LIQUID PHASE DISPERSION/MIXING INVESTIGATION IN GAS-LIQUID UPFLOW MOVING BED HYDROTREATER REACTOR (MBR) USING DEVELOPED LIQUID TRACER TECHNIQUE AND METHOD BASED ON CONVOLUTION REGRESSION AND WAVE MODEL

Vineet Alexander[1], Hamza Albazzaz[2], Muthanna Al-Dahhan[*,3]

[1,*] *Department of Chemical & Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO-65409*
[2] *Kuwait Institute for Scientific Research, Safat, kuwait*
[3] *Cihan University, Erbil, Iraq*
Email: [1] *vineet.alexander@gmmail.com,* [*,3] *aldahhanm@mst.edu*

Abstract

Liquid phase dispersion/mixing studies have been performed for the first time on the catalyst bed of a cold flow scaled-down upflow moving bed reactor (MBR) using residence time distribution (RTD) at various flow rates including the scaled down condition. MBR is hydrotreater and its design includes catalyst bed with conical bottom and plena. The catalyst bed is modeled using Wave Model, and its mixing parameters are estimated using a mathematical approach based on convolution and regression. A study is also shown to illustrate the limitation of Axial Dispersion Model (ADM) while modeling the flow which noticeably deviates from plug flow. In addition, a

dimensionless variance is also estimated for the bed region from the RTDs. Overall liquid dispersion/mixing is seen high in MBR, with more dispersion/mixing in the expanded bed region. Scaled down conditions are seen best when considering the overall catalyst utilization and liquid mixing for hydrotreatment.

Keywords: Residence Time Distribution (RTD), Wave Model (WM), Moving Bed Reactor (MBR), Liquid Tracer, Liquid Dispersion Coefficient, Peclet Number, Axial Dispersion Model (ADM)

1. Introduction

Gas-Liquid-Solid reactors are widely used for industrial processes and are designed according to the hydrodynamics, heat, and mass transfer requirements of the process [1]. Two-phase upflow fixed bed reactors are used for hydrotreatment applications, as it satisfies the principal design requirement of hydrotreatment process which is to provide desired gas to liquid flow ratio, the low residence time of liquid, better liquid distribution, and fully wetted catalyst along the length of the reactor [[2], [3]]. Although, the two-phase upflow fixed bed design provides a good working condition for hydrotreatment applications, but it could fail in the proper handling of the hydrocarbon feed with a high level of contaminants. As at hydrotreatment condition of temperature around 400-410°c and pressure of 100-200 bar [3] the contaminates of crude oil deactivates catalyst fast and results in the frequent shutdown of the reactor for catalyst replacement. Ebullated bed technology, which

is upflow gas-liquid over liquid fluidized bed [3] with provision for catalyst replacement, is used for handling heavier crude oil feed. As the catalyst replacement enables reactor to run continuously without frequent shutdown, but the catalyst activity is less for an economic size of the reactor to handle a higher flow rate of the feed stream, and it is mainly due to the fluidized state of the catalyst bed [3]. The new design of catalyst bed with conical bottom called upflow moving bed reactor (MBR) [4] solves issues pertaining to hydrotreatment of heavy crude oil. The peculiarity of MBR is the conical bottom attached to the catalyst bed (Figure 1), which enables the replacement of the catalyst during hydrotreatment operation. The gas-liquid feed stream is fed upflow through the MBR and maintaining the operating conditions to keep bed expansion less than 10 percent by volume [5]. The catalyst deactivates and move downward due to weight and removed from the conical bottom, and then fresh or regenerated catalyst are added at the top of the bed [6]. The replacement operation is not so often, and all the other times the bed behaves as upflow packed or slightly expanded bed condition. The successful reactor design is key to provide proper hydrodynamics, heat and mass transfer conditions [7]. One of the most important design parameters is liquid mixing/dispersion which is never studied for MBR reactor.

Inside the reactor, there is random fluctuation in the movement of the phase's which is superimposed on the general flow of that phase, and it is mainly due to the velocity variations and fluctuation due to varying convective force and bulk flow fields along the length of the reactor. This variations

and fluctuations is termed as convective dispersion/mixing of any phase and is one of the most critical hydrodynamic phenomena which directly affects mass and heat transport [8]. Hydrotreating is a liquid limited reaction and hence it is essential to understand the liquid hydrodynamics. Liquid dispersion/mixing is critical design parameter and this information is needed from bench scale/pilot scale and scaled-up to the industrial scale [2]. The dispersion/mixing is mainly due to velocity variations and fluctuations, and it is difficult to estimate the local velocities along the entire length of the reactor to quantify mixing [1]. The easier way is to conduct residence time distribution studies (RTD) for the region of interest in the reactor. Then fitting the RTD with an appropriate model having dispersion/mixing parameters to estimate it. These parameters quantify three-dimensional mixing and dispersion phenomena of liquid in the reactor.

RTD studies for the liquid phase are widely conducted on gas-liquid-solid reactor [9], but the signals are usually estimated for the entire reactor, where the liquid tracer is injected at the reactor inlet and detected at its outlet. In MBR, the area of interest is the packed bed, and RTD signals are needed for the bed section alone which is accompanied by an additional volume of plena below it and extra space on top of it. The common approach to extract the RTD signal of the bed is to employ detection of tracer below and above the volume of interest [[10], [11]], but due to the complexity of this reactor, injections are done below and top of the bed and detection is done at reactor outlet. The obtained RTDs are followed through a methodology based on

convolution and regression with appropriate mass transfer model describing dispersion phenomena. The most widely uses model to explain the dispersion phenomena is Axial Dispersion Model (ADM) [7], and is due to the simplicity of the ADM equation having a single parameter which accounts for the spatial complex velocity and concentration fluctuations inside the reactor [12]. ADM is obtained by superimposing diffusional phenomena on a plug flow and based on the assumption that phase dispersion is analogous to diffusional phenomena [8]. This assumption is not valid for the cases where the velocity and timescale of the dispersion phenomena are much deviating from the time and velocity scale of the diffusion processes [12]. In two-phase packed bed reactors, the dispersion is due to the combination of various factors such as velocity variations and fluctuations (Taylor dispersion), blending and separations due to flow through a tortuous path, mass exchange between stagnant and dynamic zone, molecular diffusion. The time and length scale of all these phenomena are different, and using ADM to find the dispersion phenomena fails in these cases. ADM is fundamentally second order partial diffusion equation, which has the property of infinite signal propagation [8] which necessitates the condition of applicability of ADM limited to the case of slow temporal and spatial variation of concentration field [[13] [14]]. This condition is only possible when the time scale of the transport process is extremely low and moves at infinite speed, which is the case of diffusion [[8] [12]]. For the cases, when the spatial concentration change is drastic during the time-scale of transport, such as the case when the system is noticeably

deviating from plug flow conditions, ADM fails. A case study is shown in the section 5 below to emphasize this effect.

