# WALL-TO-FLUID HEAT TRANSFER IN A CATALYTIC REACTOR AT SUPERCRITICAL CONDITIONS

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## Abstract

Computational fluid dynamics (CFD) studies can be used for improving the understanding of fluid flow and heat transfer in packed bed systems. The objective of this work was to study the heat effects in packed bed reactor under supercritical conditions using CFD comparing the simulations with empirical correlations. Simulations were done for a geometrical model of packed bed of cylindrical catalysts at high pressure supercritical conditions. The packed bed tube was heat on the walls and fluid mixture of carbon dioxide ($CO_2$), methanol ($CH_3OH$) and triolein ($C_{57}H_{104}O_6$), is flown into the packed bed at 250 bar. The flow field is described by three-dimensional (3D) Navier-Stokes equations coupled with the energy and species governing equations, which are solved by a finite volume code. The heat transfer coefficient is obtained in terms of wall Nusselt number ($Nu_w$) from simulation data and compared against empirical models for different flow rates.

**Keywords:** Computational Fluid Dynamics; Packed bed; Heat transfer; Supercritical fluids; Laminar flow; Constant wall heat flux;

## 1 Introduction

### 1.1 Packed bed wall-to-fluid heat transfer

Packed beds are widely used in chemical industries due to their simplicity in structure and effectiveness in terms of providing abundant contact area for surface reaction or for heat or mass transfer area. The study of heat transfer rate in packed beds is important not only important for design of heat exchangers but also for catalytic reactors. In shell-and-tube heat exchanger type packed bed reactor, heat is added (or removed) through the packed tube wall from a surrounding heat exchange fluid. To attain optimal performance, it is necessary to have good model for heat transfer.

A two-dimensional model was developed in which heat transfer in radial direction is superimposed upon the heat transfer by convection in the flow direction (Wasch and Froment, 1972). There are several mechanisms in radial heat flow, so to limit the complexity, the packing material and the fluid are taken as a continuum, neglecting the temperature differences between the fluid and solid phases, through which heat transfer is considered to occur by ‘effective conduction’. This ‘conduction’ is characterized by ‘effective conductivity’ $k_{er}$. This conductivity, when calculated at various locations perpendicular to the flow, is found to be decreasing strongly near the wall (Coberly and Marshall, 1951). This extra resistance near the wall causing the temperature jump, is described by as wall heat transfer coefficient $h_w$, which described the heat rate as:

$$q_A = h_w(T_w - T_i) \quad (1)$$

A two-dimensional model which has been a standard model, was presented by of Coberly and Marshall, (1951), Hatta and Maeda, (1948) which is described as pseudo-homogeneous model, is a classic heat balance equation given by Equation(2), for a cylindrical packed bed operated as a steady-state heat exchanger, assuming phase continuum. The steady state temperature profiles can be described by this equation solution. The solution of the two dimensional model is used for determining effective radial thermal conductivity $k_e$, and wall heat transfer coefficient $h_w$ from axial temperature profiles. This model is preferred over the heterogeneous model which is more complicated and requires more transport parameters.

$$GC_{p,f}\frac{\partial T}{\partial z}=k_r\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+k_{ax}\left(\frac{\partial^2 T}{\partial x^2}\right) \tag{2}$$

Experimental data has been expressed in terms of $h_w$ and $k_r$ (or in terms of dimensionless parameters $Nu_w$ and $k_r/k_f$), obtained from models with temperature profiles from experiments. Considerable amount of discrepancy exists with these literature data.

The wall heat transfer coefficient and effective thermal conductivity are found to be influenced by the length of the packed bed. Li and Finlayson, (1976) have compiled experimental data and correlated which reduced effect of length. The correlation (for $20 \leq Re \leq 800$; $3.3 < N < 20$) they presented for cylindrical packing is:

$$\frac{h_w\, d_p}{k_f}=0.16\left(\frac{G d_p}{\mu}\right)^{0.93} \tag{3}$$

Heat exchanger studies in packed beds are commonly carried out in wall-heated cylindrical beds with steam jackets (Gunn and Khalid, 1975; Wasch and Froment, 1972). Many difficulties are encountered in accurately measuring temperature profiles inside packed beds. Direct intrusive measurement would mean obstructing the flow and disturbing the geometry of the bed. This poses as an influential issue especially at low *Re* when temperature profiles very flat, making measurement errors very significant. This questions the accuracy of experimental data and their corresponding correlation predictions (Freiwald and Paterson, 1992). Another way would be to obtain temperatures at the outlet of the bed. A non-disturbing experimental methods that could be used to obtain flow patterns in packed beds is magnetic resonance imaging (MRI). However, this is restricted to low flow rates, up-to *Re*=100, and for fluid that can produce suitable signal for measurement, like water. Gas flow has not been investigated using MRI. CFD studies can be of significant use in estimating the flow profiles (Harris et al., 1996).

