Comparative Study of Different Mathematical Models of Ozone Mass Transfer in a Kenics Static Mixer

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Abstract

Static mixers have been successfully employed in water and wastewater treatment, particularly in water ozonation for disinfection and oxidation purposes. Producing higher concentration of ozone requires new contactors that operate efficiently at low gas/liquid ratio. The Kenics static mixer (KM) can meet these requirements and therefore enhance the ozone mass transfer rate [1]. The main objective is to investigate the correspondence between the transient BFCM of Romer and Durbin [2] and the axial diffusion model (ADM) and the continuous flow stirred tanks in series(CFSTR's in series) in their prediction to the residence time distribution of the gaseous solute inside a Kenics static mixer. The residences time distribution (RTD) curves produced from the experiment of Madhuranthaam et al. [3] have been used to validate and compare the predicted RTD curves of the three models. The BFCM model provides accurate, reliable, flexible and easy design model to describe the back-mixing in the liquid phase inside the Kenics static mixer.

Keywords: Static mixer; Back flow cell model; Axial diffusion model; Water ozonation.

1. Introduction

A lot of processes in the field of chemical engineering are based on the chemical reaction between the solute gas and soluble species present in liquid. In nature, gas diffuses into the liquid through gas–liquid interface due to the concentration difference of the gas between the liquid at the surface and the liquid bulk without mechanical energy. But, the gas mass transfer rate is low and the reaction rate is also low. Therefore, gas-liquid contactors such as static mixers are used to obtain a higher gas mass transfer rate and correspondingly faster reaction. These contactors enhance the mass transfer rate by increasing surface area between the gas and liquid and increasing the intensity of turbulence [4, 5]. The ozonation process is practiced by dissolving gaseous ozone into the liquid water so as to react with target contaminants. Water ozonation is usually consists of four steps: convection and back mixing of the liquid flowing through contacting chambers inside the static mixer. These two processes occur simultaneously with two other processes: ozone gas mass transfer from gas phase to the liquid phase, ozone decomposition and reactions of ozone with organic material in the water [6]. The Kenics static mixer consists of a series of fixed helical elements or blades installed inside tubular housing as shown in Figure 1.1. KM provides continuous blending and dispersion of the flowing materials, with no moving parts, and no external power or regular maintenance, by redirecting the flow patterns present in the open pipe. The Kenics static mixer has an advantage over other types of static mixer in that; it enhances the rate of mass transfer without wasting energy or material blockage. Moreover, the helical elements promote plug flow in continuous processes. The pressure drop increases along the mixer providing the energy need for mixing process [7, 8, 9].

Almost all the mathematical models that are developed to predict the performance of the ozone contactors are based on one of the following two assumptions: complete mixed flow or plug flow exist in the liquid phase. Applying these assumptions in modeling the gas-liquid contactors will underestimate the performance of the ozone contactor. Because of phe-

Figure 1.1: The structure of Kenics static mixer

nomena of the axial dispersion of the liquid phase, the real flow regime is closer to mixed flow than the plug flow, but it is not perfectly mixed flow. Thus, the back flow cell model (BFCM) has been developed as an alternative way to describe the hydrodynamics and mass transfer of the ozone inside the Kenics static mixer [11]. The BFCM is a general form of stage-wise backmixing models and it can be used to characterize the backmixing in the liquid phase for co-current or counter-current gas-liquid contactors at steady state or unsteady state operating conditions [12].