Many modifications of the ADM is found to account for various dispersion causing factors in packed bed reactor. Like Piston-Exchange Model (PE) model which consider stagnant and dynamic liquid zones without dispersion, Piston-Dispersion-Exchange (PDE) model which accounts Dispersion also [15]. These modifications are just adding up additional parameters to fit but not solving the fundamental issue related to partial differential equation's infinite signal propagation property which drastically limits the applicability of ADM for the cases of large deviation from plug flow. To account these issue [8] developed Wave Model (WM).

The proposed wave model by [8] consists of a set of two hyperbolic equation based on the simple extension of the concept formulated by [14] for ADM. The one equation is for the concentration change averaged over cross section and other is for the dispersion flux, the equations are shown in the section 4.2. For linear problems, the equation is combined to one-second order partial differential equation, which has an analytical solution. For the normal pulse injection propagation of tracer in an non-reactive system, the analytical solution of Wave Model is in the form of transfer function similar to Gauss Jordan Distribution function [16]. The simplicity and overcoming the conceptual difficulties of Partial Differential Equation (PDE) makes Wave Model a best alternative for ADM for the limitations and conditions mentioned above.

In this work, a liquid tracer system is developed for two-phase upflow moving bed reactor (MBR), and RTD studies are conducted based on an injection-sampling concept called two-point injection and one detection method. The obtained RTD are processed by following a methodology based on convolution, regression and Wave Model (for catalyst bed) for estimation of mixing parameter (D_l, Pe) of liquid. The results indicate the liquid mixing is deviating noticeably from plug flow and a case study demonstrates that ADM failed in explaining the flow behavior of liquid in the catalyst bed of MBR. In addition, dimensionless variance (σ_D^2) are estimated for the bed section of MBR, and it also indicates the extent of dispersion/mixing in the bed section. Overall liquid dispersion/mixing is seen higher in MBR, with dispersion/mixing being more in the expanded bed operating conditions.

2. Experimental Setup

The experimental setup consists of scaled down to pilot plant form industrial scale moving bed reactor based on matching the dynamic and geometric similarity. The dynamic similarity is matched by keeping the pressure drop same through the internal holes for both industrial and pilot scale unit. Pressure drop is calculated for industrial scale at its operating condition and similarly, the pressure drop is estimated at pilot plant scale at the scaled down conditions. The scaled down conditions is determined by matching the LHSV and gas to liquid volumetric flow rate ratio same between industrial and pilot plant scale.

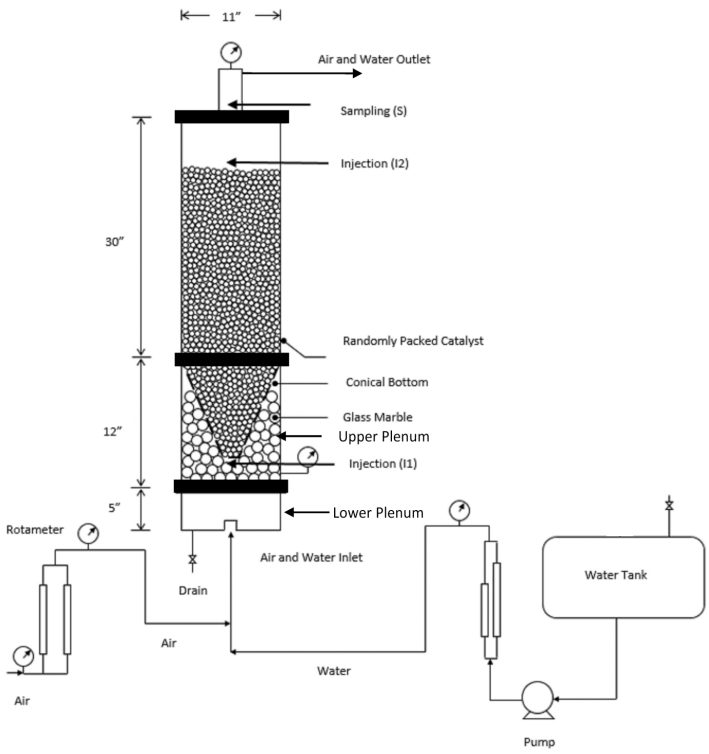


Figure 1: Schematic diagram of scaled down MBR setup for liquid dynamics studies

Figure 1 shows the schematic of the pilot scale upflow moving bed reactor (MBR). The design of this reactor is peculiar in terms of its design. It has a catalyst bed with a conical bottom, and plena classified as upper and lower plenum. The lower plenum contains deflector, 19 chimneys attached to the distributor plate in triangular pitch. Upper plenum is the compartment between the conical bottom and upper plenum wall, and this region is tightly packed with passive spheres and above the distributor plate. We conducted cold flow experimentation with gas and liquid phases as air and room temperature water. The gas phase is controlled by rotameter (Dywer-RMC-

106-SSV, Dywer-RMC-102-SSV) and the liquid phase by rotameter (Omega FL7301, Omega FL-75C). The flow is set at desired values and fed to the reactor below the bottom plenum in a premixed manner. The phases enter the reactor through the inlet of lower plenum, and it enters to the deflector which has slots on the lateral wall. The phases are pushed out through these slots to move upward to the chimney region. The chimneys are hollow cylindrical pipes having a hole on its wall, these chimneys are screwed to the distributor plate holes, such that the chimney side holes are just below the distributor plate. At scaled down operating condition, the phases coming from the distributor will make a gas pocket formation around the chimney side hole, the liquid will enter through the chimney bottom, and the gas will mix with the incoming liquid phase from the side hole, and mixed phases will be sprayed to the upper plenum. In the upper plenum, the phases will distribute due to the packed spheres, and this mix then moves to the bed region through the perforations on the conical bottom. Then phases will move upward through the bed region and air-water mix coming at the outlet is sent to the drain, as this mix will contain liquid tracer in it while conducting experimentation, which if recycled will cause calculation error for the methodology described in section 4.