## 1.2 Use of CFD in packed bed heat transfer simulation

The use of computational fluid dynamics to simulate the fluid flow and heat transfer phenomena is becoming a standard approach. It was found to be useful in wide areas of applications including reaction engineering (Harris et al., 1996; Ranade, 2002)

Actual temperatures and velocities in the bed are required for determining the effective heat transfer parameters. Logtenberg and Dixon, (1998) studied wall-to-fluid heat transfer to a small number of spherical particles of a packed bed. They studied the heat transfer parameters from CFD, experiments and correlations for plug flow models and axial axially dispersed plug flow model at different temperatures. Particles with no internal voids showed better performance in heat transfer. Guardo et al., (2005) done simulations of wall-to-fluid heat transfer in a packed bed 44 randomly-packed spheres studying the influence of various turbulence models. With the increasing computational power full bed packed columns are used for CFD work. Behnam et al., (2013) used a validated full bed 3D CFD model temperature profiles to test the 2D pseudo-continuum model (given by Equation (2))

Fixed bed models have been usually developed for high tube-to-particle diameter ration (N) beds, in which temperature gradients are less and could be averaged. In the current problem studied, the tube-to-particle diameter ratio (N) is 9. Guardo et al., (2006) have performed simulations for heat transfer from particle-to-fluid which occurs during an endothermic reaction. The simulations were performed for low and supercritical high pressure conditions. Only some studies are available for CFD studies for packed beds at supercritical conditions are available. The properties of supercritical fluids vary generally between those of liquids and gases. This is due to the fact that gaseous phase and liquid phases merge together and become indistinguishable at critical point. These properties, especially density, are highly sensitive to small changes in temperature and pressure near the critical point. (Baiker, 1999)

## 2 Simulation Strategy

In modelling fixed beds, there has to be good qualitative understanding and accurate quantitative description of fluid flow and heat transfer. The platform used to construct the geometry has to be one which allows for the feasibility of generating good mesh and able to capture all the phenomena of the problem.

The packed bed is based on the geometry of a packed bed catalytic reactor which is of length 152mm and diameter 17.5mm. This reactor is filled with cylindrical particles of diameter 1mm and length of 5mm, resulting in tube-to-equivalent spherical particle diameter ratio of 9. A wall-segment (WS) model geometry is used, which takes less computational effort. WS model is a 120º segment of the packed bed as opposed to a complete wall (CW) full bed model. The WS model geometry was found to have overall axial velocities and temperatures only slightly different as compared to a full bed (CW) model (Taskin et al., 2007). By taking the cut parts as symmetrical, one third of the tube is run for simulations decreasing the computational effort. The arrangement of the cylindrical particles is random. The particles are arranged at random with angle of cylindrical particle axis varying from 0º to 90º to the axis of the tube. Arranging particle at random to avoid bad flow distribution and channelling. Each particle is arranged by sequential operations in the software for moving the particle around in the tube. The cylindrical particles are arranged such that their axis is at angle 0º, 15º, 30º, 45º, 60º, 75º, 90º with the axis of the tube. The overall voidage of the bed is about 0.6. Because of slight overlapping (about 1 to 2% of the volume) the bed void is not exactly the volume deducted due to the particles volume. The whole bed consists of 3780 cylindrical particles. The tube has extensions before and after the bed of cylinders, in order to minimize the end effects, and the back flow temperature condition at the outlet.

