32nd Conference of the Canadian Nuclear Society
Niagara Falls, Ontario, Canada, June 5 – 8, 2011

Entropy Generation Minimization for a Packed Bed Reactor in Nuclear Hydrogen Production

K. Pope and G. F. Naterer
Faculty of Engineering and Applied Science
University of Ontario Institute of Technology, Oshawa, Ontario

Abstract

The thermochemical copper-chlorine (Cu-Cl) cycle is a promising method to produce hydrogen with nuclear energy. In this paper, the fluid flow and heat transfer processes are examined for a packed bed chemical reactor in the Cu-Cl cycle. The heat transfer rate is predicted by a heat-momentum analogy for external flow over a particle, using the friction factor and Reynolds number. The Nusselt number correlation compares well against three prior methods to predict the Nusselt number in a packed bed (for various combinations of the void fraction, Reynolds and Prandtl numbers). The analysis is extended to minimize the entropy generation due to heat transfer and fluid flow irreversibilities in the packed bed reactor.

Nomenclature

A	area [m^2]
D	diameter [m]
f	friction factor
F	force [N]
h	heat transfer coefficient [W/m^2K]
k	thermal conductivity [W/mK]
L	bed depth [m]
N	number
p	pressure [Pa]
q	heat transfer rate [W]
r	radius [m]
S_0	cross-sectional area of empty bed [m^2]
s_p	surface area of one particle [m^2]
T	temperature [k]
v_p	volume of one particle [m^3]
V	velocity [m/s]

Greek

ε	void fraction
Φ	sphericity
μ	viscosity [Pa-s]
ρ	density [kg/m^3]

Subscripts

D	drag
H	hydraulic
i	inertial

p particle
s surface
sp sphere
v viscous
∞ superficial

1. Introduction

Nuclear thermochemical hydrogen production offers a promising alternative to carbon-based methods of hydrogen production, by splitting water into hydrogen and oxygen by a series of thermally driven chemical reactions. The U.S. Argonne National Laboratory has identified the copper-chlorine (Cu-Cl) cycle as the most viable for temperatures under 600°C due to its several advantages; including potentially lower capital costs, and promising engineering feasibility, when compared to other nuclear thermochemical processes [1]. It consists of four main steps to split steam into hydrogen and oxygen; all of the other copper-chlorine compounds in the cycle are recycled, providing a sustainable option for hydrogen generation. It does not use fossil fuels or emit carbon dioxide gas, thereby offering a promising alternative to conventional hydrogen production techniques. Thermochemical hydrogen production can reduce fossil fuel dependence, particularly if the cycle can be coupled with a nuclear power source [2].

A solid-gas reaction with $CuCl_2$ for steam hydrolysis is one of the key steps in the Cu-Cl cycle. The efficiency of the hydrolysis reactor is an important factor in the effectiveness of the overall hydrogen production. Several different reactor types can be used, including packed and fluidized beds or spray reactors, each offering various advantages and disadvantages which can be integrated into different Cu-Cl cycle designs. The focus of this paper is a packed bed reactor which offers an effective and relatively simple method to expose a large total surface area of solid $CuCl_2$ particles to steam. In a packed bed reactor, large temperature gradients can be a serious concern, as they lead to non-uniformities of chemical reactions. A packed bed reactor design is commonly used if very high conversion rates are required.

The parameters affecting a packed bed's efficiency include, but are not limited to, particle size, shape, roughness, surface area, temperature, pressure and fluid velocity. Many of these factors will have an opposite effect on the heat transfer and fluid flow characteristics within the system. For example, increasing the flow rate will also increase the rate of heat transfer between the bed material and the fluid; however, this will increase the losses within the system from fluid friction and thermal irreversibilities [3]. Designing the system to minimize the entropy generation within the packed bed is an effective method to optimize these variables to operate at higher system efficiencies.

The flow paths taken by the fluid through a packed bed are very complex and irregular. This makes it difficult to obtain exact solutions and precise representations of the fluid motion. The radial fluid velocity is significant because the irregularity of the packing material causes highly variable flow paths and large differences between local and average velocities [4]. Typical methods to predict the pressure drop through a packed bed rely on the experimental correlation developed by Ergun [5], or other similar correlations. Most extensions of the Ergun equation use a similar approach [4], but including additional parameters [6]. This includes effects of the vessel walls [4] to extend the correlation to other systems. Other correlations [7] extend the flow regimes and flow conditions, by developing correlations over a wider range and lower limit of Reynolds numbers, than with previous studies.