2. Mathematical Models of Ozone Mass Transfer in a Kenics Static Mixer

2.1. Transient Back Flow Cell Model (TBFCM)

The developed models for designing gas-liquid reactors must describe the flow and mixing conditions inside the reactor. The most common ideal reactors are that used to design ozone contactor are the plug flow reactor (PFR) and the continuous flow stirred tank reactor (CFSTR). The PFR approaches the plug flow conditions. Therefore, the mixing between the adjacent flow cells is not permitted whereas, the CFSTR is considered to be perfectly mixed and has uniform concentration along the column [13]. Due to backflow, short-circuiting and stagnant zone, these two ideal flows are no longer applicable to describe the real flow inside the ozone contactors. The residence time distribution can be used to analyse these complicated flow characteristic in the ozone contactor [11]. The ordinary stirred tanks in series model which assume perfect mixed cells has been employed to describe the mixing process. However, this model does not take into consideration the upstream mixing of material i.e. the mixing in direction opposite to the direction of the main flow. In order to overcome this problem, the backflow cell model has been developed by Mecklenburg and Hartland [12]. The BFCM introduces the backflow between the cells inside the gas-liquid contactor. The backflow ratio, B is the main parameter in the BFCM. The performance of the back flow cell model varies according to the value of the backflow ratio from ordinary tanks in series ($B \to 0$) to single stirred tank ($B \to \infty$) [2, 14, 15]. The BFCM is a mathematical model that is applied to characterise the performance of the Kenics ozone static mixer. In order to describe the axial dispersion in the liquid phase, the BFCM assumes a back flow between the cells in direction opposite to the main liquid flow and exchange flow in the same direction of the main liquid flow. These two flows have been expressed as back flow ratio (B) and exchange flow ratio (B) and both of them are assumed to be equal and constant along the mixer. Generally, BFCM is composed of two series of equal number of completely mixed cells in which one series describe the liquid phase and the other describes the gas phase [16]. In this model, the backmixing in the gas phase was assumed to be negligible because of the large buoyancy of the gas bubbles, gas and liquid flow rates, interfacial and gas hold-up are constant along the contactor. Roemer and Durbin [2] have developed very efficient TBFCM to describe the residence time distribution inside the chemical reactors as shown in the Figure 2.1 below.

This model consists of number of completely mixed cells (N) that have an equal volume $\left(V_c = \frac{VT}{N}\right)$ with equal backflow rates between the cells. The cells: (0 and $N+1$) have negligible volume or hold-up and they allow the boundary conditions to be easily determined. The material balance has been carried out around each cell with respect to the inert tracer and the following equations are produced:

$$\delta(t) = (1+B)\,E_0 - Bg_1 \qquad \Rightarrow n = 0 \quad (2.1)$$

$$\frac{1}{N}\frac{dE_n}{dt} = (1+B)E_{n-1} - (1+2B)E_n + BE_{n+1} \qquad \Rightarrow 1 \le n \le N \quad (2.2)$$

$$0 = E_{N-1} - E_N \qquad \Rightarrow n = N \quad (2.3)$$

These equations have been transformed to the following equations:

$$Et(\theta) = \sum_{i=1}^{N} [A_i\, exp(s_{i\theta})] \quad (2.4)$$

Where $E(\theta)$ is the impulse response of the Nth cell

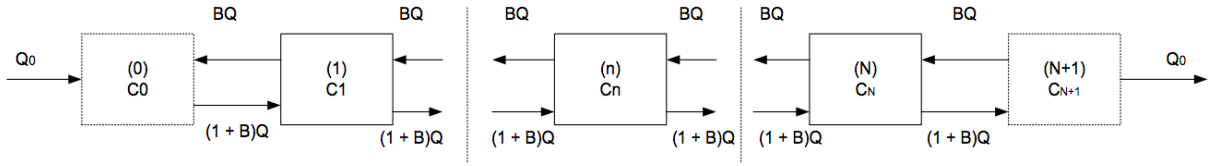


Figure 2.1: The transient back flow cell model

at time θ, $\left(\frac{C_i(\theta)}{C_i^*}\right)$

For $(0 < B < \infty$ or $0 < \lambda < 1)$, the distinct poles of the transfer function can calculated as:

$$s_i = \left(\frac{N}{1-\lambda}\right)\left[2\lambda^{0.5}Cos(\theta_i) - (1+\lambda)\right] \qquad (2.5)$$

Where $1 \leq i \leq N$

$$A_i = \left(-2N\lambda^{-N/2}\right)\left(\frac{Sin^2(\theta_i)}{D'(\theta)}\right) \qquad (2.6)$$

$D'(\theta_i)$ is the derivative of the function $D(\theta_i)$ which is equal to:

$$\begin{aligned} D(\theta) =& \lambda^{0.5}Sin\left((N+1)\,\theta\right) - 2\,Sin(N\theta) \\ &+ \lambda^{0.5}Sin(N-1)\theta \end{aligned} \qquad (2.7)$$