The bed structure can change from upflow packed bed to three-phase fluidized bed based on the flow conditions but for the scaled down operating condition the bed is in the incipient fluidized conditions. At this state, the bed is almost in packed bed with slight expansion at the top part of the

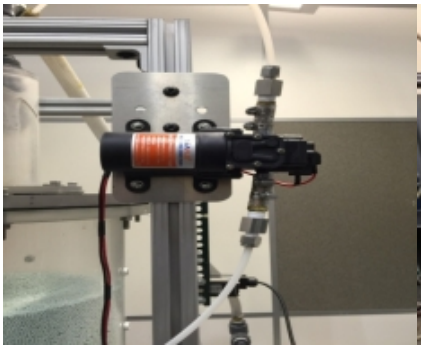
bed. In this study, we investigate the impact of flow conditions including the scaled-down conditions on liquid dispersion mixing inside the bed. Table 1 shows the operating conditions and dimensions of the experimental setup.

Table 1: Experimental setup specifications and operating conditions for liquid dynamics study

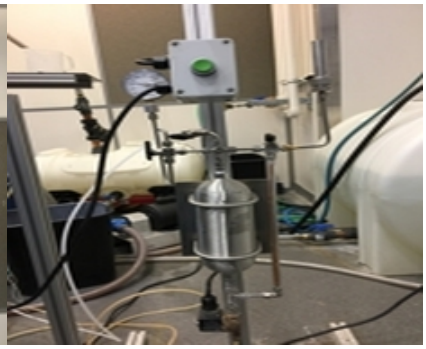
Parameters	Value/Range	Comment
Column Diameter	11 inch	
Column Height	46.46 inch	
Bed Height	24.8 inch	Height from top of the cone to the top of the bed at no flow rate
Liquid (Water) Superficial Velocity	0.01 to 0.4 cm/sec	
Gas (Air) Superficial Velocity	1.28 to 5.13 cm/sec	
Scaled Down Liquid Flow Rate	0.0175 cm/sec	By matching LHSV of industrial and scaled down reactor
Scaled Down Gas Flow Rate	7.7 cm/sec	By matching Gas/liquid volumetric flow rate of industrial and scaled down reactor

(a) Conductivity Probe

(b) Nitrogen(For Injection Unit



(c) Water Pump



(d) Injection Unit

Figure 2: Liquid tracer components

3. DYNAMIC LIQUID TRACER TECHNIQUE FOR RTD STUDIES OF LIQUID PHASE IN GAS-LIQUID UPFLOW MOVING BED REACTOR

3.1. Dynamic Liquid Tracer Technique

Figure 2 shows the component of the of the dynamic liquid tracer technique. KCL solution is used as the liquid tracer, after trial and error, we found 1.1 M KCL solution is needed for best response with the minimum

of KCL for our reactor volume. KCL solution qualifies to be used as tracer as it is non-reactive, completely miscible in the liquid phase, and have the similar physical property of liquid phase [17] . The tracer is stored in an in-house developed injection unit having a cylinder and solenoid valve attached to the bottom of the cylinder (Figure 2d). The injection unit is pressurized using nitrogen gas (Figure 2b). The solenoid valve powered to open for the small amount of time using a push button, this provides a pulse injection of tracer inside the reactor. Other types of injection such as step, sinusoidal, ramp, etc. [17] can be achieved by programming the solenoid valve opening accordingly. A water pump (Figure 2c) draws the sample out from the outlet and feeds it to the conductivity probe. The Conductivity probe (Figure 2a) is used to detect the tracer concentration. The probe connects to the data acquisition (edaq) and samples the signal at a frequency of 25 Hz. The conductivity probe gives linear variation in the voltage signal based on the conductivity of the passing liquid. The KCL solution has higher conductivity than pure water and conductivity is proportional to the concentration of KCL solution, and it is even sensitive to small traces of concentrations of KCL.

3.2. Liquid Tracer System of MBR

The liquid tracer system is shown in Figure 3, the system consists of two injection points (I1 and I2) and one sampling point (S). In our previous work on gas dispersion/mixing studies in upflow moving bed reactor, we used three

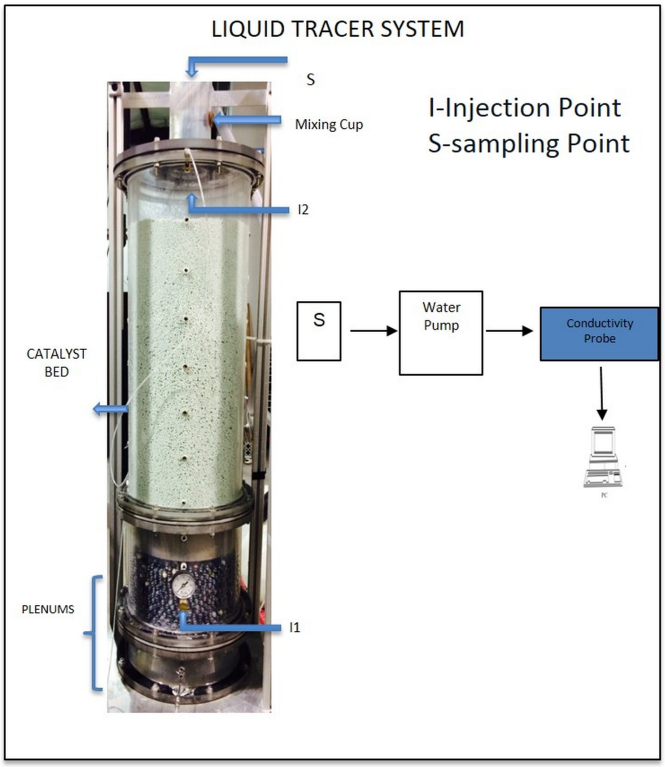


Figure 3: Liquid tracer system of MBR

injection and one detection [4], the different injection-sampling is due to the usage of different models and way it is solved. The methodology and models used in this study is explained in section 4. Injection points are connected to the injection unit and is the path of entry of tracer into the system. The sampling point (S) is at the outlet of the reactor and above the mixing cup, from where the gas-liquid mix is drawn out and fed to the conductivity probe using the water pump (Figure 2c). The mixing cup provides a uniform concentration cross-sectionally at the sampling plane, which is essential to neglect the effect of small tracer loss at the sampling point. Each injection

Table 2: Injection and sampling assembly for liquid dynamics study in MBR

Measurement	Injection	Sampling	Dispersion Zones
C(1)	I1	S	**Zone(1)**: Catalystbed + Upper external Volume + Sampling Line (measurement Volume)
C(2)	I2	S	**Zone(2)**: Upper External Volume + Sampling Line (measurement volume)

and sampling point gives the residence time distribution (RTD) of the section in between, Table 2 shows the zones covered by injection-sampling point to measure of the RTD. These assemblies of the injection/sampling are used for a method to obtain mixing parameter of the catalyst bed only and will be discussed later.