In this paper, the fluid motion through a packed bed is considered with different flow rates and particle geometries. Friction factors from the Ergun equation are used to predict the Nusselt number. A new model of the Reynolds analogy that relates the momentum and energy equations is presented. Experimentally determined Nusselt numbers are compared with the analytical predictions and close agreement is achieved. The predictions are further compared with three different predictive methods from the archival literature [8, 9, 10]. Current techniques to represent the entropy generation are extended to predict the entropy generation in a packed bed. A correlation to determine the operating conditions that minimize the entropy production is presented via the entropy generation number. This technique utilizes the Nusselt number based on the friction factor and Reynolds numbers, thereby having the potential to represent a wide variety of packed bed configurations and operating conditions.

2. Formulation of Fluid Flow and Heat Transfer

In the section, analytical techniques to predict the fluid flow and heat transfer characteristics through a packed bed reactor are presented. Assuming that the drag force (F_D) is equivalent to the sum of viscous (F_v) and inertial forces (F_i) [11],

$$\frac{F_D}{A_s} = \frac{F_v}{A_s} + \frac{F_i}{A_s} \tag{1}$$

where the viscous and inertial forces are represented by $\frac{F_v}{A_S} = k_1 \frac{\mu V_\infty}{r_H}$ and $\frac{F_i}{A_s} = k_2 \rho V_\infty^2$. The Reynolds number for a packed bed, Re_p, can be expressed as [11, 12],

$$Re_p = \frac{\rho V_\infty D_p}{\mu\,(1-\varepsilon)} \tag{2}$$

As expressed by Ergun [11], applying experimentally correlated values for k_1 and k_2 of 150/36 and 1.75/6, substituting the above equations into Eq. (1), and after manipulation, the friction factor can be expressed as

$$f_p = \frac{150}{Re_p} + 1.75 \tag{3}$$

which, for a packed bed, is defined as follows,

$$f_p = \frac{\Delta p\, D_p}{L \rho V_s^2}\left(\frac{\varepsilon^3}{1-\varepsilon}\right) \tag{4}$$

The Ergun equation is valid for flows with a Reynolds number from 1 to 1,000.

The Reynolds analogy offers a convenient relationship between fluid friction and heat transfer within a packed bed. To represent the flow in the tiny conduits within a packed bed, the bulk mean properties for wall friction and heat transfer can be expressed as follows [13],

$$\left.\frac{d(u/V)}{d(y/L_c)}\right|_{y=0} = \frac{f}{2}\frac{\rho V L_c}{\mu} = \frac{f}{2} Re \tag{5}$$

$$\left.\frac{d(T-T_s)/(T_\infty-T_s)}{d(y/L_c)}\right|_{y=0}=\frac{h\,L_c}{k}=Nu \qquad (6)$$

If the momentum and heat diffusivities match, i.e. $Pr \approx 1$, than so too will the normalized velocity and temperature profiles. Thus, the derivatives of the profiles, at the surface, Eqs. (5) and (6), will coincide, allowing for the following expression relating fluid friction and heat transfer in a packed bed, $\frac{f}{2}Re \approx Nu$. The Prandtl number is 0.71, assumed close to 1, leading to the following relation,

$$Nu=\frac{1}{2}Re_p f_p\,Pr \qquad (7)$$

In the above formulation, the Nusselt number predictions vary with friction factor, Reynolds and Prandtl numbers.