The above equations were solved using Matlab® Version R2014 in order to produce the impulse residence time distribution of the ozone solute and also to investigate the effect of the cells number and back flow ratio on the concentration of the tracer inside the Kenics static mixer. Before measuring the impulse response, the roots, θ_i of the function $D(\theta)$ have been determined by developing a Matlab code based on the Newton-Raphson method. Newton method is modified Taylor series method and uses iterative techniques to solve the non-linear algebraic equation $D(\theta) = 0$. Initial guess of the θ_i has to be made in the interval $(0 < \theta_i < \pi)$. Newton method is very fast and efficient and it has the following general formula:

$$\theta(i+1) = \theta(i) + \frac{D(\theta_i)}{D'(\theta_i)} \qquad (2.8)$$

The iteration stops when the function $D(\theta)$ value satisfies the following conditions:
$D(\theta_i) \leq \delta_{abs}$ (tolerance) [17]. It should be noted that the number of the roots, θ_i of the function $D(\theta)$ is equal to the number of cells used and their values depends on the cell number and the back flow ratio which is expressed in this model by the term (λ).

After estimating the roots of the function $D(\theta)$, a Matlab® code is built to produce the impulse and step residence time distribution, $E(\theta)$ and $F(\theta)$ respectively. Another aim of this code is to investigate the effects of the number of cells and the backflow ratio on the residence time distribution of the ozone solute inside the Kenics static mixer. Other objectives of this code are to compare the prediction of the transient BFCM, the ADM and CFSTR's in series at different operating conditions and also to validate the models with experiment data. After implementing the code in Matlab software, several graphs have been produced as shown later in this research.

2.2. The Axial Dispersion Model (ADM)

This model simply characterizes the backmixing by one-dimensional and diffusion process superimposed on plug flow equation which is expressed by the Fick's law [18]. The ADM uses only one parameter (Peclet number) to characterize the back mixing. Thus, ADM became simple and widely used model [11]. If an ideal tracer is injected to the reactor, it will spread as it travels through the column. The dispersion coefficient $D\,(m^2/s)$ exemplifies the spreading process. According to the dispersion coefficient value, we have three cases: firstly, when D is equal to zero, no spreading, thus plug flow. Secondly, small D results in slow spreading of the tracer curve. Thirdly, large D results in rapid spreading [13]. The dispersion coefficient can be represented by the dimensionless Peclet number $(Pe = \frac{D}{uL})$ in order to characterize the spreading in whole reactor, Pe is used to define the degree of backmixing. When $(Pe = 0)$, we have complete backmixing, and if $(Pe = \infty)$, plug flow exists. For the ADM, the residence time distribution (E_θ) can be expressed by [11]:

$$E_\theta = \frac{1}{2\sqrt{\pi/Pe}}\, exp\left(-\frac{Pe(1-\theta)^2}{4}\right) \qquad (2.9)$$

2.3. Continuous Stirred Tank in Series Model (CSTR's in series)

It is the simplest among stage-wise models for characterization backmixing in the multiphase reactors. In the CSTR's in series model, the reactor is viewed as a series of completely mixed stages. The degree of backmixing is determined by stage's number. The smaller the number of stages, the more significant is the backmixing [11]. Generally, CSTR's in series model is more reliable than the ADM at high values of the dispersion coefficient [19]. The residence time distribution (E_θ) can be determined by [7]:

$$E_\theta = \frac{N_{CFSTR}(N_{CFSTR}\,\theta)^{(N_{CFSTR}-1)}}{(N_{CFSTR}-1)\,!} \qquad (2.10)$$

2.4. The Relationship Between ADM and TBFCM

The transient BFCM is easier to formulate and solve than the ADM. This is because the BFCM produces non-linear algebraic equations whereas; the ADM produces non-linear differential equations which have to be converted to non-linear algebraic equations. Both transient BFCM and ADM characterize the backmixing of the liquid phase but in different ways. BFCM describes the backmixing by using the back-flow ratio (B) and number of the cells (NBFCM) whereas the backmixing in the ADM is characterized by the dimensionless Peclet number. The back flow ratio (B) and Peclet number (Pe) can be interrelated by the following equation:

$$B = \frac{N_{BFCM}}{Pe_L} - 0.5 = \frac{D_L \varepsilon_L N_{BFCM}}{u_L L} - 0.5 \qquad (2.11)$$

$$\lambda = \frac{B}{1+B} \qquad (2.12)$$

Where: NBFCM = cells number, B = Back flow ratio = exchange flow ratio, D_L = axial dispersion coefficient in the liquid phase (m^2/s), u_L = superficial liquid velocity, ε_L = liquid phase hold-up [14, 16, 18].

