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# Challenges and progress on the modeling of entropy generation in porous media: A review

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## Abstract

Depending upon the ultimate design, the use of porous media in thermal and chemical systems can provide significant operational advantages, including helping to maintain a uniform temperature distribution, increasing the heat transfer rate, controlling reaction rates, and improving heat flux absorption. For this reason, numerous experimental and numerical investigations have been performed on thermal and chemical systems that utilize various types of porous materials. Recently, previous thermal analyses of porous materials embedded in channels or cavities have been re-evaluated using a local thermal non-equilibrium (LTNE) modelling technique. Consequently, the second law analyses of these systems using the LTNE method have been a point of focus in a number of more recent investigations. This has resulted in a series of investigations in various porous systems, and comparisons of the results obtained from traditional local thermal equilibrium (LTE) and the more recent LTNE modelling approach. Moreover, the rapid development and deployment of micro-manufacturing techniques have resulted in an increase in manufacturing flexibility that has made the use of these materials much easier for many micro-thermal and chemical system applications, including emerging energy-related fields such as micro-reactors, micro-combustors, solar thermal collectors and many others. The result is a renewed interest in the thermal performance and the exergetic analysis of these porous thermochemical systems. This current investigation reviews the recent developments of the second law investigations and analyses in thermal and chemical problems in porous media. The effects of various parameters on the entropy generation in these systems are discussed, with particular attention given to the influence of local thermodynamic equilibrium and non-equilibrium upon the second law performance of these systems. This discussion is then followed by a review of the mathematical methods that have been used for simulations. Finally, conclusions and recommendations regarding the unexplored systems and the areas in the greatest need of further investigations are summarized.

**Keywords:** Entropy generation; Heat transfer; Forced convection; Chemical reactors; Solid material; Porous media.

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## Nomenclature

$a_{sf}$	interfacial area per unit volume of porous media, $\text{m}^{-1}$	$S_L$	lower wall-fluid interface entropy generation rate, $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$
$B$	A dimensionless parameter used in Eqs. (10) and (11) which depends on the thermophysical properties of the system	$S_U$	upper wall-fluid interface entropy generation rate, $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$
$B_0$	magnetic field, T	$T$	temperature, K
$Bi$	Biot number	$U$	dimensionless velocity
$Br$	Brinkman number ( $\text{Pr} \cdot \text{Ec}$ )	$u$	velocity, $\text{m} \cdot \text{s}^{-1}$
$Da$	Darcy number	<b>Greek symbols</b>	
$E$	flow strain rate tensor	$\beta$	temperature jump coefficient
$\text{Ec}$	Eckert number	$\kappa$	permeability, $\text{m}^2$
$h_{sf}$	fluid-to-solid heat transfer coefficient, $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	$\varphi$	porosity
$h$	Characteristic length of the system, m	$\phi$	nanoparticles volume fraction
$\mathbf{J}^D$	diffusion flux	$\mu$	dynamic viscosity of the fluid, $\text{Kg} \cdot \text{s}^{-1} \cdot \text{m}^{-1}$ , chemical potential, $\text{Joul} \cdot \text{Kg}^{-1}$
$\mathbf{J}^s$	entropy flux	$\theta$	dimensionless temperature
$k$	thermal conductivity of the medium, $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	$\Pi$	shear stress tensor
$k_{ef}$	effective thermal conductivity of the fluid ( $\varepsilon k_f$ ), $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	$\sigma$	electrical conductivity of fluid, $\text{S} \cdot \text{m}^{-1}$
$k_{es}$	effective thermal conductivity of the solid ( $(1-\varepsilon)k_s$ ), $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	<b>Subscripts</b>	
$N''$	dimensionless local entropy generation rate within the fluid phase of the porous medium	$ef$	effective fluid characteristic
$M$	Hartmann number	$es$	effective solid characteristic
$\text{Pr}$	Prandtl number	$f$	Fluid
$Q_L$	Lower interface heat flux	$i$	$i^{\text{th}}$ species
$Q_U$	Upper interface heat flux	$m$	Mean
$q'''$	volumetric internal heat generation rate, $\text{W} \cdot \text{m}^{-3}$	$s$	Solid
$\dot{S}'''$	local entropy generation rate, $\text{W} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$		