In the geometries previously reported (called near-miss model) by Dixon group, the particles have small gaps (and assumed zero velocity) between each other to avoid convergence problems, (Nijemeisland and Dixon, 2001). But Guardo et al., (2006) has the particles overlap about 1% at the contact points and found no convergence problem. For the model used current work, particle-to-particle contact areas were overlapped about 1 to 2% of the particle volume with adjacent particles. Some particles were chipped near the wall of the tube, and within the segment sides. This helps in treating the whole particles as a single volume so having ease of mobility of particles and avoiding meshing errors causing convergence problems. The particles are however avoided contact with the tube wall by having a very small gap at the wall contact points. This was done to avoid errors during meshing. No convergence problems were detected during simulation runs. The Finite volumes mesh is based on 3D tetrahedral elements. The wall surfaces are meshed using an unstructured triangular mesh and this surface mesh is used to construct the volume mesh. And the particles surfaces are refined by unstructured quadrilateral mesh. The mesh is checked for independence with various levels of refinement by checking velocity for flow of water through the packed bed geometry. And optimum mesh refinement is selected for the heat transfer study.

The fluid, mixture of carbon dioxide ($CO_2$), methanol ($CH_3OH$) and triolein ($C_{57}H_{104}O_6$), (reactants for transesterification reaction with supercritical solvent $CO_2$) is flown into the packed bed at 250 bar pressure and 473.15K temperature, is taken to be Newtonian, in laminar flow. Pure component properties are taken at this pressure as a function of temperature. Density, viscosity, thermal conductivity and specific heat of the fluid components are estimated as a function of temperature. Dilute approximation mass diffusivity coefficients are estimated for methanol-carbon dioxide and triolein-carbon dioxide. Methanol and triolein are taken to be dilute species for the diffusivity estimations. The tube wall is maintained at temperature 483.15K. The mixture properties are based volume weighted for density and specific heat, and mass weighted average for thermal conductivity and viscosity. The components form a single phase by the presence of supercritical $CO_2$.

Fluid flow is basically described by mathematical models (governing equations) which are based on physical principles of conservation of mass, and conservation of momentum. These are accurately described by three dimensional (3D) Navier-Stokes equations. These models coupled with energy and species models are solved in by various CFD codes. The standard numerical solution methods for these models are finite differences (FD), finite volumes (FV), finite elements methods (FE) (continuum flow methods). A Finite volume (FV) code is employed for this study. For all types of flow, the FV code solves the mass and momentum conservation equations. Energy conservation equation is solved for flows involving heat transfer. Species conservation equation is solved for flows involving multiple species mixing or reactions.

## 3 Results and Discussion

The solution to Equation (2) with boundary conditions is given by Hatta and Maeda, (1948) and later, by Coberly and Marshall, (1951):

$$\frac{T_w - T}{T_w - T_0} = 2\sum_{n=1}^{\infty}\frac{J_0\left(a_n r/R\right)e^{-a_n^2 y}}{a_n\left(1+\left(a_n/Bi\right)^2\right)J_1\left(a_n\right)} \tag{4}$$

Equation **Error! Reference source not found.**) gives the temperature profile in the packed bed. The heat transfer wall heat transfer coefficient $h_w$, is determined from measurements of axial temperature profiles i.e. $T = T_c$ at $r = 0$ using Equation **Error! Reference source not found.**). The temperature profiles at any radial position will do, but the temperature measurements along the central axis of the bed, where radial temperatures level off, are most preferable.

As mentioned earlier, the fluid mixture enters at temperature 473.15K and the wall is heated at temperature 473.15K. Figure 1 shows the temperature spread more at lower flow rate (*Re*=0.37) than at higher flow rate (*Re*=7.82). For the higher *Re* there is mixing near the wall because of higher kinetic energy. And because of more fresh lower temperature fluid molecules, the heat transfer rate is higher. The fluid with flow *Re*=0.37, is nearer to an equilibrium temperature because of more residence time of fluid molecules.