3. Formulation of Entropy Generation Minimization for a Packed Bed

The entropy generation minimization can be expressed as [14],

$$\dot{S}_{gen}=\frac{q^2}{T_\infty T_s}\frac{1}{h\,A_s}+\frac{F_D V_\infty}{T_\infty} \qquad (8)$$

where the first and second terms on the right-hand-side of Eq. (8) represent the entropy generation due to heat transfer and fluid flow. The definition of the drag coefficient can be rearranged for F_D,

$$C_D=\frac{F_D/(A_s)}{\rho V_\infty^2/2} \qquad (9)$$

where $C_D = f_p/4$. The surface area (A_s) is represented by the product of the number of particles (N_p) and surface area of a single particle (s_p), i.e. $A_s = N_p\, s_p$. The number of particles can be calculated from the volume ratio of total solids to a single particle, as follows,

$$N_p=\frac{volume\ of\ solids}{volume\ of\ one\ particle}=\frac{S_0 L\,(1-\varepsilon)}{v_p} \qquad (10)$$

The volume of a single particle can be determined from the ratio of the particle surface area to volume, as follows, $\frac{s_p}{v_p}=\frac{6}{\Phi D_p}$. The variable Φ represents the sphericity $\Phi=\frac{s_{sp}}{s_p}$, where s_{sp} and s_p are the surface areas of a sphere and particle, respectively (with the same hydraulic diameter). The sphere surface area is determined by $s_{sp}=\pi D_p^2$. The heat transfer coefficient (h) is determined from the definition of the Nusselt number.

$$Nu=\frac{h\widetilde{D}}{k}=\frac{1}{2}Re_p f_p Pr \qquad (11)$$

Eq. (11) can be rearranged to predict h, which is dependent on the friction factor, in addition to the Reynolds number of the flow, where, $\widetilde{D}=N_p D_p$. The hydraulic radius is calculated from the ratio of the perimeter to the area of the flow channels. It can be shown that the hydraulic radius for a packed bed can be further simplified to get the following definition,

$$r_H = \frac{perimeter\ of\ flow\ channels}{cross\ sectional\ area\ of\ flow\ channels} = \frac{S_0 L \varepsilon}{A_s} = \frac{\varepsilon v_p}{(1-\varepsilon) s_p} \tag{12}$$

Substituting Eqs. (8) – (12) into Eq. (1), the following expression for the entropy generation rate within a packed bed can be obtained.

$$\dot{S}_{gen} = \frac{48\,\mu\, q^2\, S_0\, \Phi\,(1-\varepsilon)^2}{\pi\, T_\infty T_s\, A_s\, k\, \mathrm{Pr}\, \rho\, V_\infty\, D_p^3 f_p} + \frac{2\, V_\infty^3\, \rho\, A_s\, f_p}{T_\infty} \tag{13}$$

In this equation, the first and second terms on the right side of the equality represent the entropy generation from heat transfer and fluid flow, respectively.

The optimum (minimum) entropy generation ($\dot{S}_{gen,opt}$) can be determined from the optimal Reynolds number ($Re_{p,opt}$) as follows,

$$\dot{S}_{gen,opt} = \dot{S}_{gen}(Re_{p,opt}) \tag{14}$$

where $Re_{p,opt}$ can be determined from the following expression,

$$\frac{\partial \dot{S}_{gen}(Re_{p,opt})}{\partial Re_p} = 0 \tag{15}$$

The entropy generation number (N_s) can be expressed as:

$$N_s = \frac{\dot{S}_{gen}}{\dot{S}_{gen,opt}} \tag{16}$$

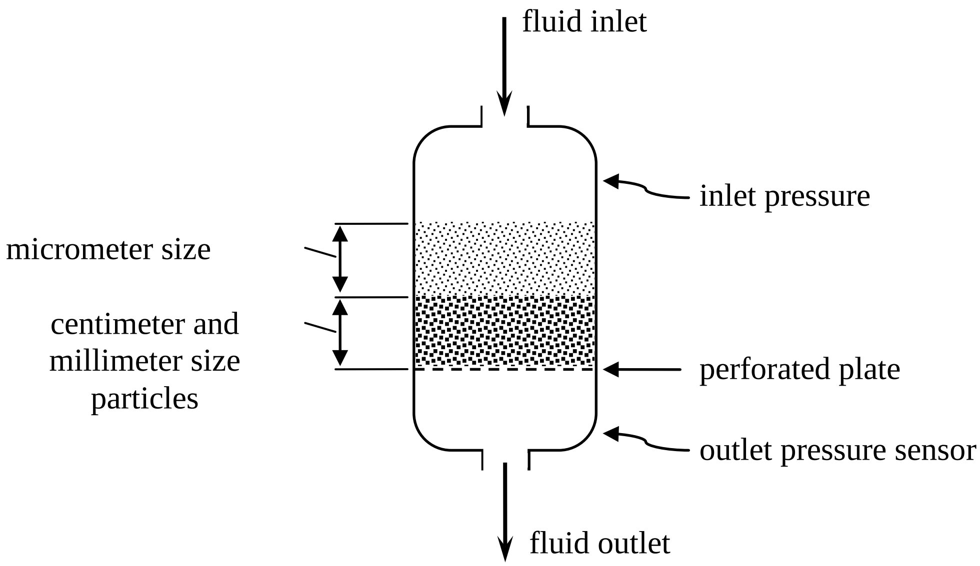
This formulation can be used to optimize the flow conditions in a packed bed, by minimizing the entropy generation from fluid flow and heat transfer.