## 1. Introduction

The use of porous media in thermal and chemical systems can provide significant operational advantages. This has led to increased interest in potential applications involving promoting a more uniform temperature distribution, increasing the heat transfer rate, controlling reaction rates, and improving heat flux absorption. For this reason there is a renewed interest in the modeling of porous materials for use in scientific and industrial applications [1]. Understanding and formulating the characteristics of porous materials has the potential to significantly impact the thermal performance of a large number of natural and artificial processes. For example, porous material play a significant role in physicochemical and biochemical reactions of methane to carbon dioxide through the bacterial

activity in the methane oxidation layer [2,3], which are used in connection with various approaches to waste disposal processes [4]. Porous materials have also been used in solar systems to enhance both the quantity and quality of the absorbed heat flux and temperature within these microstructures [5]. Porous materials have also been proposed for use in battery electrodes and other electrochemical systems [6]. In all of these application, the use of porous media can result in enhanced heat transfer, reductions in system weight, better reaction control, and sound isolation making them highly desirable for a wide range of applications [1,7].

Historically, porous media have been extensively used in thermofluidics, due to their ability to increase the Nusselt number and consequently decrease the temperature of heat transfer systems [8]. To simulate the physical processes occurring inside porous media, a number of different macroscopic and microscopic approaches have been used to capture the requisite engineering characteristics. Among these, the volume averaging theory (VAT) [9] and pore scale modeling (PSM) [10] are most frequently utilized. The well-known VAT was identified and applied by Whitaker in his pioneering article in 1969 [9]. The VAT approach exploits volume averaged quantities, *e.g.* volume-averaged velocity. When the VAT approach is employed, two modelling approaches can be adopted to simulate the porous system. A classical model is the local thermodynamic equilibrium approach, which assumes that at any point the fluid and solid phases of the porous medium are in full thermodynamic equilibrium [11]. This includes thermal, chemical and mechanical local equilibria. Under the local thermal equilibrium (LTE) approach, a single energy equation is used to model the temperature field of the porous system [12,13], since a thermal equilibrium exists between the two phases at any local point. The second approach, local thermal non-equilibrium (LTNE), assumes a local difference between the temperature fields of the two phases and hence two energy equations are required to simulate the system [14,15]. Although LTNE is more accurate, it is computationally more expensive as it relies on two energy equations coupled together with a heat transfer coefficient parameter [14,15]. It has been shown that LTNE approach should be used when the system under investigation has a low internal Biot number or the difference between the thermal conductivities of the solid and fluid materials is high [16,17]. Further, it has been demonstrated that LTNE is the preferred method for the analysis of systems that feature internal heat generation [17–20]. When the internal Biot number approaches to a high value, the temperature distribution obtained from LTNE model would be similar to that of the LTE model, and hence the simulation can be carried out using the one-energy-equation methodology [17]. This is also true for a porous system with similar thermal conductivities for solid and fluid materials. Alternatively, PSM of porous media delivers velocity and temperature distributions through the general governing equations of fluid and heat flow and without resorting to porous media phenomenological equations [21–23]. It is noted that the high demand of computational resources has restricted the application of PSM to simple porous structures [10]; there also exists a limited number of PSM attempts in thermochemical systems [24–27]. The latter method and the classical governing equations, however, exhibit identical mathematical equations [28]. Therefore complex turbulent flows within porous media can be analyzed with this technique [29][30] since Navier-Stokes equations are solved in PSM approach. The following paragraph discusses the differences between investigations on the first and the second thermodynamic laws in porous media.

