing in bulk polymerization.

#### 2.1.3 CFD approach

Paul et al. (2004) has reviewed the potential of Computational Fluid Dynamics to reveal the effect of mixing. This review focused on competitive-consecutive and competitive-

14

parallel reactions. However, polymeric reactions were not included in his review even though the polymerization is most significant area related to mixing. In contrast to former mathematical approaches, one can integrate real impeller geometry to simulate the flow field using the CFD approach. This approach has the potentiality to exceed mathematical models that are merely based on homogeneity and segregation assumptions.

McKenna et al. (1998) modeled the heat transfer phenomena on catalyst surface for olefin polymerization process. They found that the particle-particle interaction had profound effect on heat transfer coefficient. They also established that the heat transfer from the catalyst particle surface had a significant contribution over the heat conduction, particularly for particle size less than 100µm in diameter. They showed that Nusselt number correlations of typical form were not enough to describe heat transfer for the modern highly active catalysts. However, this model cannot be incorporated in the simulation of reactor, as it would be highly computational demanding.

Kolhapure and Fox (1999) carried out a CFD analysis of a tubular LDPE reactor. They coupled the four environment micro-mixing model with the CFD and reduced the computational time. Their simulation results were in good agreement with full Probability Density Function (PDF) simulations used by Tsai and Fox (1996). However, this modeling approach consists of arbitrarily defined mixing parameters, which limit the application of the model to simple flow domains. They found that the mixing became more important for high monomer feed temperature and for the initiator injection point at

the reactor center. They showed that imperfect mixing reduced the conversion and increased the polydispersity index.

Mahling et al. (2000) used the CFD to analyze the heat transfer and the initiator mixing performance in a LDPE high-pressure tubular reactor. They simulated 2D tubular reactor using a four-environment CFD micro-mixing model. It was assumed that, for fast chemical reactions, the reaction rate was controlled by transport process at molecular level. They noticed that the heat transfer rate slowed down near the entrance due to newly formed polymer and it increased further down in the stream. They also simulated 3D polymer reactor without polymerization kinetics to study the effect of tube diameter at the injection point on the initiator mixing. They found that a narrow tube diameter improves the initiator mixing. Since there was no polymerization kinetic, the effect of viscosity on the initiator mixing might not be evaluated properly.

Randick (2000) used paired-interaction closure to model the turbulent concentration fluctuations of the turbulent reacting species in the CSTR. The paired-interaction model is based on a simple probability function. The CFD with paired interaction model is used to simulate fast reacting competitive-consecutive reaction in the stirred tank. He found that the reactant feed location, had significant effect on the product yield. Feeding reactants in the impeller zone improved the yield for the fast reacting reactions. Higher yield was obtained increasing the impeller speed or the impeller diameter. He concluded that a scale-up based on simplified criteria was not adequate enough and resulted in a low yield. He verified that only using the CFD for detailed flow field calculations fulfilled the requirements for the scale-up. However, the study was limited to low molecular weight reactant and no fluid property variation due to the reaction was included.

Bakker et al. (2001) gave a comprehensive review to calculate the source term for the turbulent reacting species using the Magnussen-Hyertage model (1976) and its variants. The model consists of source term calculation primarily by two means: Arrhenius type kinetic scheme and turbulence mixing time. Smallest of these source term was considered in species transport equation. In the region of high turbulence, eddy lifetime is so short that the mixing is fast, and Magnussen-Hyertage model permits to calculate the reaction rate based on the local turbulent intensity, for slow mixing. They also proposed brief guideline to design the reactor using CFD. They used Magnussen-Hyertage model coupled with the CFD to calculate reacting species consumption rate for the LDPE polymerization reactor. They calculated temperature and species concentration over the flow domain. However, Magnussen-Hyertage model was originally developed for simple, one or two-step reaction and mainly for combustion applications.

Wells and Ray (2001) combined the CFD and the compartment model approach to investigate imperfect mixing in LDPE autoclave. The scheme required the selection of number of different zones having uniformity of the field variables. However, the selection process was arbitrary and may differ from person to person. Moreover, full CFD simulation was undertaken to determine the interaction parameters of selected compartments. They reduced the computational time but they scarified the details achievable from CFD. The autoclave impeller pushed the materials from the inlet to outlet, and essentially avoided a back mixing. Getting converged CFD solution for this type of reactor was straightforward and the computational time requirement was manageable.

Alexopoulos et al. (2002) developed a two-compartment model for calculating droplet/particle size distribution in suspension polymerization reactors. Their model comprised two mixing zones, namely, an impeller zone of high local energy dissipation rates and a circulation zone of low kinetic energy. They used CFD model to extract parameters for the model and then they used it for a non-homogeneous liquid-liquid dispersion process to calculate the time evolution of droplet size distribution in the mixing vessel. Good agreement was found between experimental data and model predictions of the droplet size distribution.

Zhou et al. (2001) used a CFD approach to simulate 2D tubular and 3D LDPE autoclave reactor and hence predicted the initiator consumption and the molecular weight distribution of the polymer, in the reactor. For a modeling purpose, they considered five monomer units in a radical chain, which was not a reasonable assumption and gave inaccurate reaction rate. Moreover, physical transport properties were assumed constant in the 3D autoclave simulations. Hence the effect of viscosity and density on the flow patterns and polymer quality were not accounted for. Few more studies on polymerization using CFD have been reported but mostly of them were limited to LDPE polymerization (Tosun and Bakker, 1997).

18

Meszena and Johnson (2001) demonstrated that the CFD approach could be used to predict the molecular weight distribution of the polymer formed in a living polymerization tubular reactor. The CFD approach predicted higher polydispersity index, much close to data than a simple plug-flow model of the process. However, they used the mass averaged velocity field, extracted from the continuity and the momentum equations, to solve the species transport equations in the concentration form.

Zhu et al. (2005) investigated the mixing mechanisms in a reactive extrusion using the CFD approach. They analyzed the bulk polymerization of  $\varepsilon$ -caprolactone in co-rotating twin–screw extruders. The simulation showed that increasing the screw pitch increased the mixing intensity, which accelerated the reaction rate. A first order reaction rate was assumed in the CFD model. It means that the reactive source term was inherently linear with respect to monomer mass fraction. Hence, convergence of the species transport equation was relatively fast. Moreover, the velocity field, derived from continuity and momentum equations, was used to solve the modified species transport equation. The velocity field, satisfying mass conservation law, might result in overshoot or undershoots for the modified species transport equations. Moreover, convective term of the momentum equation was ignored without any explanation.

The literature review of the CFD approach studying the polymerization system, suggests that the CFD approach has the capability to extract the flow patterns in details. However, simplifications of the CFD model were required to avoid convergence problems and to keep the computational time manageable.

#### 2.2 Objective

Objective of the presented thesis is to study the effect of mixing parameters, in particular impeller speed and residence time, on styrene conversion in a CSTR polymerization reactor using the CFD approach. Another objective is to determine effective ways to ensure good homogeneity in the CSTR for better polymer quality.

### 2.3 Motivation

Present work using the CFD approach to study the effect of mixing on the polymerization in continuous stirred tank reactor reactors, can be justified for the following reasons:

- Polymer exhibit wide range of molecular weights. The polymer molecules cannot be easily separated from each other in the later stage of the manufacturing, to obtain the desirable specifications. Therefore, it would be more appropriate to obtain the desire specifications at the polymerization stage itself. This demands well understanding of the effect of mixing on polymerization.
- The bulk polymerization process takes place in the highly viscous media, and the literature review suggests that there is a strong relationship between the mixing and the final polymer quality.
- The mathematical and the experimental approaches are not capable enough to give the full details about the spatial variations of the field variables.
- Generally, new product is introduced first in the pilot plant, for the verification purposes. The mixing efficiencies are different on the pilot plant scale and on the industrial scale. There is often a lack of fundamental understanding of the underlying phenomena of mixing. As a result, scale-up from pilot-plant

experiments remains unreliable. The CFD approach has been employed to better understand the mixing in such scale-up process.

- The recent advancements in the computational power have made CFD an attractive approach to study the polymerization process. The CFD approach has been adopted fruitfully for the tubular reactors.
- Despite the importance of CSTR in polymerization area, the CFD approach has not been exploited yet, to extract the details about the non-homogeneity in the CSTR.

It can be concluded from the above discussion that there is a strong need to identify the effect of mixing on the CSTR polymerization, using the CFD approach.

## **Chapter 3 : CFD Theory**

Computational fluid dynamics (CFD) is a computer based simulation tool to analyse a system of fluid flow, heat transfer and species transport with eventually other associated phenomena such as chemical reactions. The CFD technique has been integrated in the aerospace industries since1960 but it has recently been extended to chemical industries. Some of the advantages of using the CFD in chemical engineering are as follow:

- The CFD simulation gives in-depth details about the fluid flow. These details may not be available from traditional simulations and practical approaches.
- The CFD results can be used in process designing to eliminate trial and error methods and hence save time and cost.
- The CFD technique can be used for conducting the experiments when the safety is at risk.

CFD is a very vast growing subject and it is not possible to include every detail here. Hence, a brief review is presented. Versteeg and Malalasekera (1995) gave an excellent review of the CFD method. The CFD analysis of a flow domain consists of the following steps:

- Defining the computational domain
- Selecting the chemical and physical phenomena
- Simplifying the transport equations
- Defining the transport properties
- Specifying the boundary conditions

- Selecting the numerical solution technique
- Selecting the discretization techniques
- Selecting the pressure-velocity coupling
- Solving the algebraic equations using iterative methods
- Checking for convergence
- Analysing the result and validating the model when possible

These stepwise procedures are explained briefly in the following sections.

#### **3.1 Computational domain**

In order to employ the CFD method for a flow domain analysis, the first task is to define the computational domain and to create the geometry of the flow domain. Once the geometry is generated, the geometry volume is then divided into a very large number of small control volumes. The process of making small control volumes is called the grid generation or discretization and these control volumes are called cells. The cells consist of faces and nodes. The grid can be a structured grid or an unstructured grid. In 3D, structured grid consists of hexahedral (six faces) cells. In 3D unstructured grid, possible cell shapes are tetrahedral (four faces), prisms (five faces), pyramids (five faces) and hexahedra (six faces). Structured grid is preferred if the flow is aligned to the grid lines. However, the advantage of using unstructured grid is that, a complex geometry can be meshed easily with the various shapes available for the cells. Using the cell shapes available for the unstructured grid, the curved geometry can be meshed more accurately without deforming the original shape of the geometry. Therefore, the unstructured grid is preferred if the geometry contains curved surfaces.
Once the grid is generated, the next step is to check the quality of the grid, because accuracy of a solution depends on it. The quality of a grid is measured in terms of skewness of the cells. The skewness is the measure of the variation between the shape of any cell and the shape of an equilateral cell of the same volume. High skewness of cells lowers the accuracy of the solution, and even single highly skewed cell in a domain can destabilize the solution.

# 3.2 Chemical and physical phenomena

The solution of a flow problem gives the values of the flow field variables (temperatures, pressures, species mass fractions and velocities) on the cell centred nodes. The accuracy of these CFD solutions strongly depends on the number of cells in a grid. Increasing the number of cells in a grid increases the accuracy of the solution, but it also increases the computational time for the solution. Therefore, the number of cells is reduced to save the computational time, in regions having low gradients of the flow field variables, and alternatively it is increased to get high accuracy of the solution, in regions having high gradients. High gradient regions usually exist near the wall hence the grid resolution is made high near the wall.

Next task is to identify the physical and chemical phenomena involved in the flow domain. This involves the identification of operating flow regime, which is classified as inviscid flow, laminar flow, transitional flow or turbulent flow. The inviscid flow is the simplest possible flow regime, and complication increases from laminar to turbulent flow. One of the most popular criteria to classify the flow regime is based on Reynolds number. For the mixing tanks, the modified Reynolds number is defined as:

$$Re = \frac{ND^2 \rho}{\mu}$$
(1)

where N is the impeller speed (rev/s), D is the impeller diameter,  $\rho$  is the density of the fluid and  $\mu$  is the viscosity of the fluid. The flow is purely laminar for Re below 50 and purely turbulent for Re above 5000. Between these limits, the flow is in transitional regime. If the flow is in transitional or turbulent regime, then extra closure equations for the turbulent fluctuations are needed. There are various classical turbulence models that exist like k-epsilon model, k-omega model, Reynolds stress model etc. However, none of these models is universally accepted for the turbulence, but the k-epsilon model is used for the wide varieties of flow problem and it is proven to give good results over other models. Versteeg and Malalasekera (1995) have presented a quick review of these available turbulence models.

In addition, it is necessary to identify the flow as compressible or incompressible. In the compressible fluid flow, the equation of state provides the linkage between the energy transport equation and momentum transport equation. However, in the incompressible fluid flow, no such linking equation exists, therefore the continuity and momentum equations are solved to get the flow field and the energy equation is solved separately.

Moreover, if the flow is reactive then the species transport equations are also solved. A species transport equation has a reactive source term. The reactive source term incorporates the production rate or the consumption rate of the species in a reaction. In

this case, the species transport equations are coupled with the momentum transport equations, via bulk flow velocities and transport properties such as density, viscosity etc. Therefore, appropriate formulation of the reactive source term is necessary to accurately predict the reaction progress in the flow domain.

# 3.3 Transport equations

The governing transport equations (Bird et al., 2002; Fluent user's guide, 2007) can be formulated for the stationary and the rotating reference frames separately.

## 3.3.1 Equations in the stationary reference frame

The governing transport equations of continuity, momentums, energy and species can be written in the following forms for the stationary frame:

#### 3.3.1.1 Continuity

$$\frac{\partial \rho}{\partial t} + \left( \nabla \bullet \rho \vec{\upsilon} \right) = 0 \tag{2}$$

where  $\rho$  is the density and  $\vec{v}$  is the velocity vector.

#### 3.3.1.2 Momentum

$$\frac{\partial}{\partial t}(\rho\vec{\upsilon}) + \nabla \bullet (\rho\vec{\upsilon}\vec{\upsilon}) = -\nabla P + (\nabla \bullet \vec{\tau}) + \rho g + \vec{F}$$
(3)

in which,

$$\vec{\tau} = \mu \left[ \left( (\nabla \vec{\upsilon}) + (\nabla \vec{\upsilon})^T \right) - \frac{2}{3} \nabla \bullet \vec{\upsilon} \right]$$
(4)

and P is the pressure, g is the gravitational force,  $\vec{\tau}$  is the stress tensor, and  $\vec{F}$  is the external force.