3. Results and Discussion

3.1. Transient Back Flow Cell Model (TBFCM)

3.1.1. Effete of Number of Cells on Residence Time Distribution of TBFCM

Figure 3.1 depicts the effect of the number of cells at constant back flow ratio on the RTD curves of the transient BFCM.

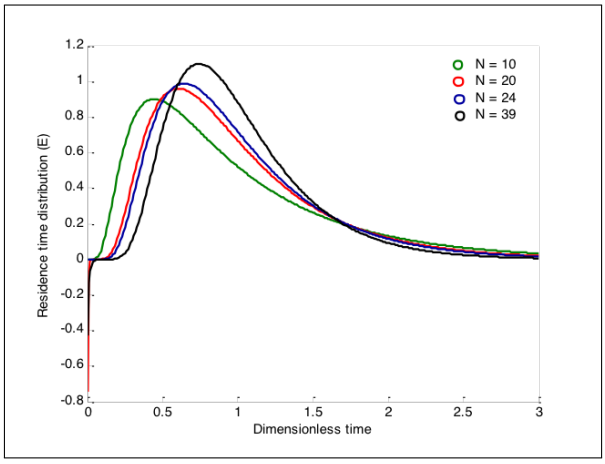


Figure 3.1: Impulse residence time distribution of ozone at constant back flow ratio

From Figure 3.1, it has been concluded that as the number of cells increases and therefore the Peclet number increases, the impulse RTD curves narrow and become more symmetrical and also the peaks of the impulse RTD curves increase. This can be explained by the fact that the liquid phase flow approaches the plug flow regime at high values of Peclet number. The RTD curves at small cell numbers are quite broad and non-symmetrical and this can attributed to the fact that the pulse tracer slowly passes through the mixer. At constant back flow ratio and according to this relationship, $\left(B = \frac{N_{BFCM}}{Pe_L} - 0.5\right)$, as the cells number increases and therefore the Peclet number increases, the liquid phase flow is approaching the plug flow regime and the RTD curves are becoming more symmetrical.

3.1.2. The Effect of Backmixing Ratio on Residence Time Distribution of TBFCM

Figure 3.2 shows the impulse RTD curves for 24 cells at different back flow ratio which is expressed in term of $\left(\lambda = \frac{B}{1+B}\right)$.

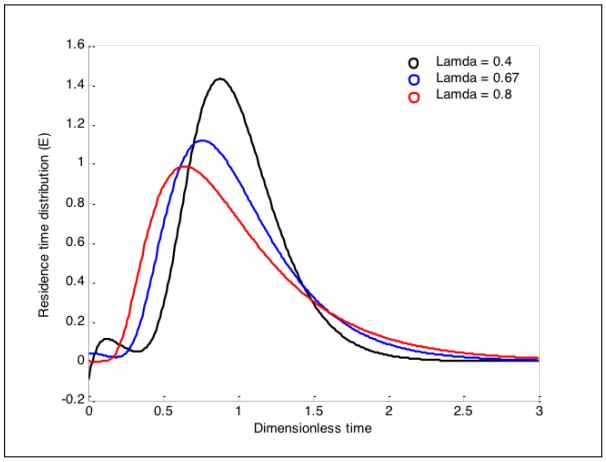


Figure 3.2: The effect of the backflow ratio on Impulse response of the ozone solute