4. Results and Discussion

In this section, the results of the entropy generation minimization formulation for a packed bed are presented and compared with experimental data. The experimental unit is illustrated in Fig. 1a. The system's primary component is the cylindrical pressure vessel, which represents the packed bed reactor. Within the vessel, a support mesh is installed to hold the packed solids. Compressed air enters through the top and exits through the bottom of the vessel, to a maximum operating pressure of 2 atm (absolute). As illustrated in Fig. 1b, two pressure sensors are installed within the vessel, one near the top and one near the bottom to gather data of the pressure drop through the packed bed. The input pressure is acquired at the top of the reactor cylinder, while the output pressure is measured near the bottom of the vessel.

The experiments gathered 1,000 samples for each of the various packing configurations. The void fraction is estimated from a water displacement measurement technique for the various particle sizes. Other experimental parameters are presented in Table 1. The measured pressure drop data, obtained for the various bed heights, are presented by the average values in the following analysis.

(a)



(b)

Figure 1: Experimental packed bed reactor a) photograph and b) schematic

Table 1: Packed bed parameters

Packing size	Packing material	Bed heights [cm]	Void fraction	Reynolds number
1 cm	glass beads	10, 20, 30	0.38	14 - 138
4 mm	peas	10, 15	0.33	5 - 51

As illustrated in Fig. 2, the predicted Nusselt number is compared with three published correlations that predict the Nusselt number of flow through a packed bed. The following functional form is assumed for Methods 2 and 3 – $Nu = a + b\,Re^{n}\,Pr^{m}$ – where the coefficients and exponents can be correlated from various methods.

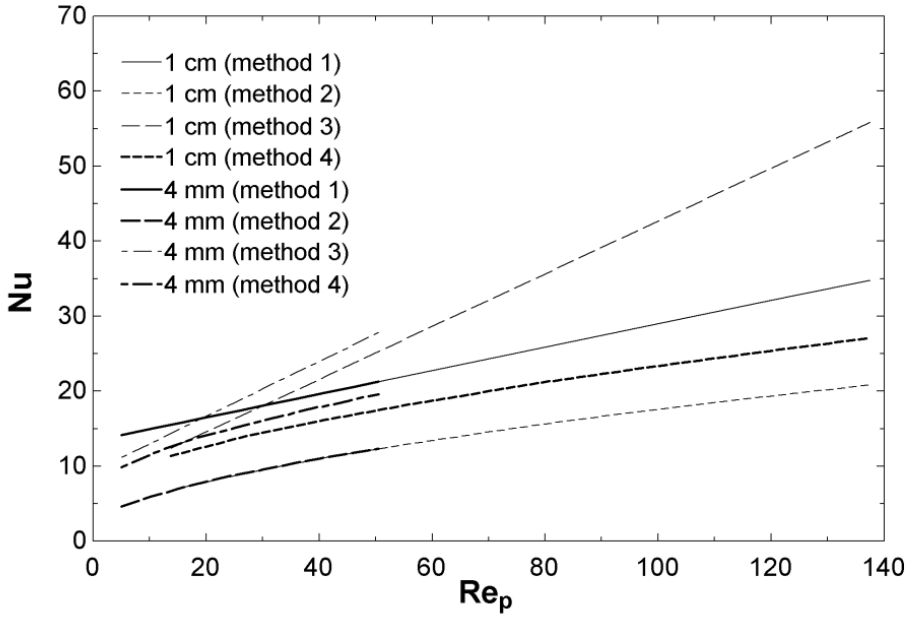


Figure 2: Predicted Nusselt number at various Reynolds numbers with (i) current method, (ii) [8], (iii) [9], and (iv) [10]