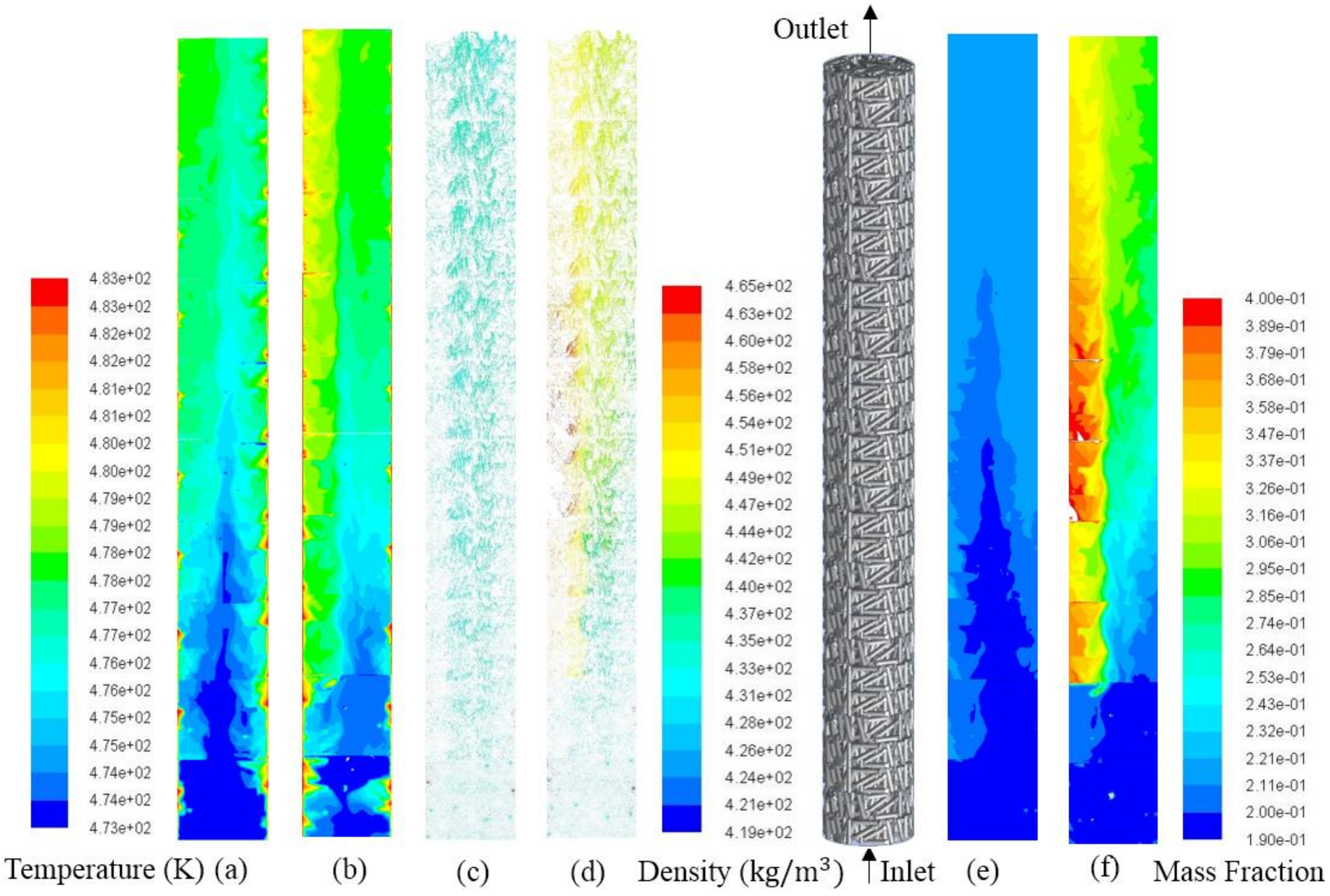

**Figure 1.** Temperature contour plots (a, b); axial velocity vector fields coloured by density (c, d); and methanol mass fraction plots (e, f) for *Re* =7.82 (a, c, e) and *Re* = 0.37 (b, d, f) along the axis of the bed on symmetrical surface cuts. Packed bed geometry with flow direction.