#### 3.3.1.3 Energy

$$\frac{\partial}{\partial t}(\rho e) + \nabla \bullet (\vec{\upsilon}(\rho e + P)) = \nabla \bullet (k \nabla T - \sum h_j \vec{J}_j + (\vec{\vec{\tau}} \bullet \vec{\upsilon})) + S_h$$
(5)

where,  $e = h - \frac{P}{\rho} + \frac{\upsilon^2}{2}$ (6)

for incompressible flow, 
$$h = \sum_{j} W_{j} h_{j} + \frac{P}{\rho}$$
(7)

$$h_j = \int_{T_{ref}}^{T} C_{p_j} dT$$
(8)

In these equations, *e* is total energy, *h* is the static enthalpy,  $h_j$  is the enthalpy of species  $j, C_{p_j}$  is the specific heat of  $j^{\text{th}}$  species, *k* is the thermal conductivity,  $S_h$  is the heat source term, and *T* is the temperature.  $T_{ref}$  is the reference temperature,  $J_j$  is the diffusive flux of  $j^{\text{th}}$  species, and  $W_j$  is the mass fraction of  $j^{\text{th}}$  species.

3.3.1.4 Species

$$\frac{\partial}{\partial t} \left( \rho W_j \right) + \nabla \bullet \left( \rho \, \vec{\upsilon} W_j \right) = - \nabla \bullet J_j + R_j + S_j \tag{9}$$

where

$$\vec{J}_j = -\rho D_j \nabla W_j \tag{10}$$

where  $J_j$  is the diffusive flux of species *j* in the mixture,  $D_j$  is the diffusivity of species *j* in the mixture,  $R_j$  is the reactive source term for production of  $j^{th}$  species and  $S_j$  is any source related to the  $j^{th}$  species.

Then, governing equations are simplified according to the flow conditions. For example, in steady state simulations, unsteady-state terms of the transport equations are ignored. The transport equations (2) to (10) are valid only for the laminar regime, but for the turbulent regime, some additional closure equations are needed.

## 3.3.2 Equations in the rotating reference frame

Consider the rotating frame (co-ordinate system) with the angular velocity  $\vec{\omega}$ . Let's say that the position vector  $\vec{r}$  from the origin of the rotating frame can locate any arbitrary point in the computational domain, then, the fluid velocities can be transformed from the stationary frame to the rotating frame using:

$$\vec{v}_r = \vec{v} - \vec{u}_r \tag{11}$$

where  $\vec{v}_r$  is the velocity viewed from the rotating frame (relative velocity),  $\vec{v}$  is the velocity viewed from the stationary frame (absolute velocity), and  $\vec{u}_r$  is the velocity due to the moving frame ("whirl" velocity) which is defined as:

$$\vec{u}_r = \vec{\omega} \times \vec{r} \tag{12}$$

When the equation of motion is transferred to the rotating reference frame, additional terms appear due to the Coriolis acceleration and centripetal acceleration of the frame.

The continuity and momentum equations (2) and (3) become, respectively:

$$\frac{\partial \rho}{\partial t} + \nabla \bullet \rho \vec{\upsilon}_r = 0 \tag{13}$$

$$\frac{\partial}{\partial t}\rho\vec{\upsilon} + \nabla \bullet (\rho\vec{\upsilon}_r\vec{\upsilon}) + \rho(\vec{\omega}\times\vec{\upsilon}) = -\nabla P + \nabla\vec{\vec{\tau}} + \vec{F}$$
(14)

where  $(\vec{\omega} \times \vec{\upsilon})$  contains the Coriolis and centripetal accelerations of the rotating reference frame. The absolute velocity  $\vec{\upsilon}$  is a dependent variable.

# 3.4 Transport properties

The transport properties like density, viscosity, thermal conductivity, and diffusivities of the species appear in the transport equations. They also contribute to the coupling among the transport equations. In the flow problem, with more than one chemical species, the properties of the mixture depend on the mass fractions of each individual species. The density of the mixture is usually calculated as the volume-weighted average of the individual species densities. The remaining transport properties of the mixture are estimated using the mass-weighted average of the individual species properties.

# 3.5 Boundary conditions

The most common boundary conditions are defined as follow:

- Inlet
- Outlet
- Wall
- Symmetry

#### 3.5.1 Inlet boundary

The boundary conditions at the process entrance are used to specify the inlet flow condition, and this boundary condition is further divided into Velocity Inlet, Mass Flow Inlet and Pressure Inlet boundary conditions.

The Velocity Inlet boundary condition is suitable for the incompressible flow only, and it gives non-physical results, if applied to a compressible flow. The inlet flow velocity and all other scalar properties (temperature, species mass fraction) have to be defined at the Velocity Inlet boundary. These input values are then used to estimate the mass flow rate at the process inlet and to compute the fluxes of momentum, energy and species at the process inlet. Only the velocity component normal to the boundary is considered in calculating the fluxes. The mass flow rate received by the cells, neighboring the velocity inlet boundary, can be expressed as:

$$m = \int \rho \, \vec{v} \bullet d\vec{A} \tag{15}$$

where *m* is the mass flow rate entering the cells,  $\vec{A}$  is the vector normal to the area.

The Mass Flow Inlet boundary condition is mainly used in the compressible flow, to specify the inlet mass flow. In this type of boundary, the total pressure varies with the interior solutions to match the prescribed mass flux. In contrast to this, in the Pressure Inlet boundary, the pressure is fixed, and the mass flux is varied to match the prescribed pressure. The Pressure Inlet boundary is used, when the mass flow rate is unknown, and only the pressure is known at the inlet.

## 3.5.2 Outlet boundary

Outlet boundary can be incorporated in the model using either one of the following boundary conditions:

- Outflow boundary condition
- Pressure outlet boundary condition

The Outflow boundary condition is used when the existing flow is incompressible with unknown velocities and the pressure fields prior to an intermediate temporary solution of the inner flow domain. In the Outflow boundary, zero diffusion flux is assumed and the overall mass balance is corrected. The field variables on the outlet plane are extrapolated from the solution of the inner domain. Therefore, this boundary condition is more appropriate for a fully developed flow exit. The Outflow boundary condition cannot be used if the Pressure Inlet boundary condition is used in the flow problem. Moreover, Outflow boundary condition cannot be used in the compressible flow.

The Pressure Outlet boundary condition is used only, when the static pressure is known at the outlet. The static pressure is then used to extrapolate all other conditions from the interior domain. The pressure Outlet boundary condition is mainly useful for the compressible flow exit.

## 3.5.3 Wall boundary

The wall boundary condition is the most common type of boundary condition appearing in the flow problem to bound fluid to solid. No-slip and no penetration boundary conditions are applied to the momentum equations on the wall. However, heat can penetrate the wall, and therefore various options are available to model the heat transfer through the wall. The temperature, the convective heat transfer or the heat flux can be specified at the wall boundary for the energy transport equations. For a specified wall temperature, ignoring the radiation effect, the heat flux from the fluid cell to the wall is expressed as:

$$q = h_f \left( T_w - T_f \right) \tag{16}$$

where, q is the heat flux,  $T_w$  is the wall temperature,  $T_f$  is the local fluid cell temperature, and  $h_f$  is the fluid side local heat transfer coefficient.

Species cannot penetrate the wall, hence zero diffusive flux, is set at the wall, if no reaction is taking place there. A finite flux can be specified at the wall, if a reaction is taking place.

## 3.5.4 Symmetry boundary

Symmetry boundary condition is used to reduce the computational domain, by cutting on the edge having mirror symmetry. The symmetrical boundary condition imposes zero normal velocity and zero normal gradients for all variables. Therefore, it is also called slip wall boundary conditions because zero shear stress is assumed at the boundary, and it allows the flow to slip on the boundary.

Many other types of boundary conditions are available and a quick review of these available boundary types is presented in the Fluent's users guide (2007).

32

# **3.6 Numerical solution technique**

Different numerical methods have been adopted to solve the governing transport equations. The finite-difference method, the finite-element method and the finite volume method have been used for this purpose. However, the finite volume method has the following additional advantages over the other methods:

- In the finite volume method, the control volume integration of the transport equations results in statements expressing the conservation of mass, momentum, energy and species. The numerical algorithm applied to conservation principles makes the finite volume method more attractive for the CFD analysis.
- The finite volume method conserve the fluid properties, on each control volume, hence it has the conservativeness property.
- The boundedness property of the numerical method requires that the solution should be bounded by the maximum and minimum boundary values of the variables in a linear flow problem without any source term. This property is easily achievable in the finite volume method by placing the constraints on the scale and sign of the coefficients of the algebraic equations.
- In the convective flow, a change in the upstream variable affects the downstream variable hence the numerical scheme with the transportiveness property is desirable for the CFD analysis. This transportiveness is easy to design in the finite volume method, using the different discretization scheme, in the calculation of face variables (variable on the cell face).

For these reasons, the finite volume method is popular, for the general purpose CFD analysis. A brief introduction of the finite volume method is provided next.

## 3.6.1 The Finite Volume Method (FVM)

The governing transport equations of the momentum, energy, and mass, have common convective and diffusive terms. The uncommon terms in the governing equation can be hidden in the source term. Therefore, the conservation form for any general variable  $\phi$  can be written as:

$$\frac{\partial(\rho\phi)}{\partial t} + \nabla \bullet (\rho\phi \ \vec{\upsilon}) = \nabla \bullet (\Gamma \ \nabla\phi) + S_{\phi}$$
(17)

where  $\Gamma$  and  $S_{\phi}$  are the diffusion coefficients and the source term of the variable  $\phi$ , respectively, and  $\nabla \phi$  is the gradient of  $\phi$ . The integration of equation (17) on each control volume (CV) gives

$$\int_{CV} \frac{\partial(\rho\phi)}{\partial t} dV + \int_{CV} \nabla \bullet (\rho\phi\vec{v}) dV = \int_{CV} \nabla \bullet (\Gamma \nabla \phi) dV + \int_{CV} S_{\phi} dV$$
(18)

The volume integral, over a small control volume, can be transferred to surface integral using the Gauss divergence theorem, and it is rewritten as:

$$\frac{\partial}{\partial t} \left( \int_{CV} \rho \phi \, dV \right) + \oint \rho \, \phi \, \vec{\upsilon} \bullet d\vec{A} = \oint \Gamma \, \nabla \phi \bullet d\vec{A} + \int_{CV} S_{\phi} \, dV \tag{19}$$

where  $\vec{A}$  is the surface area vector. For the steady-state analysis, the first term is ignored and furthermore the surface integral is transferred into a sum of face fluxes, giving:

$$\sum_{f}^{N_{faces}} \rho_{f} \upsilon_{f} \phi_{f} \bullet \vec{A}_{f} = \sum_{f}^{N_{faces}} \Gamma (\nabla \phi)_{n} \bullet \vec{A}_{f} + S_{\phi} V$$
(20)

where  $N_{faces}$  is the number of faces in a cell,  $\phi_f$  is the value of  $\phi$  convected through the face f,  $\vec{A}_f$  is the area vector of the face,  $(\nabla \phi)_n$  is the magnitude of  $\nabla \phi$  normal to face f,  $\rho_f \vec{v}_f \bullet \vec{A}_f$  is the mass flux through the face f and V is the cell volume. If the source term  $S_{\phi}$  in (20) is a function of the same dependent variable  $\phi$ , then the it is linearized and written as:

$$S_{\phi} = b + S_{p}\phi_{p} \tag{21}$$

where the subscript p refers to the cell center, b is a specific constant and  $S_p$  is the variable part of the source term. Substitution of (21) into (20) results in the discretized equations that contains the unknown value of  $\phi$  at the cell centre and the value of  $\phi$  in the neighbouring cells (through discretization). Finally, the linearized form of these equations can be rearranged to give:

$$a_p \phi_p = \sum_{nb} a_{nb} \phi_{nb} + C \tag{22}$$

where  $\phi_p$  and  $\phi_{nb}$  are the values of scalar at the cell centre and in the neighbouring cell, respectively, the  $a_p$  and  $a_{nb}$  are their respective linearized coefficients. *C* contains the constant part of the source term and the applicable boundary source. These sets of algebraic equations are solved using an iterative method like Gauss-Seidel.

## **3.7 Discretization Schemes**

The flow variables are stored at the cell centre. However, the face values of these variables are needed to calculate the convective face flux in (20). Therefore, an

interpolation scheme is needed to estimate the face values of the variable from the cell centred values.

## 3.7.1 Upwind schemes

In the convective transport, the face value of the variable is mostly affected by the cell centred value of the upstream cell. The methods utilising this directionality concept are called upwind schemes. There are various upwind methods that exist based on the directionality concept. Some of the most common upwind schemes are explained briefly.

#### 3.7.1.1 First order upwind scheme

In this scheme, the cell centred values of the variable is assumed to hold through out the cell. Hence, the face value of the variable is the same as the cell centred value. In the flux calculation for the downstream cell (sharing the face with the upstream cell), the upstream cell centred value is taken as the face value for the down stream cell. However, the accuracy of the solution is only first order. This scheme is used only to provide a good initial guess for a higher accuracy scheme.

#### 3.7.1.2 Power law Scheme

The power law scheme utilises the exact solution of one-dimensional convectiondiffusion problem to calculate the face value of the variables. Hence, this scheme is able to incorporate the effluence of the diffusion and convection on the face value. However, in the presence of high convection, this scheme reduces to first order upwind scheme.

#### 3.7.1.3 Second order upwind scheme

The second order scheme utilises the multidimensional gradients in the upstream variable to calculate the value of the variable on the face, shared by the upstream and the downstream cells. Hence, the face value of the downstream variable  $\phi_f$  is calculated as:

$$\phi_f = \phi_{up} + \nabla \phi_{up} \bullet \nabla \vec{D} \tag{23}$$

where  $\phi_{up}$  and  $\nabla \phi_{up}$  are the cell centred value and its gradient in the upstream cell, respectively;  $\nabla \vec{D}$  is the distance vector from the cell centroid of the upstream cell to the face centroid. The gradient of a variable in the upstream cell  $\nabla \phi_{up}$  is calculated as:

$$\nabla \phi_{up} = \frac{1}{V} \sum_{f}^{N_{faces}} \widetilde{\phi}_{f} \vec{A}$$
(24)

where  $\tilde{\phi}_f$  is the average value of the  $\phi$  values in two adjacent cells sharing the face. The second order-upwind scheme gives more accuracy and it is applicable in the full range of Peclet numbers.