Besides the analysis of porous systems from the first law perspective, the second law analysis of these systems has gained considerable attention [2,13,14,31–36]. This is because the second law perspective of a system provides a qualitative insight, and hence it has attracted significant resources compared with the first law perspective, which is a quantitative approach [37]. When the energy systems are considered, the entropy generation and consequently exergy destruction have an important role [38]. Although fluid flow and heat transfer investigations in porous media have been reviewed recently by Mahdi *et al.* [39], no review on the entropy generation analyses in porous systems has been provided in the literature. Many scholars have started to re-investigate porous systems from the second law perspective, rather than the first law. These investigations have been extended from thermal to chemical and thermochemical systems [40]. The present review aims to capture the recent analyses and investigations on the entropic and exergetic performances of porous systems. These systems could be purely thermal, or include thermochemical processes. In the second case the analyses need to consist of a range of multiphysics phenomena [41,42]. Attention will be paid to porous thermal systems with nanofluid, magnetic field, radiation effect, *etc.* Further, effort is made to cover the recent investigations on the thermodynamic analyses of porous thermo-dispersive systems, exothermic and endothermic thermochemical systems, micro-combustors and micro-reactors.

This review has been divided into five sections. After this Introduction, entropy generation in thermal systems is reviewed in Section 2. Section 3 covers the entropy generation analyses in thermochemical systems. Section 4 discusses the analysis methods, *i.e.*, analytical, semi-analytical, analytical-numerical and numerical techniques that have been used in these investigations. Finally, Section 5 presents the conclusions and outlook.

## **2. Entropy generation in porous thermal systems**

As stated earlier, porous media have been used vastly in thermal systems. Porous media can bring about advantages such as better heat absorption and more uniform temperature distribution [5]. Using a porous material in cooling systems, can results in increasing the heat transfer coefficient and finally decreasing the temperature of the system, which is a desired outcome in many of these thermal processes [11]. However, there is always a trade-off between the gain in heat transfer rate and the pressure drop in designing the porous thermal systems [11,43]. Moreover, incorporating porous media in thermal systems, besides affecting the heat transfer coefficient directly, could have other indirect effects, such as those on the radiative heat transfer within the system [44], viscous dissipation [45], thermal performance and finally temperature of the system. These eventually affect the entropic behaviour of the system and influence its exergetic characteristics [34,46,47].

In general, entropy generation in any thermofluid system can be calculated directly or indirectly [48]. In the direct method that is more applicable to laminar flows, the heat transfer and viscous irreversibility terms are determined in detail and are then calculated directly. In the indirect method, the entropy partial differential equations need to be solved. This method is suitable for turbulent problems when the turbulent terms in the entropy differential equations cannot be determined or neglected [48]. Regarding the second law analyses in porous media, after the ground-breaking work of Bejan [49], many scholars re-examined porous systems from the second law perspective. For years scientists have opted in favor of LTE model to analyse the system based on the second law [50]. Not only the entropy generation

rates due to the heat transfer and viscous dissipation have been considered [50–52], entropy generation by the presence of magnetic fields has been also accounted and calculated [31,53]. By realizing the importance of the two-energy equation model for porous media, i.e., the LTNE model [54], thermal [55–57] and entropy generation [45,58] analyses of porous systems based on the LTNE model have gained considerable attention. In the following subsections, effects of some of these parameters on the entropy generation in porous media are discussed in detail.

### 2.1. Viscosity effects

As far as fluid flow through a clear channel is concerned, viscous dissipation is usually negligible [8,59]. However, when dealing with highly viscous flows, such as those in food processing industries [60], an internal heat generation term should be added to the right-hand side of the energy equation [11]. In addition to the previously mentioned viscous dissipation term, when dealing with porous media, another viscous dissipation term should be added to the energy equation as to account for the internal heat generation because of the friction between the fluid and the porous insert [1,45]. This modifies the energy equation as another added term is related to the second order of the velocity gradient and the permeability of the porous medium [31,45]. The former viscous dissipation can be written based on Darcy's law and the latter one can be modelled according to Brinkman approach in porous media [61]. As a result, when LTE model is considered and viscous dissipations have also been taken into account, the following formulation governs the energy transport of the system [8]:

$$\underbrace{(\rho c)_m \frac{\partial T}{\partial t}}_{\text{storage of energy}} + \underbrace{(\rho c)_f \mathbf{v} \cdot \nabla T}_{\text{convection}} = \underbrace{\nabla \cdot (k_m \nabla T)}_{\text{conduction}} + \underbrace{\frac{\mu_f}{\kappa} \mathbf{v} \cdot \mathbf{v}}_{\text{Darcy viscous dissipation}} + \underbrace{\mu_{ef} \nabla^2 \mathbf{v}}_{\text{Brinkman viscous dissipation}} + \underbrace{q_m'''}_{\text{heat generation}}, \quad (1)$$

where

$$(\rho c)_m = (1 - \phi)(\rho c)_s + \phi(\rho c)_f, \quad (2a)$$

$$k_m = (1 - \phi)k_s + \phi k_f, \quad (2b)$$

$$\mu_{ef} = \frac{\mu_f}{\phi}, \quad (2c)$$

$$q_m''' = (1 - \phi)q_s''' + \phi q_f''', \quad (2d)$$

which ultimately by considering a porous channel without heat generation and steady state condition, the energy equation reads

$$(\rho c)_f u_f \frac{\partial T}{\partial x} = k_m \frac{\partial^2 T}{\partial y^2} + \frac{\mu_f}{\kappa} u_f^2 + \mu_{ef} \left( \frac{\partial u_f}{\partial y} \right)^2. \quad (3)$$

The local entropy generation formulation for the above mentioned system can be written as

$$\dot{S}''' = \underbrace{\frac{k_m}{T^2} \left[ \left( \frac{\partial T}{\partial x} \right)^2 + \left( \frac{\partial T}{\partial y} \right)^2 \right]}_{\text{entropy generation due to heat transfer}} + \underbrace{\frac{\mu_f}{\kappa T} u_f^2 + \frac{\mu_{ef}}{T} \left( \frac{\partial u_f}{\partial y} \right)^2}_{\text{entropy generation due to viscous dissipation}} \quad (4)$$

As previously mentioned, by considering LTNE model two energy equations are used to visualize the temperature fields in both fluid and solid phases of the porous system. Equation (3) for a porous channel can be changed to the following equations, if the LTNE approach is considered [45,62,63]

$$\rho c_p u_{f1} \frac{\partial T_f}{\partial x} = k_{ef} \frac{\partial^2 T_f}{\partial y^2} + h_{sf} a_{sf} (T_s - T_f) + \frac{\mu_f}{\kappa} u_f^2 + \mu_{ef} \left( \frac{\partial u_f}{\partial y} \right)^2, \quad (5a)$$

$$0 = k_{es} \frac{\partial^2 T_s}{\partial y^2} - h_{sf} a_{sf} (T_s - T_f), \quad (5b)$$

where Eqs. (5a) and (5b) govern the heat transfer in fluid and solid phases of the porous medium, respectively. In the above equations the term  $h_{sf} a_{sf} (T_s - T_f)$  calculates the internal heat exchange *between* the solid and fluid phases of the system. If the value of parameter  $h_{sf}$  increases, the heat transfer rate between the two phases (interphase heat transfer) increases and, ultimately, the temperatures of solid and fluid phases converge to a certain value. This decreases the magnitude of the term  $h_{sf} a_{sf} (T_s - T_f)$  to a very low value and eventually transforms the LTNE system to an LTE one.

The local entropy generation formulation for the above mentioned porous system under LTNE condition can be written as [45,62,63]

$$\dot{S}_f''' = \frac{k_{ef}}{T_f^2} \left[ \left( \frac{\partial T_f}{\partial x} \right)^2 + \left( \frac{\partial T_f}{\partial y} \right)^2 \right] + \underbrace{\frac{h_{sf} a_{sf} (T_s - T_f)}{T_f}}_{\text{entropy generation due to heat exchange between phases in porous medium}} + \underbrace{\frac{\mu_f}{\kappa T_f} u_f^2 + \frac{\mu_{ef}}{T_f} \left( \frac{\partial u_f}{\partial y} \right)^2}_{\text{entropy generation due to viscous dissipation}}, \quad (6a)$$

$$\dot{S}_s''' = \frac{k_{es}}{T_s^2} \left[ \left( \frac{\partial T_s}{\partial x} \right)^2 + \left( \frac{\partial T_s}{\partial y} \right)^2 \right] - \frac{h_{sf} a_{sf} (T_s - T_f)}{T_s}. \quad (6b)$$