Signal Processing: The raw time series signal of tracer response is filtered using second-order butterworth filter to remove non-biased noise, such as noise due to electronics [18]. The filtered signal is normalized to a base value of zero by subtracting the signal values of filtered signal with the average signal value of the filtered signal corresponding to the air-water mixture for particular flow without any tracer. Figure 4 shows the tracer response (RTD) for injection I1-S and I2-S, the signal is again normalized to the range of 0 to 1 by dividing with maximum signal values. The shape of the RTD is dependent on the nature of flow and tracer input. For pulse input of tracer, the output response curve will be of gaussian distribution in nature and will

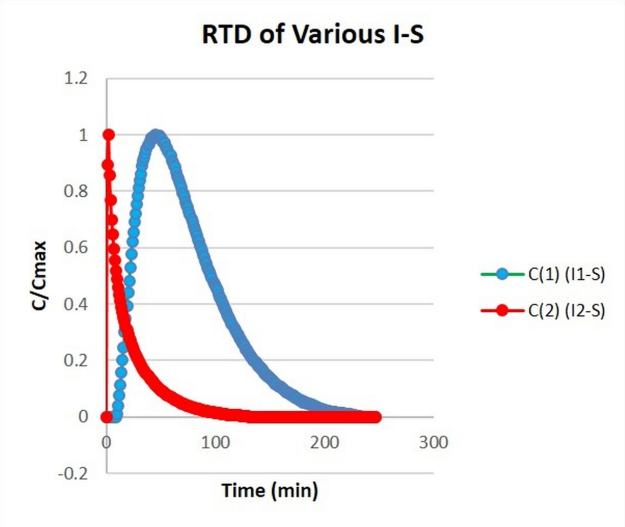


Figure 4: RTD of various injection-sampling at scaled down experimental condition

be at the extreme of the plug flow (zero dispersion) and CSTR (complete mixing) [17].

4. Methodology To Determine Dispersion/Mixing Parameter In Catalyst Bed Section Of MBR

4.1. Two Injection and One Detection Method

The area of interest is the catalyst bed section, but the catalyst bed is accompanied by additional volumes (Plenums, Upper extra volume, Sampling line) as shown in Figure 3, and to exactly obtain the RTD of the bed section we need to deconvolute the RTD signal from overall signal obtained by I-S (Table 2). Deconvolution is numerically unstable [19] and to overcome it we follow the methodology of single detection and multiple injection and a

mathematical approach of convolution and regression proposed by [19].

Usually two-point detection method [20], in which one injection two detection is used to follow the convolution principle. However due to the complexity of the MBR two-point injection and one detection is followed and mathematically both yield similar results [21]. The injection is below (I1) and above (I2) the catalyst bed and the detections is just above the mixing cup as shown in the Figure 1. Using the RTDs obtained from the injection-sampling assembly a systematic approach is followed to obtain the mixing parameters. The catalyst bed section is initially modeled using an axial dispersion model (ADM), but it failed to describe the dispersion/mixing behavior of liquid phase. The conceptual difficulty and explanation of its failure are described as a case study in section 5. In an alternative to ADM, we used a wave model (WM) to describe the liquid phase dispersion/mixing behavior, which overcomes the conceptual deficiencies of ADM.

4.2. Wave Model

Wave Model is an alternative to Fickian-Type dispersion model (ADM), and it overcomes some of the conceptual deficiencies of ADM [8]. It is a hyperbolic system of two first order equations for the average concentration (c) (equation 1) and the dispersion flux (j) (equation 2). For development of model please see [8].

$$\frac{\partial c}{\partial t} + U\frac{\partial c}{\partial x} + \frac{\partial j}{\partial x} + q(c, x, t) = 0 \tag{1}$$

$$[1 + \tau.q'(c, x, t)]j + \tau\frac{\partial j}{\partial t} + \tau(u + u_a)\frac{\partial j}{\partial x} = -D_e\frac{\partial c}{\partial x} \tag{2}$$

Where D_e is the Dispersion Coefficient, τ is the Relaxation time, and u_a is the Velocity Assymetry which are the parameters of the wave model. For the case of packed bed with no reaction, unit pulse injection of tracer and for arbitrary boundary condition and considering velocity asymmetry to be zero. The solution of wave model develops to gaussian distribution of the concentration as shown in equation 3.

$$C(t) = \sqrt{\frac{(-Pe * \tau)}{4 * \pi * t}} * \exp[\frac{-Pe * (\tau - t)^2}{4 * t * \tau}] \tag{3}$$

Where as Pe (peclet number) and τ (mean residence time) are the parameters. For detailed derivation of the solution of the wave model refers to [8] and [16].

$$PecletNumber(Pe) = \frac{U * L}{\epsilon_l * D_L} \tag{4}$$

Essentially the parameter of the solutions are ϵ_l (liquid holdup), D_l (Liquid dispersion), τ is equivalent to t_m (mean residence time), U (superficial velocity), and L (Length of the packed bed) This Gaussian function [16] relates the concentration at one position to that at another location with the degree of longitudinal mixing governed by Pe. This transfer function is used in this study to evaluate liquid behavior in the bed at the flowing conditions by estimating its parameters mentioned above.

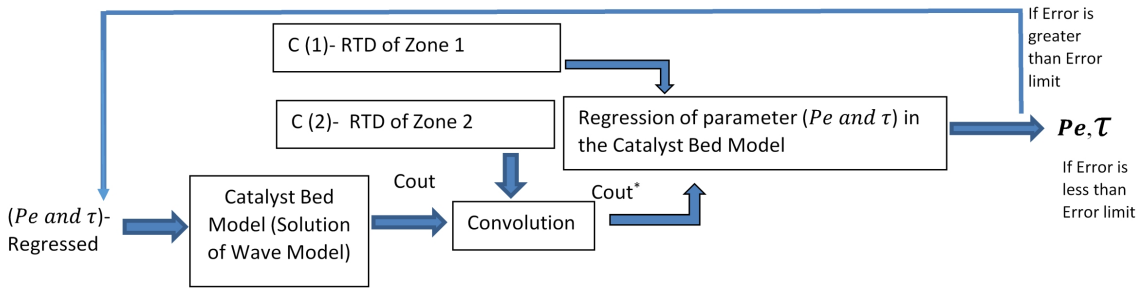


Figure 5: Schematic of convolution and regression approach to obtain liquid mixing parameters of catalyst bed

4.3. Convolution and Regression Approach to Estimate Liquid Dispersion Coefficient (D_l) and Peclet Number (Pe) of Liquid Phase in Catalyst Bed Section of MBR