#### 3.7.1.4 QUICK scheme

This scheme offers high accuracy and is similar to second order upwind scheme. However, its use is restricted to quadrilateral or hexahedral meshes. The scheme utilises the quadratic function in the calculation of face variable.

## 3.7.2 Pressure interpolation

The discretized x-momentum equation can be obtained by setting  $\phi = u$  in equation (22) giving:

$$a_p u = \sum_{nb} a_{nb} u_{nb} + \sum_{f} P_f A \bullet i + S$$
<sup>(25)</sup>

where u is the velocity in x-direction,  $P_f$  is the pressure value on the face and S is the source term. The pressure field and face fluxes are not known and have to be obtained as a part of the solution. There are some issues, regarding the storage of the pressure, due to the famous checker-boarding problem (Versteeg and Malalasekera, 1995). However, the face pressure value is needed in the equation (25) and has to be calculated from the storage value. There exist various interpolation methods to calculate the face pressure from the cell centred values viz:

- The standard interpolation scheme computes the face pressure, using the momentum equation coefficients.
- The linear scheme interpolates the face pressure by averaging the pressure values of the adjacent cells.
- The second-order scheme calculates the face pressure in the manner outlined for the convective term. This provides improvement over the standard and linear schemes, and it is recommended in the compressible flow.
- The PREssure Staggering Option (PRESTO) scheme is designed to avoid the checker boarding of the pressure. This scheme computes the face pressure using the discrete continuity balance over the staggered control volume about the face. The PRESTO scheme gives good accuracy for the tetrahedral mesh.

# 3.8 Pressure-Velocity Coupling

There are three momentum equations (in x, y, and z directions), and four unknown (three velocity and pressure). Hence, one more equation is needed for pressure. The continuity equation can be used as the density correction equation for the compressible flow. Once the density and temperature are known, they can be used in the ideal gas law to obtain the pressure field. However, in the incompressible flow, the density is not related to pressure. Therefore, in this case, if the correct pressure fields are applied in the momentum equation, the resulting velocity field should satisfy the continuity equation. This forms the basis for the various methods to solve the pressure-velocity coupling.

## 3.8.1 The SIMPLE algorithm

As mentioned earlier, the pressure does not appear in the continuity equation. Therefore, Patanakar and Spalding (1972) developed the algorithm called the Semi-Implicit Method for Pressure-Linked Equations (SIMPLE) to introduce the pressure in the continuity equation. The discretized continuity equation can be obtained by setting  $\phi = u$  in equation (22) giving:

$$\sum_{f}^{N_{faces}} J_f A_f = 0 \tag{26}$$

where  $J_f$  is the normal mass flux through the face f and  $A_f$  is the area of the face f. In the face mass flux calculation, the face velocity is needed. The face velocity is taken, as the momentum weighted averaging of the cell centred velocities of the adjacent cells. Using these velocities, the face flux is calculated as:

$$J_{f} = \hat{J}_{f} + d_{f} \left( P_{c0} - P_{c1} \right)$$
(27)

where  $P_{c0}$  and  $P_{c1}$  are the pressures in the face adjacent cells,  $\hat{J}_f$  represents the effect of the adjacent cell velocities on the face velocity.  $d_f$  is a function of the momentum coefficients of the cells adjacent to face.

The SIMPLE algorithm solves the momentum equation with a initial guess  $P^*$  of the pressure field and gives the initial face flux  $J_f^*$  as:

$$J_{f}^{*} = \hat{J}_{f}^{*} + d_{f} \left( P_{c0}^{*} - P_{c1}^{*} \right)$$
(28)

However, this face flux does not satisfy the continuity equation. Therefore, a correction is required for the face flux  $J_f^*$  to satisfy the continuity. The corrected face flux  $J_f$  is obtained by adding the correction  $J_f'$  to the initial guess of the face flux  $J_f^*$ .

$$J_{f} = J_{f}^{*} + J_{f}^{\prime}$$
(29)

The correction in the flux  $J'_f$  is related to the pressure difference in the face adjacent cells. Therefore, the SIMPLE algorithm assumes that

$$J'_{f} = d_{f} \left( \hat{P}_{c0} - \hat{P}_{c1} \right)$$
(30)

where  $\hat{P}$  is the pressure correction in the cell. Equation (29) and (30) are substituted in the discrete continuity equation in order to derive the equation for the pressure correction  $\hat{P}$  in the cell as follow:

$$a_p \hat{P} = \sum_{nb} a_{nb} \hat{P}_{nb} + b \tag{31}$$

where b is the net flow rate into the cell:

$$b = \sum_{f}^{N_{faces}} J_{f}^{*} A_{f}$$
(32)

Once the pressure correction is obtained from the solution of (31), the cell pressure and the face flux are updated as follows:

$$P = P^* + \alpha_p \hat{P} \tag{33}$$

$$J_{f} = J_{f}^{*} + d_{f} \left( \hat{P}_{c0} - \hat{P}_{c1} \right)$$
(34)

where  $\alpha_p$  is the under-relaxation factor for the pressure. The under-relaxation factor is applied to limit changes in the pressure and hence to stabilize the solution process.

## 3.8.2 The SIMPLEC

The SIMPLEC (SIMPLE-Consistent) is the variants of the SIMPLE algorithm. The only difference between the SIMLEC and the SIMPLE is in the expression of the face flux correction  $\hat{J}_f$ . The correction equation is written as:

$$J_{f} = J_{f}^{*} + d_{f} \left( \hat{P}_{c0} - \hat{P}_{c1} \right)$$
(35)

However, the coefficient  $d_f$  here is different from that in SIMPLE and it is redefined as a function of  $(a_p - \sum_{nb} a_{nb})$ . The customized pressure correction equation of the SIMPLEC method accelerates the convergence, whenever the pressure-velocity coupling is the main constraint in achieving the convergence.

# 3.9 Solving the algebraic equations

The solution process of the governing transport equations consists of the solution loops and iterative method. The solution loop, also known as a solver, is discussed in the solver section. The iterative methods are explained in section 3.9.2.

## 3.9.1 Solver

The segregated solver and the coupled solver are the two approaches available to solve the governing equations iteratively. Both type of solvers are available in FLUENT 6.3.26 and are discussed here.

#### 3.9.1.1 Segregated solver

The segregated solver was traditionally developed for the incompressible flow to solve the governing equations sequentially. The governing equations are non-linear and coupled hence several iterations are required to reach the convergence. The scheme of iterative solution loop for the segregated solver is shown in Figure 3.1. The loop consists of the following steps:

- 1. The initialization step provides the initial guess of the solutions for all field variables (velocity, temperature, etc.).
- 2. On the first iteration, the fluid properties are updated using the initial guess, and subsequently, it is updated using the current solution of the flow field variable.
- The momentum equations are solved using the current pressure field and the face mass fluxes. This step provides the updated velocity field.

- 4. The updated velocity may not satisfy the continuity equation. Hence, the pressure correction equation is solved to get the correction to the pressure, the velocity and the mass flux such that they satisfy the continuity equation.
- 5. The other scalar equations such as energy and species are solved using the updated variables.
- 6. The solution is checked for the convergence criteria. The iteration is stopped, if the solution meets the set of convergence criteria.



Figure 3.1: Segregated solver loop

#### 3.9.1.2 Coupled solver

The coupled solver is mainly used to deal with high-speed compressible flow. The solution loop for the coupled solver is shown in Figure 3.2.

The continuity, momentum, species and energy transport equations are solved simultaneously in this approach. Any other scalar equation is solved sequentially. The coupled solver needs more computer memory than the segregated solver. However, faster convergence is possible with the coupled solver for some fluid problems.



Figure 3.2: Coupled solver loop

## 3.9.2 Iterative method

The algebraic equations, shown in equation (22), result in a huge coefficient matrix for a 3D fluid problem. Direct inversion of the matrix is not possible hence iterative methods are used. A point-implicit iterative method like Gauss-Seidel can be used. The Gauss-Seidel method reduces very rapidly high frequency local errors, but it is slow in removing low frequency global errors. The acceleration in removing the global error can be achieved using the accelerator like the Multi-Grid method. In the Multi-grid method, various levels of coarse grids are built on the top of fine grid. Then, the errors on fine grids are transferred to coarse level grids, and computed corrections on the coarse grids are transferred back to the fine level grids. Building a coarse level grid may be difficult for various reasons in the unstructured grid. Hence, in the Algebraic Multi-Grid method (AMG), coarse level equations are generated without the use of any geometry. A matrix operator, called restriction, transfers the error from the fine level to the coarse level. But, a prolongation operator transfers the corrections back to the fine level. The construction of these operators and various cycles are given in the Fluent's users guide (2007). The use of Algebraic Multi-Grid method (AMG) with the Gauss-Seidel method greatly reduces the number of required iterations and CPU time.

# **3.10 Checking the convergence**

The solution method is an iterative process hence it becomes necessary to monitor the convergence. The obvious is to monitor the residuals (errors) of the equations. The residual for the general variable  $\phi$  is defined below.

The discretized conservation equation for the general variable  $\phi$  at the cell *P* can be written as:

$$a_p \phi_p = \sum_{nb} a_{nb} \phi_{nb} + C \tag{36}$$

where  $a_p$  is the centre coefficient,  $a_{nb}$  represents the influence of the neighbouring cells on  $\phi_p$ . *C* is the contribution from the constant part of the source term and from the applicable boundary fluxes. The "un-scaled residual"  $R^{\phi}$  is defined as the imbalance in equation (36) summed over all the cells in the computational domain, and it is written as:

$$R^{\phi} = \sum_{cells \ P} \left| \sum_{nb} a_{nb} \phi_{nb} + C - a_{p} \phi_{p} \right|$$
(37)

However, the un-scaled residual is of limited use to assess the convergence since no scaling is done to compare with. Hence, scaling the residual, with the representative flow rate of  $\phi$  through the cells, helps in assessing the magnitude of the residual. The scaled residual is defined as:

$$R_{SC}^{\phi} = \frac{\sum_{cells P} \left| \sum_{nb} a_{nb} \phi_{nb} + C - a_{p} \phi_{p} \right|}{\sum_{cells P} \left| a_{p} \phi_{P} \right|}$$
(38)

Similarly, un-scaled residual for the continuity equation is defined as:

$$R^{C} = \sum_{\text{cells } P} |\text{rate of mass creation in the cell } P|$$
(39)

and the scaled residual is defined as:

$$\frac{R_{iteration N}^{C}}{R_{iteration 5}^{C}}$$
(40)

where the denominator is the largest continuity imbalance in the first five iterations.

These scaled residuals can be used as a guide to assess the convergence. As the solution approaches the convergence, the scaled residuals decrease to a very low value. In Fluent's user guide (2007), it is stated that the scaled residual should decrease below  $10^{-3}$  for the continuity and momentum equations, and below  $10^{-6}$  for the species and energy equations.

Particularly, in the continuity equation, the initial absolute residuals are very high, if the initial guess is not good. Hence, the scaled residuals decrease to  $10^{-3}$  even if the solution is not converged. Therefore, the scaled residual cannot be used as the absolute indicator for the convergence, and additional monitoring of the integrated quantities such as flow rate at the process outlet, overall heat transfer coefficient etc., are needed to assess the convergence. These integrated quantities should remain constant regardless of iteration when the solution reaches the convergence.

## 3.11 Results analysis and Validation

Once the simulation is completed, next step is to show the grid independency of the solution. Then, the grid independent solution can be used for the visualization of the flow fields. Since vectors, contours etc., cannot be displayed in 3D, various kinds of surfaces can be generated to visualise the flow fields of 3D problems. The surface integral or volume integral quantity should be checked, and compared with the experimental or other model data to validate the reliability of the CFD model.

# Chapter 4 : CFD Model and Simulation

Styrene can be polymerized under the thermal effect, even in the absence of an initiator. The CFD model development for styrene polymerization in a CSTR is divided into four sections, namely:

- 1. Geometry creation
- 2. Formulation of the reactive source term
- 3. Physical properties of the reaction mass
- 4. Simulation method

The stepwise model development procedure is explained in the following sections.

# 4.1 Reactor Geometry

Styrene polymerization in a lab-scale CSTR was simulated in this study. The reactor geometry was generated using, the software called Mix Sim 2.1, a CFD tool for the simulation of agitated mixing vessels. The MixSim 2.1 uses another software package called GAMBIT in the background, in order to build and mesh the geometry models required for the CFD. The reactor specifications used for the model simulations are tabulated in Table 4.1. Two reactor geometries, with different input-output locations, were considered. The discretized domains of these reactor geometries are shown in Figure 4.1 and Figure 4.2. Figure 4.1 and Figure 4.2 contain 372571 and 371784 cells, respectively. The tetrahedral cells were used to generate the unstructured grid for the simulation of the reactors.

Tabl	e 4 1	1.	React	or	specif	ficat	tion
1 a0	ic +.	1.	Reaci	U.U.I	speen	inca	non

Parameter	Value	Parameter	Value
Tank diameter	14 cm	Impeller diameter	8.4 cm
Liquid level	26 cm	Impeller elevation	8.0 cm
Outlet diameter	1.5 cm	Impeller type	45° Pitched blade
No. of blades	4	Inlet pipe elevation	20 cm (Figure 4.1)
Inlat diamatar	neter 1 cm	Outlet pipe elevation	3 cm (Figure 4.1) & 20 cm
miet diameter			(Figure 4.2)



Figure 4.1: Reactor grid for the side inlet (near liquid level) and outlet

In both the geometries, fresh styrene or styrene-initiator mixture can enter the reactor from the inlet. Under thermal effect, styrene reacts inside the reactor to produce polymer. The polymer and the un-reacted styrene leave the reactor through the outlet pipe. The residence time was varied from 48.84min to 143.65min (corresponding flow rate from



 $4.942 \times 10^{-3}$  to  $1.680 \times 10^{-3}$  m<sup>3</sup>/hr) for the thermal polymerization study and from 150min to 326min (corresponding flow rate from  $1.609 \times 10^{-3}$  to  $7.405 \times 10^{-4}$  m<sup>3</sup>/hr) for the initiated polymerization study. The impeller speed was varied from 100rpm to 1000rpm in both types of polymerization simulations. The inlet temperature and the reactor wall temperature were kept same to impose the isothermal flow condition inside the reactor. The inlet temperature and the wall temperature were kept constant at 140°C for the thermal polymerization simulations and, at 120°C for the initiated polymerization. In the initiated polymerization, benzoyl peroxide (BPO) was used as the initiator. The inlet initiator was assumed perfectly mixed with the inlet monomer stream. The inlet initiator concentration was kept 0.01mol/L for all BPO initiated polymerization simulations. A summary of these process experiments is given in Table 4.2.