It is clear from the above formulations that the viscous dissipation plays a significant role in the entropy generation formulation as it has two terms on the right hand side of the governing equations. From these equations, it can be concluded that the velocity, viscosity and temperature of the fluid participate in entropy generation due to viscous dissipation. For a specific fluid, the velocity impact is substantial as increasing the velocity can increase the entropy generation by a substantial amount as illustrated in previous investigations [15,63]. A simple comparison between the values for the vertical axes in parts *a* and *b* of Fig. 1 shows that, for a set of parametric values used in this investigation [15], the irreversibility due to the fluid friction is much more than the irreversibility of the heat transfer. In this figure,



Model 1 incorporates the viscosity effects in the energy governing equations, while Model 2 neglects these effects. From Fig. 1a it is apparent that the heat transfer irreversibility for Model 1 is much higher than for Model 2. These illustrations reflect the importance of the two irreversibility terms that result from the fluid friction and demonstrate the relative importance of these effects for the case of irreversibility analyses in porous media. Further discussion about the effects of the volumetric concentration rate on the entropy generation, shown in Fig. 1, is included in subsection 2.4.

If a PSM approach is used, the momentum and energy equations differ from the ones provided earlier as the Navier-Stokes equations, together with the standard energy equation for a viscous flow must be solved. As a result, the second term in Eq. (3) or the third term in Eq. (5) will not appear in the energy equation, and consequently the entropy generation equation will not have the corresponding term. Furthermore, using this approach, all of the corresponding fluid friction irreversibilities are calculated via shear stress tensors. This has been thoroughly illustrated in recent investigations for entropy generation using the PSM approach in isotropic porous media by Torabi *et al.* [21,22].

## 2.2. Electromagnetic effects

Buffers and solutions conducting electricity are used in many different types of thermofluid applications [64]. If a magnetic field is applied to the system, the interaction between the electric current density and the magnetic field produces a Lorentz body force [65]. This provides the essential force for the fluid flow. As this technique does not need an actual pump to propel the fluid, it has been extensively used in the recent investigations on microfluidic systems [64,66]. Consequently, experimental [67] and theoretical [68–70] studies on the magnetohydrodynamic flows in porous media have attracted considerable attention. If a channel under the influence of a vertical magnetic field is considered, the magnetic field shows its effect on the velocity distribution [71] and as a result, it is necessary to add another term,  $\sigma B_0^2 u^2$  to the right hand side of the energy equation shown in Eq. (3). Here,  $B_0$  is the applied magnetic field and  $\sigma$  is the electrical conductivity of the fluid [31]. Hence, the energy equation for the channel under steady-state conditions, assuming viscous dissipation and a magnetic field can be written as:

$$(\rho c)_f u_f \frac{\partial T}{\partial x} = k_m \frac{\partial^2 T}{\partial y^2} + \frac{\mu_f}{\kappa} u_f^2 + \mu_{ef} \left( \frac{\partial u_f}{\partial y} \right)^2 + \sigma B_0^2 u_f^2. \quad (7)$$

As is the case for other phenomena that have impacts on the both the first and second law performance of a thermal system, the magnetic field does have important effects on the qualitative performance of the system [31,71–75]. If the above mentioned porous channel is considered, the local entropy generation rate within the channel can be calculated by the following formulation [31,62]:

$$\dot{S}''' = \frac{k_m}{T^2} \left[ \left( \frac{\partial T}{\partial x} \right)^2 + \left( \frac{\partial T}{\partial y} \right)^2 \right] + \frac{\mu_f}{\kappa T} u_f^2 + \frac{\mu_{ef}}{T} \left( \frac{\partial u_f}{\partial y} \right)^2 + \underbrace{\frac{\sigma B_0^2}{T} u_f^2}_{\text{entropy generation due to magnetic field}} \quad (8)$$