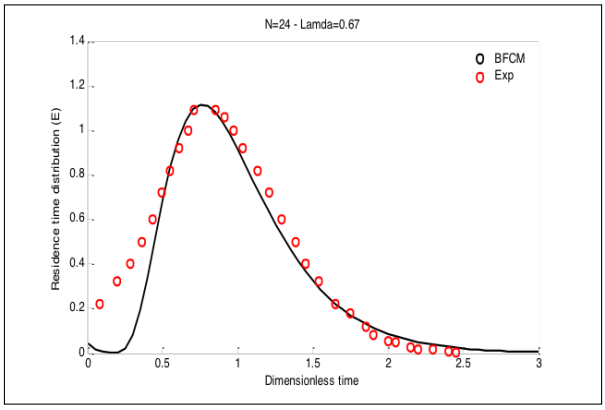


Figure 3.3: Model validation with experimental data

It can be clearly seen that as the back flow ratio decreases, the impulse RTD curves are becoming more symmetrical with higher and late peaks and shorter tails. At back flow ratio value equal 0.8, the RTD curve is symmetrical with respect to dimensionless time equal to 1 and also has no tail. These phenomena suggest that the fluid elements have uniform time distribution and no stagnant zones at this small back flow ratio respectively.

3.2. Testing of Transient BFCM with Experimental Data

The experimental tracer study of Madhuranthaam et al. [3] was used for testing the applicability of the Transient BFCM to characterize the hydrodynamic of mass transfer in a Kenics static mixer (KMX). The experimental setup used in this study consisted of a static mixer with 24 mixing elements with an internal diameter of 3.8 cm and total length of 0.98m and was operated concurrently with vertical up-flow. The fluids used were hydrogen representing the gas phase and monochlorobenzene representing the liquid phase. RTD experiment was conducted at room temperature and atmospheric pressure, and the hydrogen gas flow rate varied from 46 to 564 ml/min and liquid flow rate varied from 23 to 98 ml/min

Figure 3.3 shows the correspondence between the experimental data and the prediction Transient BFCM for gas-liquid system. There is slight difference between the experimental and predicted RTD curves and they are much more symmetrical than asymmetrical and this suggests that all the fluid elements have uniform history. Furthermore, as it can be seen from the graph we have single peaks and short tails, thus it can be said that there are no stagnant zones or channelling respectively. The Transient BFCM predictions slightly deviate from the experimental data and this has been attributed to the fact that of using a step response method and this problem can be avoided by using pulse input, but this is not applicable in this experiment due to the of the low conductivity of organic salt [3]. Even though the Transient BFCM has not been validated with experimental data of ozonation process, this does not mean this model is insufficient for this process.

3.3. Comparison Between TBFCM, ADM and CFSTR's and Testing Experimental Data

In order to compare the prediction of three modes: Transient BFCM, ADM and CFSTR's model, the RTD curves of the three models plotted together against the experimental data of the Kenics static mixer of 24 cells. In this Analysis, ADM1 refers to the model equation of Fogler that has been reported in the Madhuranthakam study [3] and the ADM2 refers to the model equation of Levenspiel [13]which has been cited by Gamal El-Din [19].

$$\text{ADM1} \quad E_\theta = \frac{1}{2\sqrt{\frac{\pi\theta^3}{Pe}}}\, exp\left(-\frac{(1-\theta)^2}{\frac{4\theta}{Pe}}\right) \tag{3.1}$$

$$\text{ADM2} \quad E_\theta = \frac{1}{2\sqrt{\frac{\pi}{Pe}}}\, exp\left(-\frac{Pe\,(1-\theta)^2}{4}\right) \tag{3.2}$$

Figure 3.4 clearly shows that the Transient BFCM and axial dispersion (ADM1) can almost predict the

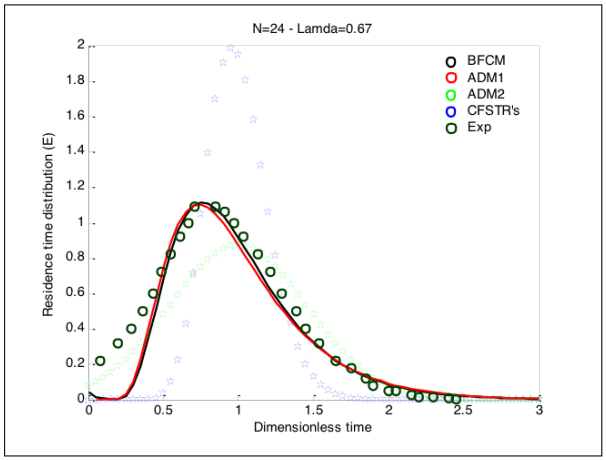


Figure 3.4: Comparison among TBFCM, ADM and CFSTR's in predicting RTD's in the Kenics static mixer