Figure 4.2: Reactor grid for the bottom inlet



Parameter	Thermal polymerization simulation	BPO initiated polymerization simulations		
Inlet Temperature, °C	140	120		
Wall temperature, °C	140	120		
Residence time, min	48, 72, 102 and 144 @500rpm	150, 200 and 326 @100rpm		
Impeller speed, rpm	100, 500 and 1000 @144min	100, 500 and 1000 @200min		
Inlet stream BPO conc., mol/L	No initiator	0.01		

Table 4.2: Process parameters for styrene polymerization simulations.

# 4.2 Formulation of reactive source term

Styrene polymerization is a sequence of chain reactions. Previous researchers have extensively studied the thermal polymerization of styrene. Hiatt and Bartlett (1959), Mayo (1968), Hui and Hamielec (1972) investigated the dependence of thermal initiation rate of styrene on the monomer concentration. Hui and Hamielec (1972) developed a third order initiation rate with respect to styrene concentration. Their kinetic model fitted well with the experimental conversion data. Therefore, the same kinetic model was used here for the thermal initiation. Dhib et al. (2000) and Gao and Penlidis (1996) have comprehensively studied initiator decomposition and chemical initiation kinetic for the styrene polymerization. Their models were tested against a very wide range of conversion. However, their kinetic models were complex, and only a simplified version of model was used here. The kinetic model was simplified by making the few assumptions listed below.

- 1. The successive steps in propagation were assumed to have the same rate constant  $K_p$ .
- 2. The chain termination was assumed to take place by combination reaction only.
- 3. The chain transfer to monomer and polymer were negligible.
- 4. Steady-state hypothesis was applicable.
- 5. The gel effect was neglected, as the conversion range considered in the simulations was low.
- 6. The monomer consumption in the initiation reaction was negligible.

Based on the assumptions above, the complete kinetic mechanism of styrene polymerization can be written in three steps namely initiation, propagation and termination.

Thermal initiation:

$$3M \xrightarrow{K_{th}} 2R_1^{\bullet} \tag{41}$$

Chemical initiation:

$$I \xrightarrow{K_d} 2R_{in}^{\bullet} \tag{42}$$

$$R_{in}^{\bullet} \xrightarrow{K_i} R_1^{\bullet} \tag{43}$$

Propagation:

$$R_r^{\bullet} + M \xrightarrow{K_p} R_{r+1}^{\bullet} \qquad r \ge 1 \tag{44}$$

Termination:

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{K_{tc}} P_{r+s} \qquad r, s \ge 1 \tag{45}$$

where M, I,  $R^{\bullet}$ , and P refer to styrene monomer, initiator (BPO), live polymer radical and dead polymer, respectively, and the subscript refer to number of monomer unit in a chain length.  $K_{th}, K_d, K_i, K_p$  and  $K_{tc}$  refer to rate constant for thermal, initiator decomposition, intermediate initiation, propagation and termination reaction, respectively.

## 4.2.1 Thermal polymerization source term

The thermal polymerization includes only thermal initiation. Assuming a steady-state hypothesis and equating the rate of thermal initiation to that of termination, the total live radical concentration can be written as follows:

$$\left[R^{\bullet}\right] = \sqrt{\frac{2K_{th}[M]^3}{K_{tc}}} \tag{46}$$

where  $[R^{\bullet}]$ , [M] refers to concentration of live polymer radicals and monomer respectively. This allows computing the thermal polymerization rate  $R_p$  as:

$$R_{p} = -K_{p} [M] [R^{\bullet}]$$
(47)

Applying equation (46) into (47) gives:

$$R_{p} = -K_{p} [M]^{2.5} \sqrt{\frac{2K_{th}}{K_{tc}}}$$
(48)

Equation (48) gives the polymer production rate per unit volume and it gives also the monomer consumption rate per unit volume, as the monomer consumption in the initiation reaction is negligible compare to that in propagation reaction.

## 4.2.2 BPO initiated polymerization

In BPO initiated polymerization, the live radicals are produced by thermal initiation and chemical initiation reactions. Hence, the total initiation rate is the sum of both initiation rates. Therefore, employing the steady-state hypothesis and equating the total initiation rate to termination rate gives the total live radical concentration, for the BPO initiated polymerization as follow:

$$[R^{\bullet}] = \sqrt{\frac{2K_{th}[M]^3 + 2fK_d[I]}{K_{tc}}}$$
(49)

where f is the initiator efficiency, which is the fraction of the radical formed in equation (42) that is successful in initiating chains by equation (43). The initiator efficiency is always less then one due to the cage effects. The initiator efficiency was taken equal to 0.8, which is in the range reported by Dhib et al. (2000). Once the total live radical concentration is known, the polymerization rate can be calculated as follow:

$$R_p = -K_p[M][R^{\bullet}]$$
(50)

$$R_{p} = -K_{p} \left[ M \right] \sqrt{\frac{2K_{th} \left[ M \right]^{3} + 2fK_{d} \left[ I \right]}{K_{tc}}}$$
(51)

Equation (51) is the polymer production rate per unit volume. The initiator (BPO) consumption rate per unit volume ( $kmol/m^3 s$ ) is given by:

$$R_{ini} = -K_d[I] \tag{52}$$

The equations (48), (51) and (52) give the consumption rate in kmol/m<sup>3</sup> s. However, the species transport equation requires source term (monomer consumption rate) in kg/m<sup>3</sup> s, so the source term in kg/m<sup>3</sup> s is given by:

$$S_{monomer} = R_P \times M_{w,monomer} \tag{53}$$

$$S_{initiator} = R_{ini} \times M_{w,BPO}$$
<sup>(54)</sup>

where  $M_{w,monomer}$ ,  $M_{w,BPO}$  are the molecular weight of the monomer and the initiator, respectively. In the equation (53),  $R_p$  is taken from equation (48) for thermal polymerization simulations, and from the equation (51) for BPO initiated polymerization simulations. Furthermore, in both thermal and BPO initiated polymerizations, the rate constants depend on the temperature through the following Arrhenius type equations:

$$K_d = A_d \exp\left(-E_d / R_g T\right)$$
(55)

$$K_{th} = A_{th} \exp\left(-E_{th} / R_g T\right)$$
(56)

$$K_{p} = A_{p} \exp\left(-E_{p} / R_{g}T\right)$$
(57)

$$K_{tc} = A_{tc} \exp\left(-E_{tc} / R_g T\right)$$
(58)

where A is the pre-exponential, E is the activation energy, and  $R_g$  is the universal gas constant. Values of pre-exponentials and respective activation energies are taken from Dhib et al. (2000) and are given in Table 4.3.

Table 4.3:	Values	of kinetic	parameters
------------	--------	------------	------------

Parameter	Values	Parameter	Values	Sources
A <sub>d</sub>	$3.816 \times 10^9 \text{ m}^3/\text{s}$	E <sub>d</sub>	$2.73254 \times 10^4$ cal/mol	[1]
$A_p$	$2.170 \times 10^7 \text{ m}^3/\text{kmol s}$	$E_p$	$7.75923 \times 10^3$ cal/mol	[2]
$A_{th}$	2.190×10 <sup>5</sup> (m <sup>3</sup> ) <sup>2</sup> /kmol <sup>2</sup> s	$E_{th}$	$2.74400 \times 10^4$ cal/mol	[1]
$A_{tc}$	8.200×10 <sup>9</sup> m <sup>3</sup> /kmol s	$E_{tc}$	$3.47129 \times 10^3$ cal/mol	[2]

Sources: [1] Villalobos et al. (1993)

[2] Gao and Penlidis (1996)

# 4.3 Estimation of physical properties

The polymerization reactions take places in high viscosity. The viscosity can significantly affect the flow behavior in the reactor (Moritz, 1989). Therefore, it is necessary to model reaction mass viscosity in the reactor. The zero shear viscosity of the reaction mass can be estimated using the following empirical correlation reported by Kim and Nauman (1992):

$$\ln(\mu_{0}) = -11.091 + 1109/T + M_{w,P}^{0.1413} [12.032w_{P} - 19.501w_{P}^{2} + 2.92w_{P}^{3} + (-1327w_{P} + 1359w_{P}^{2} + 3597w_{P}^{3})/T]$$
(59)

where  $\mu_0$  is the zero shear viscosity (Pa.s),  $M_{w,p}$  is molecular weight of the polymer.  $w_p$  is the polymer mass fraction in the mixture and *T* is the temperature (K). From the zero shear viscosity, shear dependent viscosity of the mixture can be calculated by the following correlation suggested by Kim and Nauman (1992):

$$\mu = \mu_0 / (1 + \mu_0 \gamma^{1.2} / 35000)^{0.6}$$
(60)

where  $\gamma$  is the shear rate, s<sup>-1</sup>. The average shear rate in the reactor is given by:

$$\gamma_{avg} = \mathbf{K} \, N \tag{61}$$

where K is the proportionality constant and N is the impeller speed in revolution per second. The proportionality constant K was taken equal to 11.0 for the pitched blade impeller as reported by Wilkens et al. (2003). Equation (59) and (60) are highly non-linear with respect to polymer mass fraction. This non-linearity caused difficulties in achieving the convergence. Therefore, in the CFD model, the reaction mass viscosity was calculated as explained below.

For each CFD simulation, the residence time was known. Using the same residence time in the CSTR model, monomer conversion was calculated. This calculated conversion was used to read, the weight average molecular weight of the polymer, from the data reported by Dhib et al. (2000). The polymer mass fractions, in the mixture, were also calculated using the above calculated monomer conversion. These mass fractions were used in equation 59 to get the zero shear viscosity. From the zero shear viscosity of the mixture, shear viscosity of the mixture  $\mu_{mix,CSTR}$  was calculated using the equation (60) and the average shear rate. Once the mixture viscosity was known, this viscosity was again used to extract the polymer viscosity as follow:

$$\mu_{polymer} = \frac{\mu_{mix,CSTR} - (1 - w_p)\mu_{styrene}}{w_p}$$
(62)

where,  $w_p$  is the polymer mass fraction calculated using the CSTR model.  $\mu_{mix,CSTR}$  is the mixture viscosity calculated using the CSTR model.  $\mu_{styrene}$  is the styrene viscosity ,which can be calculated using the equation 59 and putting the polymer mass fraction zero. These, polymer viscosity and the styrene viscosity, were used in the CFD model. In the CFD model, the mixture viscosity in each cell was calculated as

$$\mu_{mix,CFD} = \mu_{styrene} \left( 1 - W_{P,cell} \right) + \mu_{polymer} W_{P,cell}$$
(63)

where,  $W_{P,cell}$  is the mass fraction of the polymer in each individual cell.

The density of the mixture (kg  $/m^3$ ) can be calculated from the correlation reported by Soliman et al. (1994):

$$\rho = (1174.7 - 0.918T)(1 - w_p) + (1250.0 - 0.605T)w_p$$
(64)
The styrene density and polymer density were estimated using the equation 64, and then these densities were used in the CFD model to estimate the density of the mixture as follow.

$$\rho = \frac{1}{\sum_{j} \frac{W_{j}}{\rho_{j}}} \tag{65}$$

where  $W_j$  is the mass fraction of species j and  $\rho_j$  is the density of species j.

The specific heat and the thermal conductivity of the mixture, and the monomer diffusivity were assumed constant. The values of these properties were taken from the literature (Soliman et al., 1994) and are shown in the Table 4.4.

Table 4.4: Constant physical properties

Properties	Value
Specific heat	1880 J/kg K
Thermal conductivity	0.126 J/m s K
Monomer diffusivity	$2.0 \times 10^{-9} \text{ m}^2/\text{s}$

# 4.4 Simulation Method

MixSim 2.1 is a CFD simulation tool to analyze the flow in agitated mixing vessels, but it is limited to non- reactive flow only. Therefore, MixSim 2.1 was used only to generate the CSTR geometry and mesh, and the rest of the model was defined using the

commercial available CFD code (FLUENT 6.3.26). FLUENT 6.3.26 does not have the option to incorporate the polymerization reaction kinetics. Therefore, the FLUENT 6.3.26 code was modified using "C" language programs called as User Defined Functions (UDFs). User Defined Functions were written for the source terms defined in equation (53) and (54), and were attached to the respective transport equation in FLUENT 6.3.26. The source term of monomer species transport equation was linearized with respect to the monomer mass fraction. Similarly, the source term of initiator species transport equation was linearized with respect to the initiator mass fraction. The complete UDFs are given in appendixes.

In the thermal polymerization simulations, only monomer species transport equation was solved, and polymer mass fractions were obtained by subtracting the monomer mass fraction from one. In the BPO initiated polymerization simulations, the initiator and the monomer species transport equation were solved.

The impeller motion was incorporated in the geometry using the Multiple Reference Frames (MRF) technique. A rotating frame was used for the region adjacent to the impeller. This rotating frame region is shown in green color in Figure 4.1 and Figure 4.2. A stationary frame was used for the region far from the impeller, including the tank walls. This stationary frame region is shown, in black color in Figure 4.1 and, in gray color in Figure 4.2. For the rotating reference frame, the frame revolutions were set equal to the impeller revolutions. As a result, the impeller wall became stationary to the rotating reference frame. This method facilitates incorporation of impeller motion even with the complex geometry, and only geometry is needed to introduce the impeller motion. No other velocity specification, on the impeller, is required in this method.