Recent investigations in this area have indicated that increases in the magnetic parameter, *i.e.*, the Hartmann number, increases the entropy generation rate [72,75]. However, depending on the thermophysical specifications of the system, the impact of the Hartmann number on the entropy generation rate may, in fact, be negligible [31]. As it can be seen from the entropy generation term due to the magnetic field, this part of the entropy generation rate also depends on the electrical conductivity of the fluid and velocity field of the flow. Hence, from the above formulation which shows the local entropy generation rate in a porous channel with viscosity and magnetic field, it is intuitively comprehended that if the flow field is weak, the entropy generation from magnetic effect could be negligible. This has been also observed in previous investigations [31].

Equation (8) can be directly applied to the LTE model. However, similar to what was described previously, under LTNE conditions, an additional term should be included in the entropy generation equation. This term would account for the irreversibility due to the heat transfer between the solid and fluid phases of the porous medium. Of course, if the LTNE model is adopted, another equation, which calculates the entropy generation rate for the solid portion of the porous medium is also required [16,20]. With these considerations, the following formulations can be used to govern the local entropy generation rate in a porous channel when non-equilibrium conditions exist:

$$\dot{S}_f''' = \frac{k_{ef}}{T_f^2} \left[ \left( \frac{\partial T_f}{\partial x} \right)^2 + \left( \frac{\partial T_f}{\partial y} \right)^2 \right] + \frac{h_{sf} a_{sf} (T_s - T_f)}{T_f} + \frac{\mu_f}{\kappa T_f} u_f^2 + \frac{\mu_{ef}}{T_f} \left( \frac{\partial u_f}{\partial y} \right)^2 + \frac{\sigma B_0^2}{T_f} u_f^2, \quad (9a)$$

$$\dot{S}_s''' = \frac{k_{es}}{T_s^2} \left[ \left( \frac{\partial T_s}{\partial x} \right)^2 + \left( \frac{\partial T_s}{\partial y} \right)^2 \right] - \frac{h_{sf} a_{sf} (T_s - T_f)}{T_f}. \quad (9b)$$

To solve and illustrate the local and total entropy generation rates, the majority of the available literature considers the non-dimensional equations. In a thermofluidic system, transforming the dimensional governing equations to dimensionless equations is a nontrivial task and depends on a number of factors. For example, boundary conditions heavily influence the dimensionless equations and the aforementioned governing equations are subject to this dependence. If a specific channel size is considered, the outer thermal boundary conditions may significantly change the dimensionless method and parameters. However, for the sake of completeness, it can be assumed that the entropy generation Eqs. (4) and (6) can be non-dimensionalized to create the following expressions, respectively [16]:

$$N_f''' = \frac{\dot{S}_f''' h^2}{k_m} = \frac{\left[ \left( \frac{\partial \theta}{\partial X} \right)^2 + \left( \frac{\partial \theta}{\partial Y} \right)^2 \right]}{k(\theta + B)^2} + \frac{Br U_f^2}{Da(\theta + B)} + \frac{Br \left( \frac{\partial U_f}{\partial Y} \right)^2}{(\theta + B)} + \frac{M^2 Br U_f^2}{(\theta + B)}, \quad (10)$$

$$N_s''' = \frac{\dot{S}_s''' h^2}{k_{es}} = \frac{\left[ \left( \frac{\partial \theta_f}{\partial X} \right)^2 + \left( \frac{\partial \theta_f}{\partial Y} \right)^2 \right]}{k(\theta_f + B)^2} + \frac{Bi(\theta_s - \theta_f)}{(\theta_f + B)} + \frac{Br U_f^2}{Da(\theta_f + B)} + \frac{Br \left( \frac{\partial U_f}{\partial Y} \right)^2}{(\theta_f + B)} + \frac{M^2 Br U_f^2}{(\theta + B)}, \quad (11a)$$