Pe and τ values are assumed initially and fed into equation 3 and the resulting output C_{out} (Figures 5 and 6) represents the solution for unit pulse input of tracer at the outlet of the catalyst bed. Convolution Principle is applied using equation 5. C_{out} is input to zone-2 and C(2) (Figure 5 and 6) is the experimental response of zone 2. The output C_{out^*} (Figures 5 and 6) represents the output from zone 2 for an inlet response of C_{out} which itself is the outlet of catalyst bed for unit pulse injection. Hence, C_{out^*} is theoretical output of catalyst bed section plus zone-2, which is equivalent to zone 1. It means C_{out^*} is theoretical output of Zone-1.

$$C_{out^*} = \int_0^t C_{out}(t').C_2(t-t').dt' \tag{5}$$

Estimation of Pe and τ: C(1) (Figure 7) represents the experimental

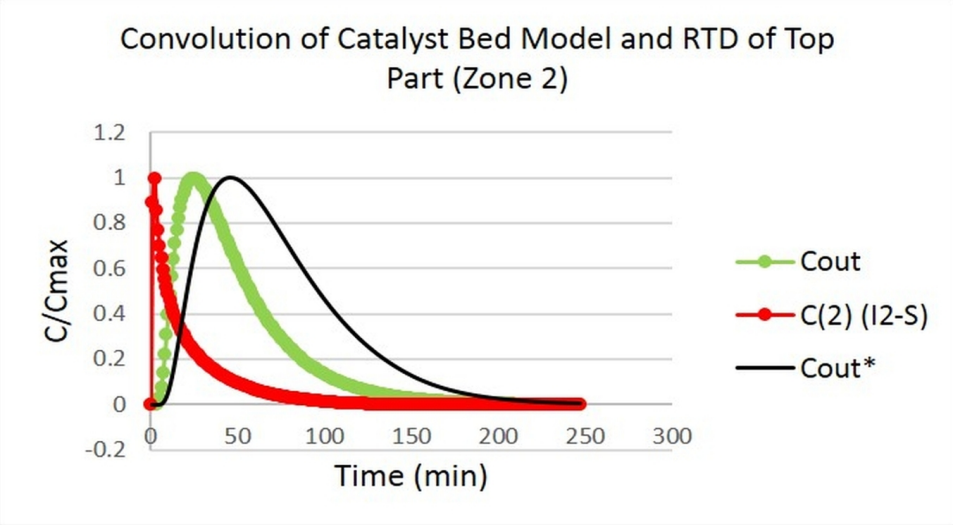


Figure 6: Cout (solution of the wave Model), C(2) (experimental output of zone-2), C_{out^*} (convoluted signal of Cout and Zone-2), at the experimental scaled down conditions

output of zone 1 and C_{out^*} (Figure 7) represents the theoretical output of Zone 1 based on the solution of Wave Model for parameter Pe and τ. $C1$ and C_{out^*} are regressed using equation(6) for minimum error for the values of Pe and τ. These values represent the actual model parameters for equation (3) representing the liquid phase flow behavior inside the catalyst bed.

$$Error = \frac{1}{n}\sum_{j=1}^{n}[C_{out^*}(t_j) - C(1)(t_j)]^2 \tag{6}$$

The minimum averaged sum of square error (equation 6) value for the case shown in Figure 7 is 0.00013, this validates that Wave Model is applicable to quantify liquid flow dynamics in catalyst bed section of MBR. The estimated parameter are Pe=3.78, and τ=32 min.

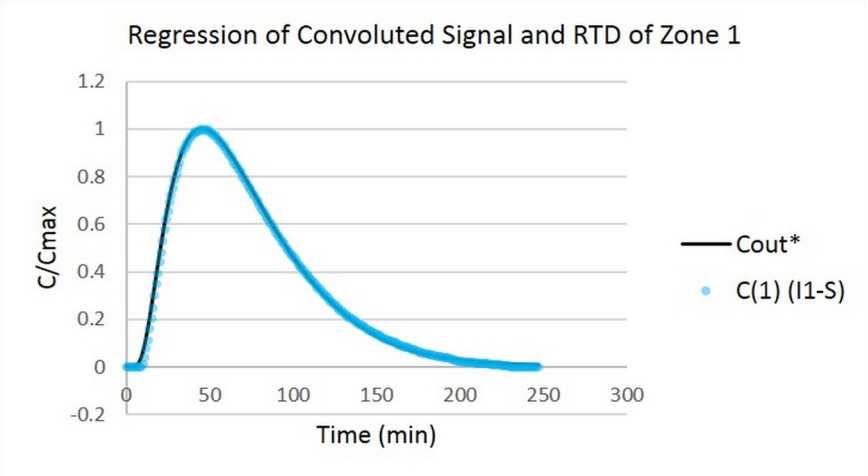


Figure 7: The regression plot for minimum error between convoluted signal (C_{out^*}) and experimental response C(1), at experimental scaled down condition

Estimation of D_l: The D_l is calculated using the equation 4, where the unknown is ϵ_l, and rest of all the quantities are known. ϵ_l can be estimated using the equation 7 and equation 9 based on RTD response [3].

$$\epsilon_{l1} = \frac{V_L}{X} * t_{m1} \tag{7}$$

Where ϵ_{l1} is the liquid holdup of zone1, V_L is the superficial liquid velocity based on empty column, X is the linear distance of zone 1, and t_{m1} is the mean residence time calculated using equation 8 for the RTD of Zone 1 (C(1)).

$$t_{m1} = \frac{\int C(1).t}{\int C(1)} \tag{8}$$

$$\epsilon_{l2} = \frac{V_L}{Y} * t_{m2} \tag{9}$$

Where ϵ_{l2} is the Liquid holdup of zone-2, V_L is the superficial liquid velocity based on empty column, Y is the linear distance of zone-2, and t_{m2} is the mean residence time calculated using equation 10 for the RTD of zone-2 (C(2)).

$$t_{m2} = \frac{\int C(2).t}{\int C(2)} \tag{10}$$

now using the equation

$$\epsilon_L = \frac{Volume of Liquid in Bed}{Volume of Bed} = \frac{\epsilon_{L1} * V_{zone1} - \epsilon_{L2} * V_{zone2}}{V_{catalystbed}} \tag{11}$$

In equation 11, all the terms (ϵ_{l1}, ϵ_{l2}) are known from equation 7 and equation 9, and V_{zone1}, V_{zone2}, and $V_{catalystbed}$ are known from reactor geometry. The estimated $D_l = 0.0065\ m^2/min$ for the experimental scaled down condition.