On the inlet, the inlet-velocity boundary condition was used. The inlet velocity, the styrene mass fraction and the temperature were supplied. The inlet boundary fluxes were calculated using these supplied variable values. On the outlet, the outflow type boundary condition was applied. For this boundary condition, zero normal gradients for all variables are assumed. Therefore, there was no diffusive flow normal to the boundary. On the liquid level, the symmetry boundary condition was used hence zero normal gradients and No-penetration were assumed for all variables.

On the tank and the impeller walls, wall boundary condition was used for all the transport equations. Zero diffusive gradients were assumed for the species transport equations on both walls. No-Slip and no-penetration conditions were imposed for the momentum transport equations on the both walls. For the energy equation, fixed temperature was supplied on the tank wall, whereas zero flux normal to boundary was assumed on the impeller wall.

Laminar region was assumed in all the simulations since, the Reynolds number calculated using equation (1) was approximately 20 for the highest impeller speed and the lowest viscosity encountered in the simulations, which is well below 50. Second-order upwind discretization scheme was used to calculate the face fluxes in the momentums, species and energy transport equations. PRESTO scheme was used for the pressure

62

discretization. Velocity-Pressure coupling was solved using SIMPLE algorithm. The governing transport equations were integrated over all the small control volumes. The resultant linear algebraic equations were solved using the Gauss-Seidel iterative method in combination with the Algebraic Multi-Grid method (AMG).

Special solution strategy was needed to achieve the convergence, due to the highly coupled nature of the transport equations in the polymerization. The momentum and energy equations were first solved assuming, that only styrene was present in the flow domain. After getting partially converged solution for the flow, species transport equations were turned on without the source term. Once the non-reactive flow field solution was converged for all the transport equations, the species source terms were introduced in their respective species transport equations. Then, the transport equations were solved in coupled conditions. The under-relaxation factor for the species transport equation was increased gradually as the iteration progresses. Convergence was checked by monitoring residuals as well as surface integral quantities of the variables.

# **Chapter 5 : Results and Discussion**

The styrene polymerizations with and without initiator were simulated. Styrene polymerization, in the presence of an initiator, integrated the thermal and initiator effects, whereas styrene polymerization, in the absence of an initiator, included only the thermal effect. Both types of the polymerization were simulated in a lab scaled CSTR with the detailed specifications given in the model formulation. The polymerization reactor was simulated using the commercially available CFD code FLUENT 6.3.26. CFD approach was adopted here to expose the effect of mixing on polymerization.

Some important issues pertaining to CFD simulations are grid independency, convergence criteria and computational time. These issues will be addressed prior to discussion of the simulation results.

# 5.1 Grid Independency Check

The accuracy of the transport equation solutions depends on the grid resolution of the flow domain. The coarse grid cannot properly resolve the gradients of the flow field variables (velocities, temperature, species mass fractions and pressure) and may give misleading results. The accuracy of the solution increases with increase in grid resolution but the solution of the transport equations on high grid resolution requires more computational time. Hence, it becomes necessary to design a grid that is optimum compromise between desired accuracy and computational cost of the solution. In CFD analysis, it is a common practice to check the dependency of the solution on the grid

resolution. Two grids, named as GRID 1 and GRID 2, were generated for the polymerization reactor using MixSim 2.1.10 software. GRID 1 and GRID 2 contained 372571 and 562435 cells, respectively. Hence, GRID 2 had 1.5 times more cell than GRID 1. On both grids, grid resolution was kept high near the impeller and tank wall to ensure that, the high gradients, present near wall region resolve properly. The continuity and the momentum transport equations, for the non-reactive flow, were solved on both the grids using FLUENT 6.3.26.

The impeller in the model (pitched blade impeller) was an axial flow impeller. Hence the axial velocity was more representative variable of the flow domain. Therefore, after getting the converged solutions for the flow field variables on both the grids, results were compared for the axial velocity just below the impeller. Impeller elevation was 8 cm therefore comparing axial velocity at 7.5 cm elevation ensured that comparison was done in high gradient region. Figure 5.1 shows the axial velocities on a line positioned at the axial location of 7.5 cm for both the grid. Abscissa represents radial position from the centre and ordinate represents axial velocity in meter per second (m/s). The negative axial velocity represents downward velocity in the reactor. The axial velocity profiles on both the grids were in good match as shown in Figure 5.1. In order to quantify the discrepancy, the Root Mean Square (RMS) deviation was calculated:

$$RMS = \frac{\left(\frac{1}{n}\sum_{i=1}^{n} \left(U_{1,i} - U_{2,i}\right)^{2}\right)^{\frac{1}{2}}}{\left(\frac{1}{n}\sum_{i=1}^{n} U_{2,i}^{2}\right)^{\frac{1}{2}}}$$
(66)

where

 $U_1$  = axial velocity on node *i* for GRID 1

 $U_2$  = axial velocity on node *i* for GRID 2

n = number of nodes

The calculated error was 0.78 %, which is acceptable with confidence in the solution accuracy. Hence, the solution of the transport equation on GRID 1 can be considered grid independent. However, it is possible to further refine the grid and get even more accurate results but further refinement in grid increases computational time drastically. Therefore, for all other simulations, Grid resolution was kept same as the resolution of GRID 1.



Figure 5.1: Axial-velocities below impeller on GRID1 and GRID 2

# 5.2 Convergence Criteria

The solution of the transport equations is an iterative process hence the field variables changes with the iteration till the convergence is reached. One of the major challenges in CFD is to assess this convergence, for the field variables of interest. Various convergence criteria exist. The most popular approach is to monitor the residuals of the transport equations with the iteration progress. According to Fluent's user guide (2007), recommended criteria to measure the convergence is that the residuals for the continuity and the momentum equations should decrease to  $10^{-3}$  whereas residuals for the species and the energy equations should decrease to  $10^{-6}$ . Figure 5.2 shows the residual against the iteration progress graph for the simulations conducted for the polymerization reactor.



Figure 5.2: Plot of the residual versus the iterations



The residual for continuity equation was dropped below 10<sup>-6</sup>, whereas for the species and energy transport equations were dropped below 10<sup>-7</sup> and 10<sup>-15</sup>, respectively. However, only residual monitoring did not ensure the convergence of the solutions as the field variables of interest were still changing with the iteration even though the residual was dropped below the recommended criteria. Hence, it became necessary to monitor the field variables itself to assure that they were not changing with the iteration near the convergence. However, monitoring the field variables on a single node may be misleading therefore the field variables were monitored on a surface made of a group of nodes, It was assured that the convergence was reached for each simulation by monitoring the surface integral quantity of the field variables such as sum of the velocity magnitudes on the top liquid surface, un-reacted styrene outflow from the outlet, and the momentum coefficient about the impeller axis. However, volume integral quantity, overall mass, was already been represented in continuity equation hence additional monitoring of volume integral quantities were not needed.

The graph of the sum of the velocity magnitudes on the top liquid surface versus iteration is shown in Figure 5.3. The sum of the velocity magnitude increased up to 40000 iterations then suddenly dropped. This behaviour of the graph was anticipated because for all simulations, initial guess for all the velocity were set to zero. Moreover, the reaction source term was introduced after 40000 iterations. It means there was only styrene in the reactor till 40000 iterations. Hence, as iterations progressed, the velocities on each node were corrected until the convergence was reached for the non-reactive flow. The nonreactive mass (no polymer) possessed low viscosity. Therefore, the impeller was able to generate motion on the top liquid surface. For this reason, the sum of the velocity magnitude increased till 40000 iterations. However, after 40000 iterations, the reaction source term started producing polymer and the reaction mass viscosity increased. Therefore, the impeller momentum was not able to generate motion on top liquid surface. Hence, a sudden drop was seen in the sum of the velocity magnitude on the graph after 40000 iterations.



Figure 5.3: Sum of velocity magnitudes on the top liquid surface versus iteration

The sum of the velocity magnitude monitor graph became flat near 50000 iterations. It means, velocity on each node of the surface was not changing with iteration anymore and the solution of momentum transport equation had reached the convergence.

The solution of the species transport equations gave species mass fractions on each node. These mass fractions on a surface were represented by the mass flow rate for that surface. Hence, monitoring the un-reacted styrene outflow from the outlet boundary, against the iteration progress represented the convergence history of the species transport equations. The convergence history for styrene transport equation is shown in Figure 5.4 for the simulation of the polymerization reactor. As mentioned earlier, species source term was introduced in transport equation of styrene after 40000 iterations. Hence the styrene outflow was constant till 40000 iterations and it can be seen as initial flat portion in the Figure 5.4.



Figure 5.4: Convergence history of the styrene transport equation

After 40000 iterations, the reaction source term (the consumption of monomer per unit volume per time) started building up in the flow domain with the iteration progress. Hence, the styrene outflow decreased with the iteration progress and finally became flat again as the solution approaches the convergence. From initial flat portion to final flat portion, the slop of the graph was changing as under-relaxation factor for the styrene

transport equation was increased in step from 0.8 to 0.99. High under-relaxation factor accelerates the convergence rate but keeping high under-relaxation from the start leads to divergence. Hence, under-relaxation factor was increased slowly as solution progressed towards convergence.

In addition to above-mentioned surface monitors, momentum coefficient about the impeller axis was also monitored to keep the track of the momentum convergence in the impeller region. However, in all simulation runs this monitor graph was getting flat well before other monitors.

In general, the species transport equation for styrene was the last candidate in reaching the convergence. The main cause for the slow convergence of the species transport equation was the non-linear source term (monomer consumption rate).

### **5.3 Computational Time**

The computational time increases with the number of cells and the number of equations in the model and also with the number of iterations required to reach the convergence. The simulated reactor model had approximately 372000 cells, three momentum equations, the continuity equation, the pressure correction, the energy equation and the species transport equation. In addition to these equations, the model had property update equations for density, viscosity, thermal conductivities and specific heat. It also had some other interpolation equations to calculate face values from cell centre values. Moreover, 230000 to 300000 iterations were required to get converged solutions for each simulation. In addition, the source term of the species transport equation was written in 'C' language, User Defined Function (UDF), and it was attached to FLUENT 6.3.26. This linking process also increased computational time because of the communication between the UDF and FLUENT 6.3.26. Each simulation would have taken approximately 96 days on single CPU. (Calculations are based on the linear CPU efficiency interpolation from the actual run).

In order to meet this computational requirement all the simulations were run on Super Computing facilities of HPCVL (High Performance Computing Virtual Laboratory). Each simulation was run in parallel with 24 to 35 dual core SUN Ultra-Spark IV, 1.8 GHz Sun Micro-Systems CPUs. The Grid was partitioned into 24 to 35 parts then one CPU was assigned to each partition. The computational time was reduced to 5 to 6 days using 24 CPUs for each steady state simulation of the polymerization reactor.

Some unsteady state simulations of the polymerization reactor were also tried. For the unsteady state simulations, the ideal time step size should be small enough to resolve all the time dependent features in the flow domain. Hence, the ideal time step size was chosen as the ratio of the cell size and the characteristic flow speed (impeller tip velocity). This ratio was around 10<sup>-9</sup> second, which was not achievable. Therefore, 10<sup>-3</sup> second was chosen to see the computational cost. However, the model required 20 to 100 iterations per time step to reach the convergence. Therefore, each second simulation of the model required 20000 to 100000 iterations approximately. Which means, to simulate the reactor for one hour reaction time, it would require 10 years on Pentium P4 with 2GB RAM and

3.0 GHz single processor CPU. However, this computational time cannot be reduced to feasible range using parallel processing due to data dependency of the current time step solution on the previous time step solution. Hence unsteady state simulation of the polymerization reactor is still in its infancy stage and we need to wait for the advancement in the computational efficiency.

## **5.4 Reactor Simulations**

Thermal and BPO initiated polymerization of styrene in a CSTR were simulated. The simulation results of thermal polymerization of styrene are discussed in section 5.4.1 whereas the BPO initiated polymerization is discussed in section 5.4.2.

### 5.4.1 Thermal polymerization

Thermal polymerization of styrene in a CSTR was simulated to find the effect of mixing on polymerization. Four simulations were conducted to explore the effect of residence time on styrene conversion. Three simulations were done to investigate the effect of the impeller speed on the monomer conversion and homogeneity. Two simulations were run to determine the effect of input-output locations on the monomer conversion and the mixing phenomena. All simulations were done at 140°C temperatures. Although, polymerization reactions are exothermic but on a lab scale reactor isothermal condition is achievable and hence for the simplicity, an isothermal condition was imposed. First, the effect of the impeller speed on mixing is discussed. Next, we will focus on the effect of the impeller speed and the residence time on conversion. The conversion predicted using CFD is compared with experimental data and CSTR model prediction. The effect of the input-output location on the monomer conversion is discussed later.

#### 5.4.1.1 The effect of the impeller speed

Three simulations were done with impeller speed of 100rpm, 500rpm and 1000rpm with the inlet-outlet locations as shown in Figure 4.1. Through the inlet, fresh styrene comes into the reactor. The un-reacted styrene and newly formed polymer leave the reactor through the outlet. In all three simulations, the residence time was kept constant at 144 minutes.

In the perfectly mixed CSTR, there is uniformity in the concentrations of the reactants everywhere in the reactor. Also, there is no variation in the product concentration in the reactor. However, the CFD simulation results showed that the polymerization reactor was not perfectly mixed. Hence, the concentration of styrene was not uniform everywhere in the reactor even at high impeller speed. Figure 5.5 shows the filled contour for the styrene mass fraction for the impeller speed of 100rpm, on a plane aligned to the impeller rotation axis. As shown in the Figure, the fresh styrene entered the reactor at a zone far from the impeller. The convective velocities in this region were low hence the convective flow was not able to sweep away the newly entered styrene fast enough. Therefore, a local styrene rich region formed near the top. The region near the impeller remained rich in polymer. These two separate regions are clearly visible in Figure 5.5. The region near the impeller was perfectly mixed whereas the region far from the impeller remained relatively unmixed.



Figure 5.5: Contour for styrene mass fraction at 100rpm impeller speed and 144min residence time

At low impeller speed, the homogenously mixed region remained small and limited. For this reason, the impeller pulled some mass out of the non-mixed region. This mass was pumped downward because of the downward pumping action of the pitched blade impeller. Then, this down pumped mass was divided into two parts near the impeller because of the impeller symmetry about the axis. Below the impeller, the combined action of the axial and the radial flow pushed the mass in an approximately 45° angled direction about the impeller axis. This flow pattern is visible in Figure 5.5. However, this pattern was not visible when the impeller speed was high. There might be two reasons for the absence of such pattern at higher impeller speed. First, the homogenous region was wide at high impeller speed hence the impeller was not able to pull the mass out of the



non-mixed region. Second, at high impeller speed, the convective velocities in the impeller region were high enough to homogenize the region.