$$N_s''' = \frac{\dot{S}_s'' h^2}{k_{ef}} = \frac{\left[ \left( \frac{\partial \theta_s}{\partial X} \right)^2 + \left( \frac{\partial \theta_s}{\partial Y} \right)^2 \right]}{(\theta_s + B)^2} - \frac{Bi(\theta_s - \theta_f)}{(\theta_s + B)}, \quad (11b)$$

where Eq. (10) provides the non-dimensional entropy generation based on the LTE model, and Eqs. (11a) and (11b) describe the non-dimensional entropy generation based on the LTNE model for the fluid and solid phases of the porous medium, respectively. Although, in general, different characteristics of the system can determine how the above dimensionless parameters are obtained, in a specific situation these parameters may read as [12,16]:

$$U = \frac{u}{u_r}, u_r = -\frac{h^2}{\mu_f} \frac{\partial p}{\partial x}, \theta = \frac{k_{es}(T - T_w)}{q_w h}, k = \frac{k_{es}}{k_{ef}} = \frac{(1 - \varepsilon)k_s}{\varepsilon k_f}, Bi = \frac{h_{sf} a_{sf} h^2}{k_{es}}, Y = \frac{y}{h}, X = \frac{x}{h}, \quad (12)$$

$$Da = \frac{\kappa}{h^2}, Br = \frac{\mu_f u_r^2}{q_w h}, B = \frac{k_{ef} T_w}{q_w h}, M = \sqrt{\frac{\sigma}{\mu_f}} h B_0$$

The dimensionless total entropy generation can be easily calculated by integrating the local entropy generation rate over the volume of the thermal system under investigation.

To date, only a handful of investigations involving the effects of the magnetic field on the irreversibility of porous systems using equilibrium assumptions have been reported [12,13,62,72,75], and no research into the effect of magnetic fields on the entropy generation rate in a porous thermal system have been reported, when thermal non-equilibrium conditions between the two phases is available. Because these two features, *i.e.*, the magnetic field and the LTNE, may overlap in many emerging fields, it is important that the local and total entropy generation rates be understood along with the impact of both LTNE model and magnetic effects.

### 2.3. Radiative effects

Previous investigations have indicated that radiative heat transfer can be significant in porous media at high temperatures [76], and thermal radiation has been included in the analyses of combustion in porous media for a relatively long time, see Refs. [77–79]. In addition, the impact of thermal radiation in porous media have been experimentally investigated by Kamimoto *et al.* [80]. Subsequent to this study, a number of investigations have begun to include the effects of radiation in porous systems such as combustors [44,81] and solar collectors [82] in the thermal modeling of these systems. From a simulation perspective, the radiative effects in porous materials have been modeled using two approaches. The first of these, employs a Rosseland approximation and considers a thermal conductivity factor in lieu of thermal radiation and adds this to the thermal conductivity of the solid structure of the porous medium [5,83–85]. This approach is computationally inexpensive, yet is only an approximation method. The second approach assumes a fourth order P1-radiative transfer model in the energy equation, which is approximately 90% accurate for optical thicknesses up to unity [86,87]. Other more complex simulation methods can be also found in the literature [88].

It has also been shown that the radiation parameter has a significant impact on the heat transfer in porous systems. This has been demonstrated in a number of theoretical [71,89–91] and experimental [92,93] investigations. As the radiation heat transfer in porous material can be simplified by incorporating the radiative effect to the thermal conductivity of the solid phase of the porous medium, it impacts the transfer rate and therefore decreases the temperature of the investigated thermal system. This has been repeatedly illustrated in the literature [84]. However, unlike the viscous dissipation and magnetic fields, this indirectly participates in the entropy generation by modifying the temperature fields of the medium [89,90,94,95]. This fact alone has been shown to be true for the entropy generation in non-porous systems [96–98]. It should also be noted that some investigators have shown that the radiation heat transfer directly affects the entropy generation rate by including a specific term in the formulation [99–101]. While the correct methodology for calculating the entropy generation rate in thermal systems, including radiation is an open question in the literature, both methods show that increasing the radiation parameter increases the entropy generation rate [94,95,100,101]. The situation for entropy generation investigations in porous thermal systems using the LTNE approach and radiation effects is similar to that mentioned earlier for electromagnetic effect. Thus, currently there is insufficient information of how the radiation effects and the LTNE conditions impact the entropy generation in porous media.