- Method 1 - current method: Eq. 7.
- Method 2 - Wakao et al. [8]:

$$Nu = 2 + 1.1Re_p^{0.6}Pr^{1/3} \tag{17}$$

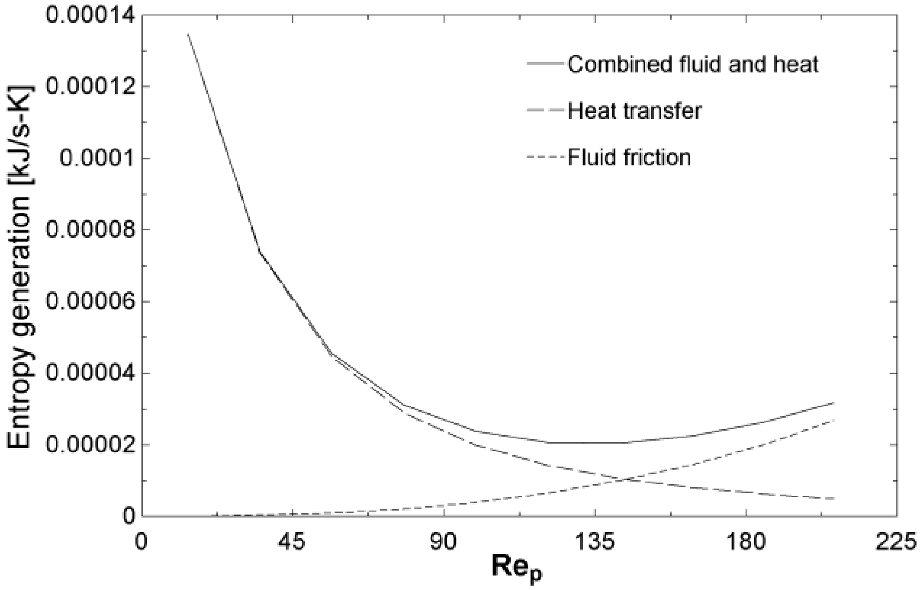
- Method 3 - Kuwahara et al. [9]:

$$Nu = \left(1 + \frac{4(1-\varepsilon)}{\varepsilon}\right) + \frac{1}{2}(1-\varepsilon)^{0.5}Re_pPr^{1/3} \tag{18}$$

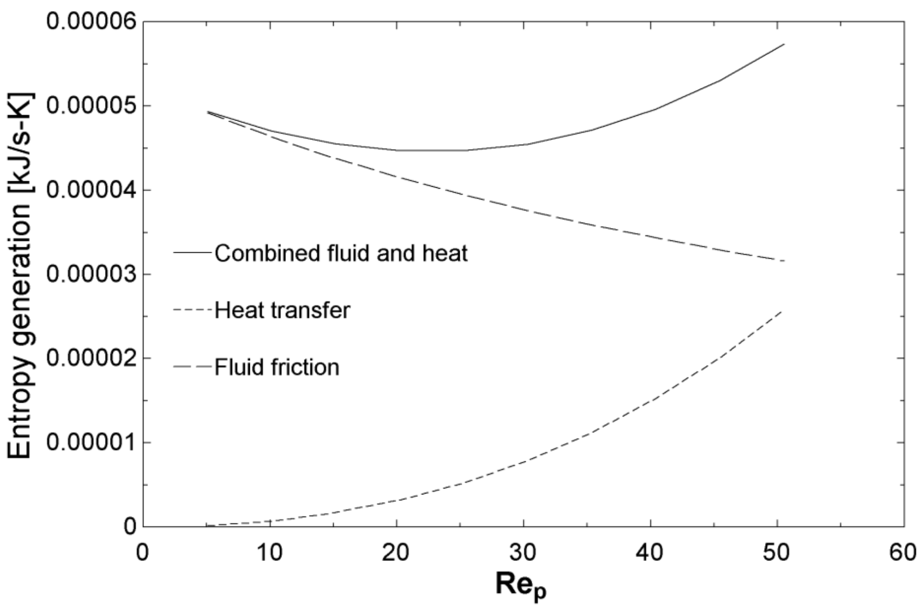
- Method 4 - Gunn [10]:

$$Nu = (7 - 10\varepsilon + 5\varepsilon^2)\left(1 + 0.7Re^{0.2}\ Pr^{1/3}\right) + (1.33 - 2.4\varepsilon + 1.2\varepsilon^2)Re^{0.7}Pr^{1/3} \tag{19}$$