5. Case Study to show failure of ADM

The methodology shown in section 4 is applied with replacing the model of catalyst bed with Axial Dispersion Model (ADM) for Dirac delta input as shown in Figure 8.

C_{out} is the solution of the ADM which is input to the zone-3. The same convolution principle of equation (5) is applied and C_{out^*} is obtained. The C_{out^*} represents the theoretical output of zone-1 and C(1) represents the experimental output of zone-1. The C_{out^*} and C(1) are regressed for D_l and

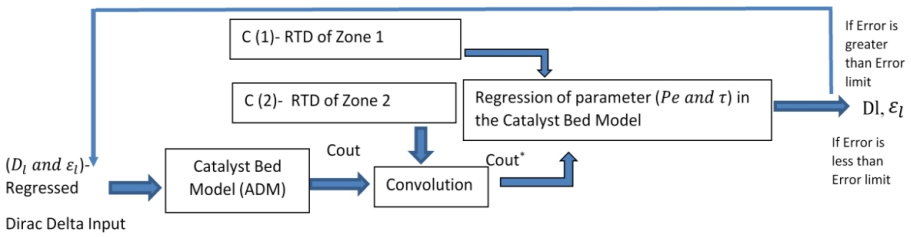


Figure 8: Schematic of convolution and regression approach using ADM model for catalyst bed

ϵ_l for minimum error using the equation 6.

$$\frac{\partial C_L}{\partial t} = D_l \frac{\partial^2 C_L}{\partial Z^2} - \frac{U_L}{\epsilon_L} \frac{\partial C_L}{\partial Z} \tag{12}$$

Boundary Conditions:

$$Z = 0, U_g.C_{in} = U_L.C_L|_{z=0} - D_l \frac{\partial C_L}{\partial Z}|_{z=0} \tag{13}$$

$$Z = L, \frac{\partial C_L}{\partial z}|_{z=L} = 0 \tag{14}$$

Figure 9 shows the regression plot for the theoretical output using ADM and Experimental Output of RTD for Zone-1. The plots show the best regression possible for least error of 0.125. The least error is much higher than the tolerance limit for good fit (max error of 0.005), whereas using Wave Model for same operating conditions, the error was 0.00035 within the tolerance (Figure 7). This indicates, ADM is not a suitable model for liquid phase dispersion studies in catalyst bed section of this reactor. On carefully analyzing the Figure 9, one can see that theoretical output has

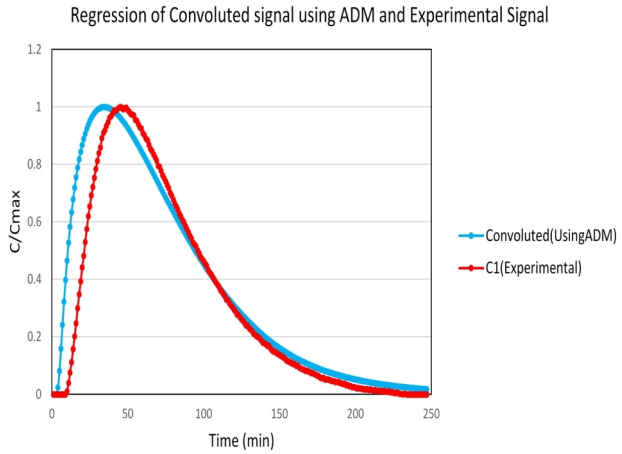


Figure 9: The regression plot for minimum error between convoluted signal (using ADM) and experimental response C(1), at scaled down experimental conditions

signal value at a time from (0 min), whereas for the experimental output, the first signal value is at (3min), This is the primary reason for the non-fit condition between theoretical and experimental output. Why theoretical output generates a signal at zero time is due to the fundamental nature of ADM equation. ADM is second order parabolic differential equation, and the solution of these equations have an infinite speed of signal propagation, which means instantaneous signal (concentration) at all the modeling space with the intensity proportional to dispersion coefficient [8]. ADM can be better understood by focusing on ficks law, based on which ADM is conceived.

Westerterp ([12]) analyzed the ficks law for diffusional phenomena at particle level scrutiny and found that, to hold ficks law, the time taken (relaxation time) for random particle movement (mean free path) shall approach zero. Hence, the velocity scale (mean free path/relaxation time) of diffu-

sional transport shall approach infinity. Hence, ADM is applicable for the cases when these conditions are fulfilled or not much deviating from it, or it is only properly applicable for the case of molecular diffusion, as infinite velocity scale of molecular diffusion justifies physically the ADM behavior of infinite signal propagation [22]. The cases, such the flow of gas phases, the relaxation time of particle movement is very slow to the order of (10^{-10} to 10^{-11} sec) which is comparable with the diffusional time scale, and hence ADM is applicable for gas phase with a reasonable level of accuracy [8]. The liquid phase flow has a time scale of particle movement higher than the diffusional phenomena and hence not reasonable to use ADM to find dispersion phenomena.

6. Dimensionless Variance (Tank in Series)

Tank in series is a one parameter model and are used to describe non-ideal reactors. In this modeling concept, n tanks are modeled as ideal CSTR in series for pulse injection of tracer. The Residence Time Distribution (RTD) obtained from the model is matched with experimental RTD of non-ideal reactor by varying n. Larger the value of n indicating the flow is towards plug flow and lower means the flow is towards CSTR. Fogler ([23]) showed that equation 15 is the generalized RTD for n tank modeled as ideal CSTR in series.

$$E(t) = \frac{t^n}{(n-1)!\tau_i^n} e^{-t/\tau_i} \tag{15}$$

Where τ_i is the means residence time in single tank, n is the number of tank, and τ_i is equal to τ/n, and τ is mean residence time of entire reactor. Equation 15 is converted to dimensionless form $E(\theta)$ as shown in Equation 16.

$$E(\theta) = \tau E(\theta) = \frac{n(n\theta)^{n-1}}{(n-1)!} e^{-n\theta} \tag{16}$$

Where θ is the ratio of t and τ. The variance of equation 16 can be found using equation 17, which is called dimensionless variance (σ_D^2), and this dimensionless variance is equal to the ratio of variance (σ^2) and square of mean residence time (t_m).

$$\sigma_D^2 = \frac{\sigma^2}{{t_m}^2} = \int_0^\infty (\theta - 1)^2 E(\theta) d\theta \tag{17}$$

[23] showed the solution of equation 17 is equal to the inverse of number of tanks (n), as shown in equation 18.