RTD experimental data. However, Transient BFCM is a slightly better than the ADM1 in predicting the experimental data and this mainly because the transient BFCM characterize the backmixing in the liquid phase using two mixing parameters: Back flow ratio and cells number, whereas, ADM1 uses only one parameter which is the Peclet number to describe the backmixing in the liquid phase. The three models: transient BFCM, ADM1 and CFSTR's predicted symmetrical impulse RTD curves which have identical spread. However, the peak predicted by the CFSTR's model is around two times higher than that of the transient BFCM and ADM1. This is maybe because of the fact that this model does not characterize the backmixing in the liquid phase and also the cells number have higher impact than the backmixing.

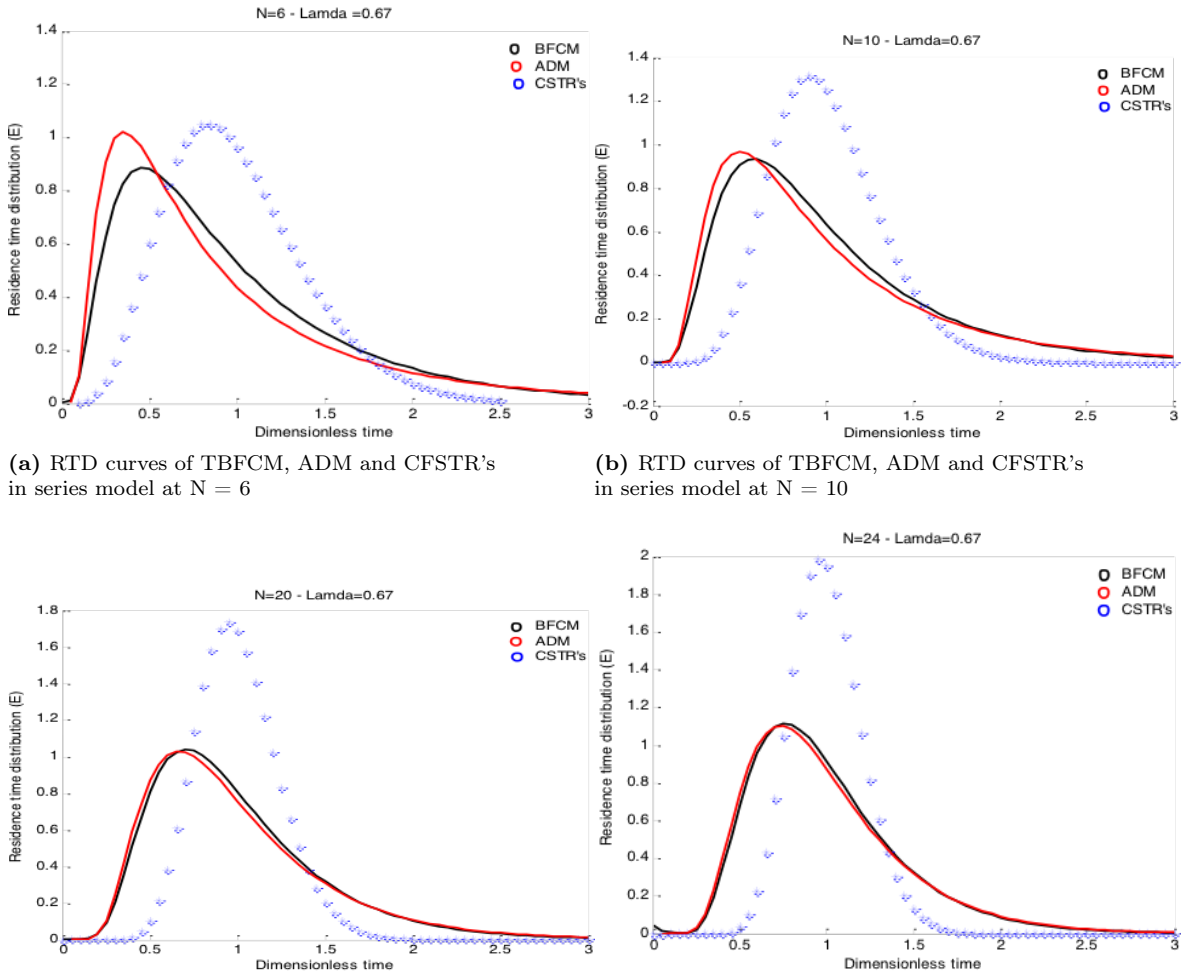
From the figure, it is evident that the ADM2 is inadequate to characterize the hydrodynamic of the static mixer. This model represents slight deviation from the plug flow regime and it is not accurate. This is may be due to the fact that real flow regime inside the mixer is closer to the completely mixed flow than the plug flow regime and also this model represents open-open boundary conditions and therefore it is not suitable because the real conditions are usually closed-closed or closed-open conditions [19]. The ADM2 predicted the broadest, the latest and the lowest peak of the RTD curve among all the other models. This can be attributed to the fact that the value of the Peclet number ($Pe_L = 10$) is very small. Thus, the assumption that the liquid flow approaches the plug flow regime is not applicable and therefore the ADM2 under-predict the backmixing in the liquid phase under such conditions. However, the CFSTR's in series model predicted the highest peak and the RTD curve is symmetrical. This is because the CFSTR's in series model does not consider the backmixing between the cells, which is has large value at such low Peclet number and it assumes completely mixed cells [13, 19].