Analysis of the inlet region in the Figure 5.5 revealed another interesting phenomenon. By tracking the pure styrene mass fraction (shown in dark red colour) at the inlet pipe, it can be seen that as soon as the styrene stream entered reactor, it was pushed upward and then rotated in the upper region. In the upper region, pure styrene mixed further with polymer and lost its identity of being pure. This flow behaviour is explained in next paragraph.





fraction)

#### 211 PG0

Antipergeneration (see all end of the second se

### 2 Singel with a second seco

Path lines of the particles released at the inlet were generated to investigate the mixing patterns inside the reactor. These path lines were coloured according to the styrene mass fraction. Therefore, these path lines represent the reaction progress of styrene particles, as they travel through the reactor. The path line behaviour shown in Figure 5.6 can be explained more appropriately by observing the impeller action. The pitch blade impeller generated circular flow oriented downwards below the impeller and upwards near the tank wall. Hence, one can imagine that an upward axial thrust was generated near the wall. This axial thrust pushed upwards any material entering the reactor inlet. This explains the styrene path near the injection point. Such path lines were generated for 100m travels of the particles released at the inlet. It may be possible to generate path lines for more traveled distance, but then path lines would look denser.

The contour for styrene mass fraction for a higher impeller speed of 500rpm is shown in Figure 5.7. There, the impeller delivered more momentum at 500rpm than at 100rpm. The increased momentum in the impeller region led to an expansion of the perfectly mixed region. Comparing the well-mixed regions at 100rpm and 500rpm, expansion of fully mixed region, becomes clear.

At higher impeller speed of 1000rpm, the perfectly mixed region expanded further and touched the inlet location. This is shown in the contour of styrene mass fraction at 1000rpm in Figure 5.8.





Figure 5.7: Styrene mass fraction contour at 500rpm impeller speed and 144min



residence time

Figure 5.8: Styrene mass fraction contour at 1000rpm impeller speed and 144min

residence time



#### 5.4.1.2 Reactive flow and non reactive flow

During a polymerization, the system viscosity increases very rapidly. For example at 35% monomer conversion, reaction mass viscosity increased to 1.9 kg/m s, which is approximately 10000 times of the initial styrene viscosity. Figure 5.9 shows the contours of the medium viscosity for a residence time of 144min and impeller speed of 1000rpm. Density change was minor during the polymerization process. Hence, the effect of the density change on the flow behaviour was insignificant compared to that effect of the viscosity on the flow behaviour.



Figure 5.9: Contour of viscosity (kg/m s) of the reactive mass at 1000rpm impeller speed 144min residence time

The sudden increase in the system viscosity forced us to modify the assumption made earlier to start process of simulation, and which presented difficulties in getting



convergence for the solution of the reactive flow. However, the non-reactive mass (pure styrene at low temperature) had low viscosity hence convergence was straightforward for the non-reactive flow. The velocity magnitude contour for the non-reactive flow is shown in Figure 5.10. The convective flow can be seen all over the interior reactor space because of the low viscosity of the reaction mass. However, when monomer reacted to produce polymer, viscosity increased rapidly. This jumped in viscosity imposed high gradient on the momentum imparted by the impeller. Hence, the convective flow remained limited to the impeller region. This information can be extracted from the contours of velocity magnitude for the reactive flow shown in Figure 5.11. It is worth to note that there is a cavern formation in the reactive flow even at very high impeller speed.



Figure 5.10: Contour of velocity magnitudes (m/s) for the non-reactive mass at 1000rpm

impeller speed and 144min residence time

PROPERTY OF RYERSON UNIVERSITY LIBRARY



#### 5.4.1.3.1 Fixed residence time and variable speed

In the first part of this study, four simulations were carried out to analyse the effect of the agitator speed on the conversion. The residence time was kept at 144 min for this part of the study. For the input-output stream locations shown in the Figure 4.1, styrene conversion versus impeller speed is plotted in Figure 5.12. Looking at the CFD results in the graph, one can see that the conversion was highest at low impeller speed and the conversion decreased as the impeller speed increased. There can be two causes for this decrease in the conversion.



Figure 5.12: Conversion versus Impeller speed for the residence time of 144min Batch data source: Dhib et al. (2000)

First, as the impeller speed increased, the impeller pumped more liquid downward. This flow movement entrained some mass from the styrene rich region into the lesser styrene region near at the bottom. In this way, there was chance for the un-reacted styrene to



leave the reactor from the outlet located near the bottom. Analogically, this flow movement resembles a short-circuiting for the un-reacted styrene at increased impeller speed in this particular type of vessel geometry. Therefore, changing the input-output position as in Figure 4.2 did not allow the occurrence of the short-circuiting, consequently in the absence of which, the conversion did not decreased with the increased impeller speed. This observation is elaborated in detail in the sub-section 5.4.14.

The second reason for the decrease in conversion can be more appropriately explained by looking at the propagation rate equation (equation 67). For a given temperature, the reaction rate constants  $K_p$ ,  $K_t$  and  $K_{th}$  are constant. Therefore, the propagation rate depends only on monomer concentration.

$$R_{p} = -K_{p} [M] [R^{\bullet}]$$
(67)

$$\left[R^{\bullet}\right] \propto \left[M\right]^{1.5} \tag{68}$$

$$[R_P] \propto [M]^{2.5} \tag{69}$$

Hence, the propagation rate was higher in the styrene rich region (near the top). However, this styrene rich region became smaller at higher impeller speed. Therefore, the average propagation rate in the reactor reduced as the impeller speed increased and ended in low polymer formation at higher impeller speed. We can call this effect as the monomer dilution effect on the propagation rate.

Both effects led to decrease in conversion at high impeller speed. This trend was also observed in the experiment conducted for the batch polymerization of styrene by Erdogan et al. (2002).

The difference in the conversion predicted using CSTR model and that predicted using CFD model, can be explained by looking at CSTR model formulation. The steady state CSTR model can be written as follow.

$$0 = -R_p + \frac{Q}{V} \left( M_f - M_e \right) \tag{70}$$

$$0 = -K_p \left[ M_e \right] \left[ R^{\bullet} \right] + \frac{Q}{V} \left( M_f - M_e \right)$$
(71)

where

- $M_f$  = Monomer feed concentration
- $M_e$  = Homogenous monomer concentration

Q = Volumetric flow

V =Reactor volume

In the above equation, the reaction source term is calculated assuming the perfectly mixed CSTR. Therefore, the monomer concentration in the source term is the homogenous monomer concentration in the reactor. However, in the CFD model, the reaction source term was calculated for each individual cell. Hence, the monomer concentration in the cells varied from pure styrene concentration to the final product concentration. Therefore, the conversion predicted using CFD was higher than that predicted using CSTR model.

It can be seen from Figure 5.12 that, the CFD prediction deviated more from the CSTR model at low impeller speed, and the CFD prediction approached the CSTR model prediction at higher impeller speed. As the impeller speed was increased, the CFD results

showed more homogenous mixing in the reactor. The completely homogenous reactor was the assumption of the CSTR model. For this reason, the CFD curve came closer to the CSTR curve with increase in the impeller speed. The CSTR model was not able to consider any non-homogeneity present in the system where the CFD model takes care of non-homogeneity. Therefore, the CFD model gives predictions close to experimental values. Unfortunately, experimental data for styrene thermal polymerization in a CSTR are limited and a full comparison with the CFD model is not possible. No experimental work is available with a detailed geometry specification of CSTR in open literature. Therefore, the batch conversion data are treated as the upper extreme because it is clear that the conversion is always higher in the batch than the CSTR for the same residence time. Experimental data for batch ampoule (no stirring) were taken from the data reported by Dhib et al. (2000). CFD was able to predict the conversion between these two case studies, which are the CSTR model and batch conversion data.

### 5.4.1.3.2 Fixed impeller speed and variable residence time

Four simulation runs were conducted to investigate the effect of the residence time on the conversion keeping the impeller speed at 500rpm. The monomer conversion is plotted against the residence time in Figure 5.13. The conversion predicted using the CFD model was also compared to those obtained from the CSTR model. The CFD curve was close to the CSTR curve at low residence time and it deviated away with an increase in residence time. As discussed in the previous section, this can be explained by the fact that the CSTR model involves the assumption of homogenous mixing. At low residence time, the conversion and the viscosity were low. This condition favoured the mixing and the
system was more mixed at low residence time. Therefore, at low residence time, the CSTR and the CFD predictions approached each other. The experimental conversion data of the batch ampoule is also plotted to show the upper bound for the CSTR conversion.





#### 5.4.1.4 Effect of input/output location

The most important issue in the design of continuous stirred tank reactor is the choice of input-output stream location. The channelling can take place if the inputs and the outputs are very near to each other and then the rest of reactor zone behaves as a dead zone. Setting the output in front of the impeller pumping direction can also lead to channelling. However, placing the input against impeller pumping improves mixing. To analyze the effect of the input-output location on the monomer conversion, two simulations were run with 100rpm and 500rpm impeller speed. The input-output locations were changed to



different positions as shown in Figure 4.2. Figure 5.14 and Figure 5.15 show the contours of styrene mass fraction for the impeller speed of 100rpm and 500rpm, respectively. At 100rpm impeller speed, the styrene jet from the inlet placed at the reactor bottom was able to rise up to the impeller elevation. As soon as the jet touched the impeller, the impeller forces dispersed the jet. Hence, there was only minor non-homogeneity, in the system even at low impeller speed. In Figure 5.14, a layer of rich styrene stretching towards the outlet is visible. This stretching layer was the result of an outlet suction force. However, this pattern was not seen at high impeller speed because at high impeller speed, the impeller forces overcome the outlet suction forces. Therefore it resulted in better homogeneity, at high impeller speed.





residence time





Figure 5.15: Contour of styrene mass fraction for 500rpm and 144min residence time

As expected, the conversion was almost independent of impeller speed and small increase in conversion was seen with the increase in the impeller speed as shown in Figure 5.16. This minute conversion increase may be due to numerical errors. However, the absence of the decreasing trend of the conversion of Figure 5.12 here advocates the absence of short-circuiting in this type of the input-output location configuration. Moreover, the system reached homogeneity at low impeller speed and further increase in impeller speed did not help in increasing homogeneity. Therefore, the strong dependency of the conversion on the impeller speed, seen in earlier configuration of input-output location, was not produced here.





Figure 5.16: Conversion versus Impeller speed for the residence time of 144min

# 5.4.2 BPO initiated polymerization

Benzoyl peroxide (BPO) is a commonly used initiator in the free radical polymerization of styrene. Therefore, the bulk polymerization of styrene in the presence of BPO was simulated to investigate the effect of mixing. CFD simulations of BPO initiated polymerization were more difficult to converge than thermal polymerization simulations. The difficulties rose because of the following two reasons:

First, styrene polymerization in the presence of an initiator involves two-step reaction where initiator decomposes and then, initiates the radical chain by reacting with monomer. Therefore, two species transport equations were required to simulate the polymerization reactor. Moreover, the monomer transport equation was coupled with the initiator transport equation, through the appearance of initiator concentration in the source term of the monomer transport equation. Second, the thermal initiation and the chemical initiation reactions were simultaneously taking place in BPO initiated polymerization. Both of these reactions contributed in forming live polymer radicals. The total live polymer concentration term appeared in the propagation rate equation. Hence, the propagation rate became highly non-linear with respect to the monomer concentration.

The coupling nature of the initiator and monomer transport equations, and the nonlinearity of the source term in monomer transport equation were additional complications compared to thermal polymerization. Moreover, initiator was present in very small quantity compare to the quantity of other species. Therefore, even small truncation error during iteration might have significant effects on initiator convergence. However, no specific rule could be established to get the converged solution and one has to follow trial and error method to get the converged solution for the given flow domain. For all the above-mentioned and some other reasons, the convergence was not straightforward and each simulation needed special treatment of under relaxation factor to get the converged solutions. Furthermore, more than 300,000 iterations were required to get the converged solution, and it took 5 to 6 days with 24 CPUs of the configuration mentioned earlier.

Only few simulations were run due to time intensive nature of the problem and the limitation of the available resources. The study of BPO initiated polymerization of styrene is divided into two parts. First part explains the effect of the impeller speed on the conversion. The effect of the residence time on the conversion will be discussed in the next part.

## 5.4.2.1 Effect of the impeller speed

In this part, three simulations were conducted to study the effect of the impeller speed on the conversion. The impeller speed was varied from 100rpm to 1000rpm. The residence time, BPO concentration at the inlet and temperatures were kept constant at 200min, 0.01mol/L and 120°C, respectively for this part of study. The contour of styrene mass fractions for the impeller speed of 100rpm is shown in Figure 5.17.



Figure 5.17: Contour of styrene mass fraction for 100rpm impeller speed, 200min residence time, temp 120°C, BPO conc. 0.01mol/L at the inlet

One can see from the Figure 5.17 that the basic flow pattern was similar to that in thermal polymerization. The path lines of the particles released at the inlet, the homogeneously mixed region near the impeller and the unmixed region far from the impeller, visually



looked unaffected with the addition of the initiator. One reason was that, the initiator quantity was very low in the mixture and therefore the density and viscosity of a mixture practically remained unaltered by the initiator presence. Even though, initiator made the reaction fast, it merely reduced the residence time for the required conversion.



Figure 5.18: Contour of the percentage conversion for 100rpm impeller speed, 200min residence time, temp 120°C, BPO conc. 0.01mol/L at the inlet

The contour of conversion was produced to investigate the reaction progress at different locations in the reactor. Figure 5.18 shows the contour of the percentage conversion in the reactor plane for 100rpm impeller speed. Less than 4% conversion took place in the inlet pipe. The quality of polymer formed in the inlet pipe would have the characteristic similar to those formed in the tubular reactor. The inlet pipe was short hence the polymer formed in the inlet pipe would not affect the overall product quality appreciably. Moreover, it



is worth to note that up to 20% conversion took place in the segregated region. The polymer formed in this segregated region has high polydispersity index and therefore, affected the overall product quality.