Method 2 [8] is developed from a Reynolds analogy from a mass transfer correlation for closely packed beds, from published data for 3 < Re < 10,000 [15]. The data is corrected for axial fluid dispersion resulting in the following mass transfer correlation for a packed bed: $Sh = 2 + 1.1\ Re^{0.6}\ Sc^{1/3}$. Equation 17 is applicable to flows with a Reynolds number between 15 and 8,500. Method 3 is developed from two-dimensional numerical simulations of a packed bed. When developing Eq. (18), a series of simulations was conducted with varying void fractions, Reynolds and Prandtl numbers. The authors [9] reported the correlation is applicable for a wide range of Re and Pr numbers, as well as $0.2 < \varepsilon < 0.9$. Method 4 is developed from four asymptotic solutions, one that bounds Nu for (i) particles with high and low Reynolds number and void fractions for particles, (ii) a single particle at low Re, and two experimentally developed correlations that bound Nu at low Re and Pr for (iii) a single particle and (iv) a packed bed. The authors [10] developed a correlation that satisfies all four of the limiting relations, i.e., Method 4 (Eq. 19).



(a)



(b)

Figure 3: Entropy generation at various Reynolds numbers with a) 1 cm and b) 4 mm particle diameters

Variations between predictions from the different correlations can be expected, not only due to uncertainties, but also the different flow conditions, bed properties, and assumptions used to develop each of the methods. Unique to the present correlation, is can predict the Nusselt number as a function of friction factor and Reynolds numbers of a system. This allows the correlation to be used to predict the entropy generation in a packed bed, due to fluid flow and heat transfer irreversibilities.

As illustrated in Fig. 3, the entropy generation, predicted by Eq. 13, exhibits the expected trend required by the Second Law of Thermodynamics, wherein the total entropy generation of any process will always increase, i.e., $\dot{S}_{gen} \geq 0$. A concave trend in the entropy generation is exhibited. For these plots, the fluid temperature (T_∞) and reference surface temperature ($\tilde{T}_s$) are assumed to be 325K, and 293K, respectively. The other conditions are the same as the experimental settings. Numerical values of $Re_{p,opt}$ and $\dot{S}_{gen,opt}$ can be determined from Fig. 3, for these representative system parameters, which are taken to be 140 and 0.0000205 kJ/s-K for D_p = 1 cm and 25 and 0.00004468 kJ/s-K for D_p = 4 mm, respectively.

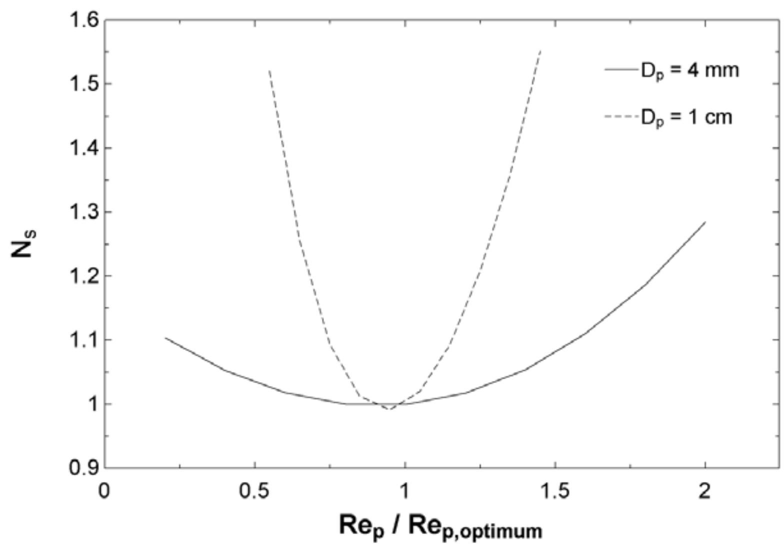


Figure 4: Entropy generation minimization with different particle diameters at various Reynolds numbers

As illustrated in Fig. 4, the numerical values of $\dot{S}_{gen,opt}$ and $Re_{p,opt}$ can be used to develop a dimensionless plot of the entropy generation number. Differences in the packing material (D_p) and operating conditions collapse onto a single plot, i.e., N_s. These results indicate this is a useful method to improve packed bed designs by minimizing the entropy generation during operation.