This indicates if σ_D^2 is zero then the flow is towards the plug flow as n tends to infinite ideal CSTR in series, and when σ_D^2 approaches one the flow is towards complete mixing as n tends to one ideal CSTR . Dimensionless variance can be determined by RTD experiments, as it is the ratio of variance (σ^2) (second moment) and square of mean residence time (t_m) (first moment).

$$\sigma_D^2 = \frac{\sigma^2}{{t_m}^2} = \frac{1}{n} \tag{18}$$

$$MeanResidenceTime(t_m) = \int_0^\infty E(t)tdt \tag{19}$$

$$Variance(\sigma^2) = \int_0^\infty (t - t_m)^2 E(t)dt \tag{20}$$

In our case, the area of interest is packed bed region, and its dimensionless variance is evaluated by finding the variance of RTD of zone 1 (t_{m1}) (Figure 4 and Table 2) and RTD of zone 2 (t_{m2}) (Figure 4 and Table 2) using the equation 19 and similarly the variance (σ_1^2 and σ_2^2) using equation 20. Volume of Zone 1 minus volume of zone 2 gives volume of bed , and as these moments are additive the bed variance will ($\sigma_1^2 - \sigma_2^2$) and mean residence time in the bed will be ($t_{m1} - t_{m2}$). Hence the σ_D^2 is calculated using equation 21.

$$\sigma_D^2(Bed) = \frac{(\sigma_1^2 - \sigma_2^2)}{(t_{m1} - t_{m2})^2} \tag{21}$$

Equation 21 shows the dimensionless variance of the liquid phase in catalyst bed region and for scaled down experimental condition (Table 1), σ_D^2 is 0.331.

7. Results and Discussion

The evaluated wave model (WM) parameters are liquid dispersion coefficient (D_l) and Peclet number (Pe). In addition, dimensionless variance (σ_D^2) in the bed region is evaluated. These parameters estimate the extent of mixing of liquid phase in catalyst bed section of this reactor. The effect

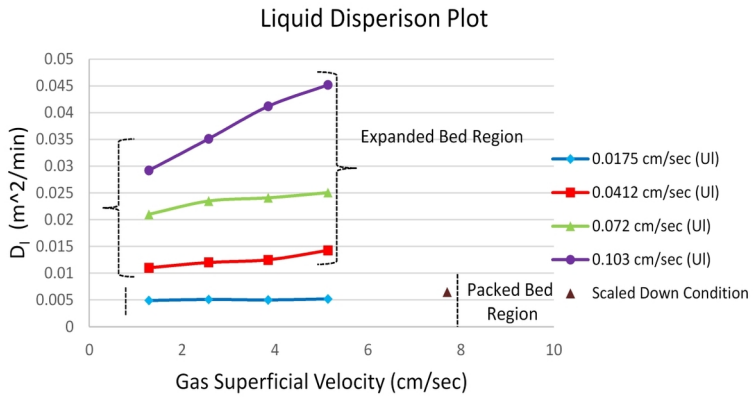


Figure 10: The liquid dispersion in the catalyst bed of MBR for varying flow rate of phases

of operating conditions on these parameters are investigated.

7.1. Effect of Operating Condition on Dispersion Inside the Catalyst Bed Section of MBR

The physical representation of D_l is the quantification of the spread of tracer signal in the catalyst bed section. The spreading is dependent on diffusive nature of tracer and spread occurring due to the external force field which is dependent on the flow condition. Hence, the dispersion coefficient (D_l) can be represented as the summation of molecular diffusivity and dispersion due to convective term [9]. Any non-ideality in the flow is reflected in the convective dispersion term. The primary source of non-ideality for liquid flow in two-phase upflow packed or expanded bed are due to non-uniform velocity profile, by passing streams of phases, velocity fluctuations due to turbulence, backflow of liquid due to velocity difference with gas phase, non-uniform flow pattern of gas phase in bed, mass transfer between dynamic and

stagnant liquid zones [24]. All these non-idealities are a function of reactor design, bed structure and operating condition of phases. Figure 10 shows the effect of gas and liquid superficial velocity on the liquid dispersion in the catalyst bed packing of this reactor. Based on the operating condition the bed structure changes form packed bed to expanded. The previous study of ([4]) indicates that for liquid flow rate (0.0175 cm/sec) and varying gas flow rate from (1 to 7 cm/sec), the bed is in packed condition, with slight expansion at the top for scaled down conditions (Table 1). For the rest of all the operating conditions the bed starts to expand, and its extent depends on flow condition. The dispersion trend of liquid is seen different for the packed bed and expanded bed case. In packed bed case (Figure 10) the liquid dispersion is not changing significantly with increasing flow rate of gas and the same observed by [11]. In packed bed region with increase in gas flow the bubble breakup phenomena increases and moves upwards as small bubbles, these small rising bubbles cause less dispersion/mixing in liquid [25]. Other main criteria which can induce non-ideality or increased spreading of liquid are liquid flow rates and bed structure, where the bed structure is not much changing for all the operating condition in packed bed case. In expanded bed case the situation changes as the bed structure changes with operating conditions.

The operating region of expanded bed is shown in Figure 10. In this region, the bed starts to expands and moves toward three phase fluidization. It is seen that for all liquid flow rates the liquid dispersion coefficient (D_l) is

increasing with increase in gas flow rate. A similar trend is observed by [7] for three-phase fluidized bed. It is also seen that D_l increases with increase in liquid flow rate and the increasing effect with respect to increase in the gas flow is greater for higher liquid flow rates. The extent of the bed expansion is proportional to the increase in the flow rate of phases for MBR ([4]). With increasing liquid flow rate the bed expansion increases which result in increase liquid spreading induced by moving solids. In expanded bed, with increasing gas flow rate results in bubble coalescence, channeling and random flow distribution of gas phase along the bed, which increases the bubble-induced turbulence and macro recirculation of liquid phase [7]. These phenomena increase dispersion of liquid phase in expanded bed region. From the results, it is indicative that the liquid dispersion is a strong function of flow rate of phases and its effect is intense for a higher flow rate of phases. Although this gives good trend to understand the dispersive nature but to identify nature of flow such as pulse flow or completely mixed, a peclet number is needed. As the calculated D_l is proportional to the convective component of liquid phase flow, and its increase will result in increasing trend of D_l, but it does not mean the flow is moving toward completely mixed flow. Hence, the comparison of bulk flow field with dispersive force field is done by finding the peclet number (Pe).