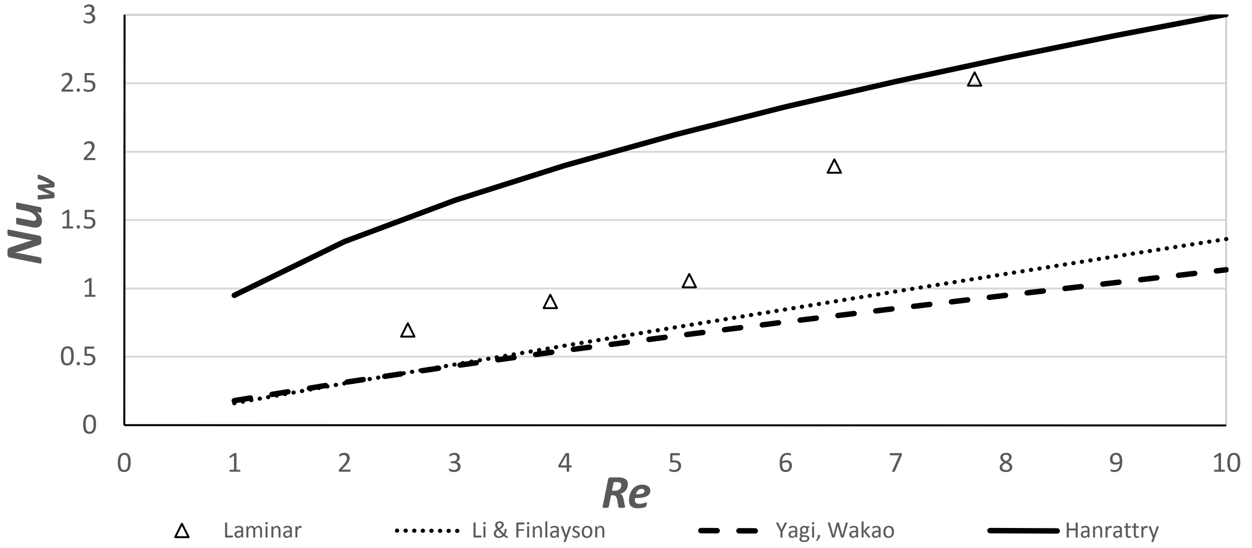

**Figure 2.** Wall Nusselt number vs Reynolds number for CFD simulations (laminar) compared with various correlations based on experiments

Velocity fields for Re=7.82 and 0.37 are shown in Figure 1. The length of the pointers indicates the velocity magnitude. The velocity vectors are coloured by density. At the entrances of the packed bed it can be seen that the vectors are uniform throughout the bed at both the Re. For the low Reynolds numbers, the wall effects and particle surface effects are at a minimum. However, at the ending of the bed crossflows can be seen. Also there is back flow (negative magnitude, dark blue regions in velocity field.) at some locations in the centre of the bed for the second half, this crossflows contribute to a more uniform temperature at the bed ending. The wall effects can be seen in this region of the bed, where the flow is more developed. Although the higher temperature at lower *Re* would indicate lower density, the velocity vector plots in Figure 1(c,d) show a higher density. This is due to accumulation of higher density methanol at lower *Re*. It can also be seen that at lower *Re* the temperature and concentration in the bed are not uniform in the radial direction in bed.

For the calculations of $Nu_w$, fluid thermal conductivity $k_f$ was kept a constant reference value. *Re* was calculated at the average values of viscosity in the bed and mass flux $G=\dot{m}/S=\rho u_0$. In Figure 2 are shown the values for $Nu_w$ for different values of *Re*. The wall heat transfer coefficient was obtained from the calculated heat flux and the temperature profiles. The heat transfer coefficient is correlated in terms of Nusselt number. The Figure 2 shows increase of heat transfer with *Re*, this effect can also be seen in the temperature contour plots of Figure 1. The empirical models by Hanrattry (1954) correlated for cylinders for *Re*~20 are shown for reference. There is agreement with the correlation at *Re*~8. However, for lower Re, there is much deviation. The other data for reference is the data correlated by Li and Finlayson, (1976) and of Yagi and Wakao, (1959). These correlations predicted lower heat transfer rate. The higher heat transfer rate could be because of higher rate of heat transfer in supercritical fluids, which is due to high density as shown in Figure 1 (c, d) and low viscosity under these conditions. The data of these correlations are modelled for non-supercritical conditions, which also contributes to their variation with the simulations.

## Conclusions

Heat transfer under supercritical conditions, is studied for packed bed catalytic reactor with constant wall heat flux. A packed bed finite element model with tube-to particle diameter *N*=9, was built. The whole bed consists of 3780 cylindrical particles. CFD simulations were done for *Re* = 0.37 up to 7.82. The temperature profiles showed higher temperature for lower *Re*. Velocity vector fields show higher velocities near the exit end of the bed. Higher density at lower *Re* can be observer, which is due to accumulation of methanol in the bed at this *Re*. Values of $Nu_w$ for different Re are calculated from temperature profiles. The results show a trend of increase with *Re*. Higher heat transfer is observed than what is predicted by some empirical correlations, which signifies the higher heat transfer for supercritical fluids.

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