5. Conclusions

In this paper, the fluid flow and heat transfer are investigated for a packed bed reactor by analyzing the entropy generation minimization. Different operating parameters were collapsed onto a single plot, predicted by the entropy generation number, thereby providing a method to compare a wide variety of designs, with a single parameter. A Reynolds analogy was used to predict the Nusselt number, which varies with Reynolds number and friction factor, connecting the fluid flow and heat transfer properties, and providing a tool for a second law analysis. The insights of this research provide a method to improve the design of packed bed reactors to achieve higher system efficiencies by reducing the entropy generation during operation.

6. Acknowledgements

The authors express their grateful appreciation to the Natural Sciences and Engineering Research Council of Canada (NSERC) for their financial support; and F. Wang, P. le-Pargneux, M. Lesire, V. Daggupati for their technical assistance.

7. References

[1] L.M. Lewis, M. Serban and J.K. Basco, "Hydrogen production at <550C using a low temperature thermochemical cycle", Nuclear production of hydrogen, second information exchange meeting Argonne, Argonne, Illinois, US, 2003. pp. 145-156.

[2] M.A. Rosen, "Advances in hydrogen production by thermochemical water decomposition: a review", Energy, Vol. 35, Iss. 2, 2010, pp. 1068-1076.

[3] A. Bejan, "Entropy generation minimization: the method of thermodynamic optimization of Finite-Size Systems and finite-Time Processes", CRC Press, 1996.

[4] T. Atmakidis and E.Y. Kenig, "CFD-based analysis of the wall effect on the pressure drop in packed beds with moderate tube/particle diameter ratios in the laminar flow regime", Chemical Engineering Journal, Vol. 155, 2009, pp. 404-410.

[5] S. Ergun, "Fluid flow through packed columns", Chemical Engineering Progress, Vol. 48, 1952, pp. 89-94.

[6] G.G. Chase and P. Dachavijit, "A correlation for yield stress fluid flow through packed beds", Rheologica Acta, 2005, pp. 495-501.

[7] J.A. Tallmadge, "Packed bed pressure drop — an extension to higher Reynolds numbers", American Institute of Chemical Engineers Journal, 1970, pp. 1092-1093.

[8] N. Wakao, S. Kaguei and T. Funazkri, "Effect of fluid dispersion coefficients on particle-to-fluid heat transfer coefficients in packed bed: Correlation of Nusselt Numbers", Chemical Engineering Science, Vol. 34, Iss. 3, 1979, pp. 325–336.

[9] F. Kuwahara, M. Shirota and A. Nakayama, "A numerical study of interfacial convective heat transfer coefficient in two-energy equation model for convection in porous media", International Journal of Heat and Mass Transfer, Vol. 44, 2001, pp. 1153–1159.

[10] D.J. Gunn, "Transfer of Heat or Mass to Particles in Fixed and Fluidised Beds", International Journal of Heat and Mass Transfer, Vol. 21, 1978, pp. 461.476.

[11] W.L. McCabe, J.C. Smith and P. Harriott, "Unit Operations of Chemical Engineering", 4th ed. Mc-Graw Hill, 1985.

[12] J.G.I. Hellström, T.S. Lundström, "Flow through Porous Media at Moderate Reynolds Number", International Scientific Colloquium, Modelling for Material Processing, Riga, 2006, June 8-9.

[13] Y. A. Cengel. Heat and Mass Transfer: a Practical Approach, 3rd ed. McGraw Hill, 2007.

[14] G.F. Naterer. Heat Transfer in Single and Multiphase Systems, CRC Press, 2003.

[15] N. Wakao, T. Funazkri, "Effect of fluid dispersion coefficients on particle-to-fluid heat transfer coefficients in packed bed: Correlation of Sherwood numbers", Chemical Engineering Science, Vol. 33, Iss. 10, 1978, pp. 1375-1384.