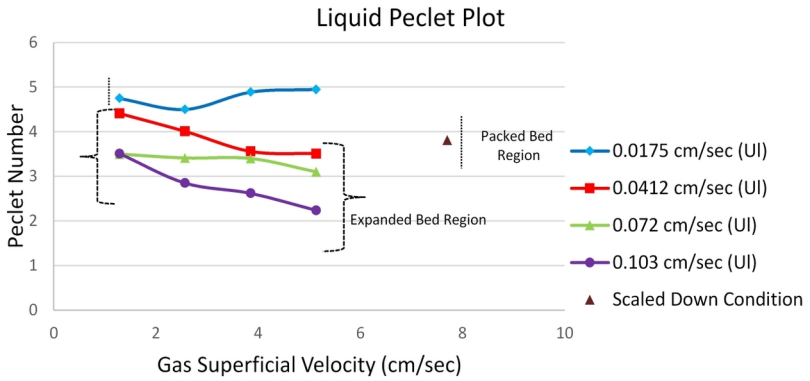


Figure 11: The liquid peclet number in catalyst bed of MBR for varying flow rate of phases

7.2. Effect of Operating Conditions on Peclet Number Inside the Catalyst Bed Section of MBR

Peclet (Pe) number is calculated using the equation 4, and it indicates whether advective or dispersive field dominates the nature of the flow. Higher the Pe, flow is towards the plug flow, and for lower Pe the flow is towards complete mixing. Figure 11 shows the peclet number plot for the liquid phase for the varying flow rate of phases. The plot shows that for both packed bed and expanded bed region, the Pe number is decreasing with increasing flow rate of gas phase and liquid phase, the decrease of Pe with increasing gas flow rate is more significant at higher liquid flow rates. For packed and slightly expanded bed cases the Pe for liquid is seen to decrease with gas flow rate [[2], [20], [26], [1]]. The small values of the peclet number clearly indicate that liquid phase non-ideality is quite significant and largely deviating from the plug flow [[9], [27]]. These non-idealities are much dominant in expanded

bed case, and is seen to be increasing function with bed expansion.

As the bed expands, dispersion of liquid phase increases as explained in the section 7.1. At expanded bed conditions the bubble coalescence and other maldistribution and catalyst particle movement is observed. These movement creates a force field for micro and macro recirculation zones in the bed for liquid phase [28]. These recirculations increases the residence time of the liquid phase and results in dominance of dispersive forces compared to convective. The dispersive forces are directly linked with hydrodynamics mixing which includes backmixing and thus decreases Pe with increasing liquid flow rate. For MBR at the hydrotreating condition, the condition of low bed expansion is preferable for maximum catalyst utilization [5]. In terms of liquid mixing the scaled down conditions are suitable, as based on its low Pe value the mixing is already quite good. Pe gives a good indication of mixing phenomena in the bed, but additionally, dimensionless variance (σ_D^2) is evaluated using the moments of experimental RTDs, as this parameter is also indicates the degree of dispersion/mixing.

7.3. Effect of Operating Conditions on Dimensionless Variance Inside the Catalyst Bed Section of MBR

The dimensionless variance (σ_D^2) indicates the degree of dispersion/mixing in the reactor. The procedure to calculate σ_D^2 is shown in section 6. If the values of σ_D^2 is zero it indicates the flow is in plug flow and if its one then flow is completely mixed. Figure 12 shows the dimensionless variance plot

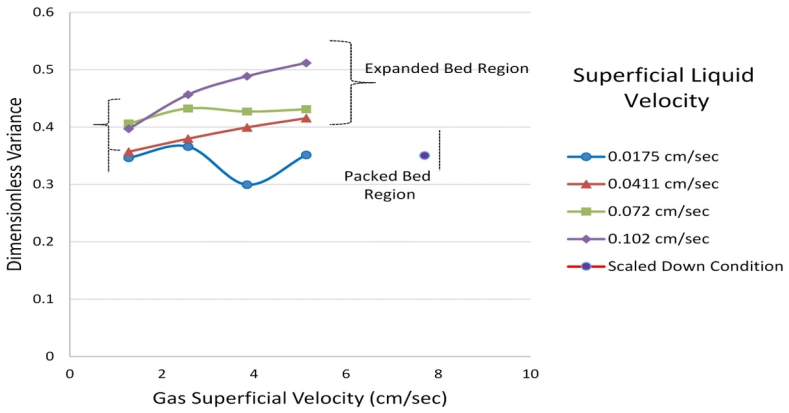


Figure 12: The liquid dimensionless variance in catalyst bed of MBR for varying flow rate of phases

for varying flow rate of phases and at scaled down conditions. The results indicates similar dispersion/mixing behavior of liquid phase in the bed as we observed with peclet plot (Figure 11). For packed bed the σ_D^2 is slightly increases with gas velocity, indicating gas phase doesnt have significant effect on liquid dispersion/mixing at these conditions. At expanded bed condition the σ_D^2 is increasing with increasing flow rate of both the phases. This indicates the dispersion or mixing is increasing and going towards complete mixing in the expanded bed case and is a direct function of bed expansion. The value of σ_D^2 is in the range of 0.3 to 0.52 indicating noticeable deviation from plug flow behavior, as σ_D^2 value of around 0.1 or less is considered to be in plug flow [29]. Scaled down experimental condition shows a σ_D^2 value of 0.33 showing high dispersion/mixing of liquid phase at these conditions, and at these conditions the bed behaves as upflow packed with slight expansion,

which is needed for better catalyst utilization.

8. Remarks

Liquid phase dispersion/mixing is successfully investigated for the first time in the catalyst bed of upflow moving bed reactor (MBR) using residence time distribution (RTD) studies. The catalyst bed is modeled using Wave Model (WM), and its dispersion or mixing parameters (D_l and Pe) are estimated using a mathematical approach based on convolution and regression. A case study is also shown to illustrate the limitation of Axial Dispersion Model (ADM) for modeling the liquid phase flow behavior in MBR. In addition, a dimensionless variance (σ_D^2) in the bed section is estimated using the first moment (t_m) and second moment (σ^2) of the experimental RTD. The D_l result indicates the liquid dispersion is not much affected by the increase in gas flow rate in packed bed region, but in expanded bed regions D_l increases with increasing flow rate of both the phases and is due to the increase in bed expansion with flow rate. Pe and σ_D^2 showed that overall liquid dispersion/mixing is higher in MBR for all the operating conditions studied, but mixing/dispersion is more in expanded bed and increases with bed expansion. The value of Pe and σ_D^2 also indicates that the liquid flow is noticeably deviating from plug flow and moving towards completely mixing with bed expansion. For hydrotreatment application in MBR, scaled down conditions are preferable, as the Pe and σ_D^2 indicates high liquid mixing, and moreover, at these conditions, the bed behavior is in upflow packed with

slight expansion at the top, which is a necessary condition for good catalyst utilization.

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