3.4. Number of Cells Effect on the Theoretical Residence Time Distribution of TBFCM, ADM and CFSTR's in Series

Figure 3.5with its subfigures shows the effect of increasing the cells number of the static mixer on the correspondence between the three models and also their predictions of the RTD curves. As shown in the graphs above, and as the number of cells is increased, the Transient BFCM approaches or converges to the axial dispersion model. As shown in Figure 3.5a at small number of cells (N = 6), there is large difference between the transient BFCM and the ADM in predicting the RTD curves. However, as you can see in Figures 3.5b, 3.5c and 3.5d that the deviation between these two models is becoming smaller and smaller and also the RTD curves are getting more symmetrical as the number of cells is increased. As shown in figure 10, the best correspondence between transient BFCM and ADM was at a number of cells equal to 24 which is the same number of cells of the Kenics static mixer that used in the experimental study. There is long tails at small number of cells, especially at N=6 or 10, which suggest the presence of stagnant zones. Therefore, this small number of cells is insufficient to provide adequate mixing between the two phases. For the CFSTR's, it has poorly predicted the RTD curves compared to other two models, and this is very noticeable at high cells' number. This is due to the fact that this model does not account for the backmixing in the liquid phase. RTD curves of the CFSTR's in series model were always symmetrical and therefore this suggests uniform distribution of the solute concentration inside the mixer of completely mixed cells.

4. Conclusion

Three different models have been used to characterize the performance of the gas-liquid system inside Kenics static mixer: the transient back flow cell model of Roemer and Durbin, [2], the axial dispersion model (ADM) and the continuous flow stirred



(a) RTD curves of TBFCM, ADM and CFSTR's in series model at N = 6

(b) RTD curves of TBFCM, ADM and CFSTR's in series model at N = 10

(c) RTD curves of TBFCM, ADM and CFSTR's in series model at N = 20

(d) RTD curves of TBFCM, ADM and CFSTR's in series model at N = 24

Figure 3.5: Number of cells effect on theoretical residence time distribution (RTD)

tank in series (CFSTR's in series). The three models have been validated with experimental data Madhuranthaam et al. [3] and they have been used to simulate the impact of different parameters: cells number and back flow ratio on the performance of the mixer.

As a result of this comparison, both BFCM and ADM have proved to be accurate, sufficient and reliable in their predictions of the performance of the ozone Kenics static mixer. However, the transient BFCM have provided slightly better results than the ADM at a high number of cells, around 24. This is because the transient BFCM uses two mixing parameters to characterise the backmixing in the liquid phase: the number of cells and the backmixing ratio whereas the ADM uses only one parameter which is the Peclet number. Interestingly, it was found that the Transient BFCM approaches or converges to the axial dispersion model at a higher number of cells.

5. Further Work

The transient BFCM should be improved to include the effect of the gas and liquid flow rates, the backmixing in the gas phase, variable backmixing ratio in the liquid phase across the static mixer.

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