Figure 5.19: Contour of initiator mass fraction for 100rpm impeller speed, 200min residence time, temp 120°C, BPO conc. 0.01mol/L at the inlet

Additionally, the polymer qualities depend on local initiator concentration. One can see, from the contour of initiator mass fraction shown in Figure 5.19, that the initiator concentration was not uniform in the region far from the impeller. Consequently, one may expect that molecular weight of polymer chains cannot be uniform, nor, the polydispersity index in the upper region. Another parameter affecting the polymer quality is the propagation rate. The effect of the impeller speed on the propagation rate can be seen from the contours of the propagation rate shown in Figure 5.20 and Figure 5.21 for



the impeller speed of 100rpm and 500rpm, respectively. It is obvious that the propagation rate was very high in the upper region of the reactor in both cases. However, the region having very high propagation rate was larger at 100rpm impeller speed than the region at 500rpm. For this reason, the overall conversion was higher at low impeller speed.



Figure 5.20: Contour of propagation rate (kg/m<sup>3</sup> s) for impeller speed 100rpm, 200min residence time, temp 120°C, BPO initiator conc. 0.01mol/L at the inlet

The overall conversion is plotted against the impeller speed in Figure 5.22. The decreasing trend of the conversion is obvious because of the reasons similar to the thermal polymerization study.





Figure 5.21: Contour of propagation rate (kg/m<sup>3</sup> s) for impeller speed 500rpm, 200min residence time, temp 120°C, BPO initiator conc. 0.01mol/L at the inlet

The conversion predicted using CFD was compared to that obtained with the CSTR model. The CSTR model for BPO initiated polymerization is as follows:

For initiator 
$$0 = -K_d I + \frac{Q}{V} \left( I_f - I_e \right)$$
(72)

For monomer 
$$0 = -K_p [M_e] \sqrt{\frac{2fK_d I_e + 2K_{th} M_e^3}{K_t}} + \frac{Q}{V} (M_f - M_e)$$
(73)

where  $I_f$  and  $I_e$  are the initiator concentration in the feed and outlet, respectively, and Q/V is the inverse of the residence time. Both equations were solved using MATLAB to



get the conversion of initiator and monomer for a fix residence time. The conversion is then plotted in Figure 5.22.



Figure 5.22: Conversion versus impeller speed for 200min residence time, temp 120°C,

BPO initiator conc. 0.01mol/L at the inlet

The CSTR model assumes a perfectly mixed reactor. However, the CFD results showed that the reactor could not be perfectly mixed up to 500rpm. Therefore, for impeller speed up to 500rpm, the monomer and initiator conversions predicted using CFD model were higher than those obtained with the CSTR model. The deviation in the conversion at 1000rpm impeller speed can be explained by analyzing the contour of styrene mass fraction shown in Figure 5.23. It is obvious that the reactor achieved complete homogeneity at 1000rpm impeller speed. Therefore, the conversion obtained using CFD should match the CSTR prediction at 1000rpm impeller speed, if no short-circuiting is taking place in the system. In contrast to this, the CFD predicted conversions were lower



than the CSTR predicted conversion at 1000rpm as shown in Figure 5.22, indicating that styrene short-circuiting was taking place in the reactor.





### 5.4.2.2 Effect of the residence time

Lastly, the effect of the residence time on conversion was investigated. Three simulations were run with the residence time of 150min, 200min and 326min. The impeller speed, the temperature and the BPO concentration at the inlet were kept constant at 100rpm, 120<sup>o</sup>C and 0.01mol/L, respectively. The monomer and the initiator conversion obtained from the CFD solutions are plotted against the residence time in Figure 5.24. The conversions



obtained from the CSTR model are also plotted in Figure 5.24 for the comparison purpose.



Figure 5.24: Conversion versus residence time for 100rpm impeller speed, temp 120°C, BPO initiator conc. 0.01mol/L at the inlet

The conversion trend was similar to that seen in the study of thermal polymerization. The differences in conversions obtained with CFD models and the CSTR model remained small at low residence time. The differences were apparent because the CSTR model could not include the non-homogeneity present in the system. However, the conversion and the viscosity were low at low residence time hence less non-homogeneity was present in the reactor. Longer residence time allowed the viscosity to increase. This raised viscosity promoted non-homogeneity in the reactor. The presence of non-homogeneity contradicted the assumptions made for the CSTR model development.

-

Therefore, the difference in the conversions predicted by both models increased with an increase in residence time.

It was noticed that the convergence became more difficult for longer residence time runs. The presence of high gradients of the flow field variables at high residence time is likely the reason causing numerical difficulties. However, high gradient simulations were easily obtained in the thermal polymerization case study.

# **Chapter 6 : Conclusion and Future Recommendations**

# 6.1 Conclusion

Computational Fluid Dynamics (CFD) technique was exploited to investigate the effect of mixing on the polymerization of styrene in a lab scale CSTR. All simulations were run on supercomputing facilities using 24 to 35 CPUs for each simulation. Difficulties were encountered in getting the converged solution for the flow field variables in the CSTR because of the complex back mixing involved in the CSTR and the highly coupled nature of the governing transport equations of the polymerization. The polymerization kinetics was simplified to avoid convergence difficulties and to reduce the computational time. However, the CFD model was able to predict the coupled transport phenomena of the polymerization reactor. The required computational time was still high for a single CPU even after the simplifications of the polymerization kinetics.

The thermal polymerization and BPO initiated polymerization of styrene in a CSTR were simulated using the CFD. Flow visualization inside the polymerization reactor was made possible using the CFD model. The path lines of the particles, released at the inlet, were analyzed for a better understanding of the flow behavior. Various contours of the variations of styrene mass fraction, viscosity, conversion, reaction rate and velocity magnitudes, were generated to show the effect of mixing. The simulation results showed that the basic flow behavior remained the same in thermal polymerization and BPO

124

initiated polymerization. The qualitative trends of conversion, exhibiting the effect of the mixing parameters, looked similar in both polymerizations.

The CFD analysis revealed the presence of non-uniform mixing regions within the reactor. Also, the CFD simulation results illustrated that the region near the impeller was perfectly mixed and the regions far from the impeller remained unmixed, due to high reaction mass viscosity.

The effects of the impeller speed, the residence time and the input-output stream location on the conversion and the flow behavior of the system were analyzed. It was found that with the increase in the impeller speed, the perfectly mixed region near the impeller expands and reduces the non-homogeneity in the CSTR. It was also observed that the non-homogeneity was larger at the high residence time than at the low residence time, for the same impeller speed. The CFD results pointed that placing the styrene feed at the bottom and near the impeller, help in achieving a high degree of homogeneity even at the low impeller speed.

The conversion was not depended on the impeller speed, when styrene feed was located at the bottom and near the impeller. However, irrespective of the input stream location, when the reactor outlet was located at the bottom, in the pumping direction of the impeller, there was a short-circuiting of the un-reacted styrene. This short-circuiting of the un-reacted styrene was found more pronounced at high impeller speed than at low impeller speed. Therefore, the conversion decreased with the increase in impeller speed.

125

The conversions predicted using the CFD model was compared to those obtained from the CSTR model and batch experimental data. It was shown that the conversion predicted using the CSTR model and the batch experimental data could be treated as the minimum and the maximum limit, respectively, of the achievable conversion in a CSTR. The conversion predicted using the CFD model lied in between these two limits. However, the conversion predicted using the CFD model deviated more from those predicted using the CSTR model, at high residence time and at low impeller speed. It was found that the presence of non-homogeneity and the short-circuiting of the un-reacted styrene in the reactor caused the observed deviation. The CSTR model was unable to consider the nonhomogeneity and the short-circuiting the conversion. It was shown that the CFD model predicted the conversion much better than the CSTR model, by taking into account the short-circuiting and the non-homogeneity of the system. The CFD model was shown to be a useful tool in simulation of polymerization reactor and helps for a better reactor design.

# **6.2 Future Recommendations**

In the presented study, some assumptions were made during the model development process to reduce the computational time and to avoid the convergence problems. However, these assumptions may have significant effects on the flow behaviour and should not be neglected in the model developed for the industrial scale reactor. Therefore, some recommendations are presented below to improve the model for wide scope applications.

- The model used for CFD analysis assumed the isothermal condition only. This condition is achievable on lab scale reactor, but industrial reactors can not be operated on isothermal conditions, because of the high viscosity. Therefore, it will be of immense benefit to the industry, if it's feasible to get the converged solutions for non-isothermal conditions within a reasonable computational time.
- One of the major challenges being faced by the polymer industry is in getting the mono-disperse or the polymer with low polydispersity. Therefore, the knowledge of spatial variation of the molecular weight distributions, inside the reactor, will be useful in the reactor design, to provide uniform polymer quality. It is possible to solve the polymer moment equations for the given flow domain. However, it would add some extra computational time, but with the advancement in computational efficiency, it would be possible to incorporate the moment equation in the model.
- Unsteady-state simulations of the polymerization reactor were tried, but it was not possible to get the converged solutions for the specified instance, due to high computational time of the simulations. Looking at the present trend of improvement in computational efficiencies, the complete unsteady-state simulations of the polymerization reactor would be possible in near future.

# Nomenclature

- $\vec{A}$  Area vector
- $A_f$  Area of the face f
- A Pre- exponential
- *a* Linearized coefficients
- *b* Constant part of source or net flow rate into the cell
- *BPO* Benzoyl peroxide
- $C_p$  Specific heat
- $D_m$  Diffusivity of species *j* in the mixture
- D Impeller diameter, m
- $d_f$  A function of the momentum coefficients of the cells adjacent to face

١

- E Activation energy
- *e* Total energy
- $\vec{F}$  External forces
- f Initiator efficiency, or face
- g Gravitational acceleration,  $m/s^2$
- h Enthalpy
- $h_f$  Fluid side local heat transfer coefficient
- *I* Initiator

- $I_f$  Initiator concentration in the feed
- $I_e$  Initiator concentration in the reactor
- J Diffusive flux
- $J_f$  Mass flux through the face f
- *K* Rate Constant or Consistency index
- *k* Thermal conductivity
- N Impeller speed, rev/s
- $N_{faces}$  Number of faces in a cell
  - *n* Number of nodes
  - M Monomer
- $M_e$  Homogenous monomer concentration
- $M_f$  Monomer feed concentration
- $M_{w}$  Molecular weight
- $\dot{m}$  Mass flow rate entering the cell
- *P* Pressure
- *Q* Volumetric flow rate
- q Heat flux from the fluid cell to the wall
- *R* Reaction rate
- $R^{\bullet}$  Radical

- $R_g$  Universal gas constant
- $R_i$  Reactive source term for the  $j^{th}$  species
- $R^{\phi}$  Un-scaled residual
- $R^c$  Un-scaled residual for the continuity equation
- $\vec{r}$  Position vector from the origin of the rotating reference frame
- *S* Source term in respective equation
- $S_p$  Variable part of the source term
- T Temperature, K
- $T_f$  Local fluid cell temperature
- $T_w$  Wall temperature
- $U_1$  Axial velocity below impeller on GRID 1
- $U_2$  Axial velocity below impeller on GRID 2
- *u* Velocity in x-direction
- $\vec{u}_r$  Velocity due to the moving frame
- *V* Volume of a cell or a reactor
- W Weight fraction in cell
- *w* Weight fraction from CSTR model
- X Co-ordinate of 3D
- *Y* Mass fraction

## Greek Symbols

- $\alpha$  Under relaxation factor
- $\rho$  Density of the mixture, kg/m<sup>3</sup>
- $\vec{v}$  Velocity vector
- $\vec{v}_r$  Velocity viewed from the rotating frame
- $\vec{\omega}$  Rotational axis vector
- $\vec{\overline{\tau}}$  Stress tensor
- $\phi$  General variable
- $\widetilde{\phi}_f$  Average value of the  $\phi$  in the two adjacent cells sharing the face
- $\Gamma$  Diffusion coefficient of the variable
- $\gamma$  Shear rate, sec<sup>-1</sup>
- $\mu$  Dynamic viscosity, Pa.s
- $\mu_0$  Zero shear viscosity
- $\nabla$  The Vector differential operator
- $(\nabla \phi)_n$  Magnitude of  $\nabla \phi$  normal to face f

## Subscripts

- 0 Zero-shear rate
- avg Average
- c0,c1 Face adjacent cells
  - d Decomposition
  - f Face value

- *i* Node index
- ini Initiation
- *j* Species index
- *m* Monomer
- *nb* Neighbors cell
- *p* Propagation or cell center value or pressure
- P Polymer
- *r* No. Of monomer units, r
- s No. Of monomer units. S
- *tc* Termination by combination
- th Thermal initiation
- *up* Upstream cell value

#### Notations

- [] Concentration of respective molecules
- \* Initial guessed value
- $\wedge$  Correction in respective variable

# References

Alexopoulos A. H., Maggioris D. and Kiparissides C., "CFD analysis of turbulence non-homogeneity in mixing vessels A two-compartment model", Chem. Eng. Sci., 57(10), pp 1735-1752, (2002)

Atiqullah M. and Nauman E. B., "A model and measurement technique for Micromixing in Co-polymerization Reactors", Chem. Eng. Sci., 45(5), pp 1267-1279, (1990)

Baade W., Moritz H. U. and Reichert K. H., "Kinetics of high conversion polymerization of vinyl acetate. Effect of mixing and reactor type on polymer properties", J. of Appl. Polym. Sci., 27(6), pp 2249-2267, (1982)

Bakker A., Haidari A. H. and Marshall L. M., "Design reactors via CFD", Chem. Eng. Progress, 97(12), pp 31-39, (2001)

Bhat S. A., Sharma R. and Gupta S. K., "Simulation and optimization of the continuous tower process for styrene polymerization", J. of Appl. Polym. Sci., 94(2), pp 775-788, (2004)

Bird R. B., Stewart W.E. and Lightfoot E.N., "Transport Phenomena", New York, J. Wiley, (2002)
Boodhoo K.V.K. and Jachuck R.J., "Process intensification: spinning disk reactor for styrene polymerization", Appl. Thermal Eng., 20(12), pp 1127-1146, (2000)

Brooks B. W., "Why are polymerization reactors special?" Ind. Eng. Chem. Res., 36(4), pp 1158-1162, (1997)

Chen M.S.K. and Fan L.T., "A reversed Two-environment model for micro-mixing in a continuous flow reactor", Can. J. of Chem. Eng., 49, pp 704-708, (1971)

Cole W. M., "Experimental Study of Mixing Patterns in Continuous Polymerization Reactors and their Effect on Polymer Structure", AICHE symposium series, 72(160), pp 51-60, (1975)

Dhib R., Goa J. and Penlidis A., "Simulation of free radical bulk/solution homopolymerization using mono- and bi-functional initiators" Polymer Reaction Eng., 8(4), pp 299-464, (2000)

Dierendonck L. L. V., Bouter J. A. and Ostendorf H. K., "The development of a special stirrer device for mixing in homogenous continuous polymerization reactors", Chem. Eng. Sci., 35(1), page 476-482, (1980)

Duerksen J. H., "Free radical polymerization of styrene in continuous stirred tank reactors", Ph. D. thesis, McMaster University, (1968)

Erdogen S., Alpbaz M. and Karagoz A. R., "The effect of operational conditions on the performance of batch polymerization reactor control", Chem. Eng. J., 86(3), pp 259-268, (2002)

Fields S. D. and Ottino J. M., "Mixing effects during polymerization by the adiabatic temperature rise technique", AICHE Journal, 33(1), pp 157-160, (1987)

Fluent's User Guide, Fluent Inc. Lebanon, NJ, USA, (2007)

Gao J. and Penlidis A., "A comprehensive simulator/database package for reviewing free-radical homo-polymerizations", J. Macromol. Sci. Rev. Macromol. Chem. Phy., C36, pp 199-404,(1996)

Harada M., Tanaka K., Eguchi W. and Nagata S., "The effect of micro-mixing on the homogeneous polymerization of styrene in a continuous flow reactor", J. of Chem. Eng. of Japan, 1(2), pp 148-152, (1968)

Heidarian J., Nayef M. G. and Wan M.A.W.D., "Effects of the temperature and mixing rate on foaming in a polymerization reaction to produce fatty polyamides in the presence of catalyst", Ind. Eng. Chem. Res., 43(19), pp 6048-6054, (2004)

Hiatt R. R. and Bartlett T., "The thermal reaction of styrene with ethyl thioglycolate; evidence for the termolecular thermal initiation of styrene polymerization ", J. Am. Chem. Soc., 81(5), pp 1149-1154, (1959)

Hosogai K. and Tanaka M., "Effect of impeller diameter on mean droplet diameter in circular loop reactor", The Can. J. of Chem. Eng., 70, pp 645-653, (1992)

Hui A. W. and Hamielec A. E.," Thermal polymerization of styrene at high conversion and temperatures an experimental study ", J. of Appl. Polym. Sci., 16(3), pp 749-769, (1972)

Hui A. W. T., "Free radical polymerization of styrene in a batch reactor up to high conversion", a thesis, McMaster University, (1967)

Kaflas G. A., "Experimental studies and mathematical modeling of aqueous suspension polymerization reactors", Ph. D. Thesis, Uni. of Wisconsin, Madison (1992)

Kemmere M. F., Meuldljk J., Drinkenburg A. A. H. and German A.L., "Emulsification in Batch-Emulsion Polymerization of Styrene and Vinyl Acetate: A Reaction Calorimetric Study", J. of Appl. Polym. Sci., 79(5), pp 944-957, (2001) Kim D. M. and Nauman E. B., "Solution viscosity of Polystyrene at conditions applicable to commercial manufacturing processes", J. Chem. Eng. Data, 37(4), pp 427-432, (1992)

Kim J. Y. and Laurence R. L., "The Mixing Effect on the Free Radical MMA Solution Polymerization", Korean J. Chem. Eng., 15(3), pp 273-286, (1998)

Kolhapure N. H. and Fox R. O., "CFD analysis of micro mixing effects on polymerization in tubular low density polyethylene reactors", Chem. Eng. Sci., 54(15), pp 3233-3242, (1999)

Lee Y. M. and Lee L. J., "Effect of mixing and reaction on a fast step growth polymerization", Int. Polym. Process, 1, pp 144-154, (1987)

Louis S. H., "Stability analysis of polymerization in continuous stirred tank reactors", Chem. Eng. Progress, March, pp 42-50, (1987)

Lu Y. and Biesenberger J.A., "Effect of reactor type on product: a back-mix reactor for polymerization and other viscous reaction media", Polym. Eng. and Sci., 37(6), pp 1036-1044, (1997)

Magnussen B.F. and Hjertager B. H.,"On the mathematical model of turbulent consumption with special emphasis on soot formation and combustion", Proc. 16<sup>th</sup> Int. Symposium on Combustion, The combustion Institute, Pittsburgh, PA (1976)

Mahling F. O., Daib A., Kolhapure N. and Fox R. O., "CFD analysis of heat transfer and initiator mixing performance in LDPE high pressure tubular reactors", European Symposium on Computer Aided Process Engineering-10, pp 427-432, (2000)

Mayo F.R., "The dimerization of styrene", J. American Chem. Soc., 90(5), pp 1289-1295, (1968)

McKenna T. F., Cokljat D. and Wild P., "CFD modeling of heat transfer during gas phase olefin polymerization", Computers Chem. Eng., 22(Suppl.), pp s285-s292, (1998)

Meszena Z. G. and Johnson A. F., "Prediction of the Spatial Distribution of the Average Molecular Weights in Living Polymerization Reactors using CFD Methods", Macromolecular theory and simulation, 10(2), pp 123-135, (2001)

Middleton J.C., Pierce F., Lynch P.M., "Computations of flow fields and complex reaction yield in turbulent stirred reactors and comparison with experimental data", AICHE Symposium series, 87, pp 239-246,(1984)

Mitchell G., "Effect of agitator geometry and speed on suspension polystyrene particle formation", A Master's thesis, McMaster University, (1986)

Moritz H. U., "Increase in Viscosity and its influence on polymerization processes", Chem. Eng. Technol., 12(1), pp 71-87, (1989)

Ozdeger E., Sudol E. D, El-Aasser M. S. and Klein A., "Role of mixing in copolymerization of styrene and n-Butyl Acrylate", J. of Appl. Polym. Sci., 69(11), pp 2277-2289, (1998)

Patanakar S. V. and Spalding D. B., "A calculation procedure for heat, mass and momentum transfer in Three-dimensional parabolic flows", Int. J. Heat and Mass transfer, 15(10), pp 1787-1806, (1972)

Paul E. L., Victor A. O. and Kresta Suzanne M., "Handbook of industrial mixing", New York, Chichester Wiley, (2004)

Prochukhan Yu A., Minsker K. S., Karpasas, Berlin A. A., Bakhitova R. K. and Yenikolopyan N. S., "Effect of mixing methods on the character of ultra-fast polymerization processes", Polymer science, U.S.S.R., 30(6), page 1317-1321, (1988)

Randick J. J., "Simulation of scale-up effects on stirred chemical reactors", A Master's thesis, University of Missouri-Rolla, (2000)

Robertson E. R., "Diffusion control in the polymerization of methyl methacrylate and styrene", Trans. Faraday Soc., 52, pp 426-437, (1959)

Soliman M. A., Aljarboa T. and Alahmad M., "Simulation of free radical polymerization reactors", Polym. Eng. and Sci., 19(34), pp 1464-1470, (1994)

Tanaka M. and Izumi T., "Application of stirred tank reactor equipped with draft tube to suspension polymerization of styrene", J. of Chem. Eng. of Japan, 18(4), pp 354-358, (1985)

Tefera N., Weickert G. and Westerterp K. R., "Modeling of free radical polymerization up to high conversion. I. A method for the selection of models by simultaneous parameter estimation", J. of Appl. Polym. Sci., 63(12), pp 1649-1661, (1997)

Tosun G. and Bakker A., " A study of macro-segregation in Low-Density Polyethylene autoclave reactors by Computational Fluid Dynamics modelling", Ind. Eng. Chem. Res., 36(2), pp 296-305, (1997)

Tosun G., "A mathematical model of mixing and polymerization in a semi batch stirred tank Reactor", AICHE journal, 38(3), pp 425-437, (1992)

Tsai K. and Fox R. O.," PDF modelling of turbulent-mixing effects on initiator efficiency in a tubular LDPE reactor", AICHE Journal, 42(10), pp 2926-2940, (1996)

Versteeg H. K. and Malalasekera W. "An introduction to computational fluid dynamics the finite volume method", Pearson Prentice Hall, (1995)

Villa C. M., Dihora J. O. and Ray W. H., "Effects of imperfect mixing on low-density polyethylene reactor dynamics", AICHE Journal, 44(7), pp 1646-1656, (1998)

Villalobos M. A., Hamielec A.E. and Wood P.E., "Bulk and Suspension polymerization of styrene in the presence of n-Pentane. An evaluation of monofunctional and Bi-functional initiation" ,J. Appl. Polym. Sci.,50(2), pp 327-343, (1993)

Villermaux J., "A simple model for partial segregation in a semi-batch reactor", AICHE meeting, San Francisco, paper 114a, (1989)

Wells G.J. and Ray W.H., "Investigation of imperfect mixing effects in the LDPE autoclave reactor using CFD and compartment models", DECHEMA monographs, 137, pp 49-59, (2001)

Wilkens R J., Henry C. and Gates L. E., "How to scale-up mixing processes in Non-Newtonian fluids", Chem. Eng. Prog., 99(5), pp 44-52, (2003) Yang B. and Takahashi K., "Effect of an unsteady agitation method on drop coalescence characteristics in suspension polymerization of styrene", The Can. J. of Chem. Eng., 79, pp 760-765, (2001)

Zhou W., Marshall E. and Oshinowo L., "Modelling LDPE tubular and autoclave reactor", Ind. Eng Chem. Res., 40(23), pp 5533-5542, (2001)

Zhu L., Narh K. A., Hyun K. S., "Investigation of mixing mechanisms and energy balance in reactive extrusion using three dimensional numerical simulation method", Int. J. of heat and mass transfer, 48(16), pp 3411-3422, (2005)

## **Appendices**

## **Appendix A: UDF for the thermal polymerization**

The following is the program written in 'C' language to incorporate the reaction source term, in the species transport equation of monomer, for the thermal polymerization simulation. The program can be linked to FLUENT 6.3.26.

#include "udf.h"
#define KTHO 2.19e+5
#define THENG 2.7440e+4
#define GASR 1.987
#define GASR 1.987
#define KTCO 8.2e+9
#define TERMENG 3.47129e+3
#define KPO 2.17e+7
#define PROPENG 7.75923e+3
DEFINE\_SOURCE(thermoini\_source,c,t,dS,eqn)
{
 real lamda;
 real source;
 real kth , ktc,kp;
 real molconc;

kth = KTHO \* (exp( (-THENG) / (GASR \* C\_T(c,t)))); /\* ktho is converted in m3 per kgmol3 per sec \*/

 $ktc = KTCO * (exp((-TERMENG) / (GASR * C_T(c,t))));$ 

 $kp = KPO * (exp((-PROPENG) / (GASR * C_T(c,t))));$ 

 $molconc = (C_YI(c,t,0) * C_R(c,t)) / 104.12;$ 

lamda = sqrt(2.0 \* kth \* pow(molconc,3.0) / ktc ) ;/\* radical concentration \*/ source = -kp \* 104.12 \* molconc \* lamda; /\* kg of monomer per m3 per time \*/ dS[eqn] = -kp \* lamda \* (C\_R(c,t) / 104.12) ; /\*derivative of source term \*/ return source;

}

## Appendix B: UDF for the BPO initiated polymerization

The following is the program written in 'C' language to incorporate the reaction source term, in the species transport equation of monomer and initiator, for the BPO initiated polymerization simulation. The program can be linked to FLUENT 6.3.26.

#include "udf.h" #define KTHO 2.19e+5 #define THENG 2.7440e+4 #define GASR 1.987 #define KTCO 8.2e+9 #define TERMENG 3.47129e+3 #define KPO 2.17e+7 #define PROPENG 7.75923e+3 #define KDO 3.81600000e+9 #define KDENG 2.732540000e+4 DEFINE SOURCE(sty source,c,t,ds,eqn) { real lamda; real source; real kth ,ktc ,kp ,KD; real molconc; real iniconc; real parta, partb, partup, partdown;

kth = KTHO \*  $(exp((-THENG)/(GASR * C_T(c,t))));$ 

ktc = KTCO \* (exp((-TERMENG)/(GASR \* C\_T(c,t))));

 $kp = KPO * (exp((-PROPENG)/(GASR * C_T(c,t))));$ 

 $KD = KDO *(exp((-KDENG)/(GASR * C_T(c,t))));$ 

molconc =  $(C_YI(c,t,0) * C_R(c,t))/104.12;$ 

iniconc =  $(C_YI(c,t,1) * C_R(c,t))/242.00;$ 

parta =  $(2.0 * \text{kth} * \text{pow}(\text{kp},2.0) * \text{pow}((C_R(c,t)/104.12),5.0))/\text{ktc};$ 

 $partb = (2.0 * 0.8 * KD * pow(kp,2.0) * pow((C_R(c,t)/104.12),2.0))/ktc;$ 

partup = -(( $5.0 * \text{ parta } * (\text{pow}(C_YI(c,t,0),4.0)))$ +( $2.0 * \text{ partb } * C_YI(c,t,0))$ );

partdown = (2.0 \* sqrt((parta \* (pow(C\_YI(c,t,0),5.0)))+(partb \*

(pow(C\_YI(c,t,0),2.0))));

lamda = sqrt(((2.0 \* kth \* pow(molconc, 3.0))+(2.0 \* 0.8 \* KD \* iniconc))/ktc);

source = -kp \* 104.12 \* molconc \* lamda;

```
ds[eqn] = partup / partdown ;
```

return source;

}

```
DEFINE_SOURCE(ini_source,c,t,ds,eqn)
```

```
{
```

```
real sourcei;
```

real KD1;

real iniconc1;

 $KD1 = KDO * (exp((-KDENG)/(GASR * C_T(c,t))));$ 

iniconc1 =  $(C_YI(c,t,1) * C_R(c,t)) / 242.00;$ 

sourcei = -KD1 \* 242.00 \*iniconc1;

 $ds[eqn] = -KD1 * (C_R(c,t) / 242.00);$ 

return sourcei;

}