#### 2.4. Nanofluid effects

Nanofluids have been used for nearly two decades to increase the thermal conductivity of the base fluid, so that the Nusselt number increases and consequently the temperature of the system decreases [102,103]. So far, many theoretical [104–106] and experimental [107,108] investigations have been conducted on thermal performance of porous media saturated with nanofluids. The inclusion of nanofluids in a system can also affect its second law performance. In recent years, scholars have started to analyse porous thermal systems accommodating nanofluid flow from both a first and second law perspective [15,19,20,35,63,74,90,95,109].

The total entropy generation rate in these thermofluid systems is the result of the combined effects of heat transfer and fluid friction irreversibilities. The addition of nanoparticles to the base fluid, affects the total entropy generation [103]. It has been shown that the inclusion of nanofluids decreases the temperature of the systems and hence the heat transfer contribution to the total entropy generation rate decreases [15,35]. However, nanoparticles increase the viscosity of the fluid and therefore intensify the exergy loss due to the heat generation and hence, the pressure drop in the system increases [15,63]. Mathematically speaking, if a LTNE model is considered, the nanoparticles increase the  $\mu_f$  to  $\mu_{nf}$  in the third and fourth terms on the right hand side of Eq. (9a); this ultimately increases the fluid friction portion of the entropy generation rate. For the LTE model, a similar change occurs for the second and third terms on the right hand side of Eq. (8). Interestingly, it has been illustrated that, if the LTNE approach is used, the entropy generation rate in the fluid phase of the porous section increases with the volume fraction, while it decreases in the solid phase of the porous section [63]. Due to the different effects of nanoparticles on the entropy generation rate of a system, the overall effect of adding nanoparticles to the base fluid is a complicated phenomenon and may include competing effects. These competing effects have been illustrated in a recent investigation by Ting *et al.* [63], and are

illustrated in Fig. 2. In general, it has been shown that the incremental increase caused by the fluid friction irreversibility due to the addition of nanoparticles to the base fluid, overtakes the irreversibility reduction because of lower temperature within the solid phase of the porous system. As a result, it has been reported that the addition of nanoparticles, normally increases the irreversibility of a porous thermal system [15,19,20,35,63,95]. As an example, Kefayati [35] analyzed the entropy generation rate in a porous cavity filled with a nanofluid, and showed that increasing the nanofluid volume fraction would ultimately increase the total entropy generation rate of the process. This effect has been illustrated in Fig. 3. A similar study was also carried out by Hoseinpour *et al.* [110]. In this investigation, the authors showed that it may be possible to minimize the entropy generation in the system by varying the porosity of the medium.

## 2.5. Effects of velocity slip and temperature jump

Although in macro channels, the continuum conditions at the wall are valid, it has been shown that in micro channels this assumption may not be valid [111]. The continuum approximation breaks down when the mean free path of the fluid molecules becomes comparable to the length scale of the system. This is represented by Knudson number, which is the ratio of mean free path of the fluid to the length scale of the system [112,113]. A thorough discussion of the Knudson number and the effect of this parameter on the mass flow rate in microchannels can be found in a relatively new investigation by Lv *et al.* [114]. When the Knudson number is below 0.01 the length scale of the systems is dominant and the continuum assumption should be considered [115]. However, if this ratio is higher than 0.01 the mean free path of the fluid molecules is large enough that the velocity slip and temperature jump boundary conditions at the interface of the solid walls and the fluid, should be considered [13,115].

Consideration of the velocity slip and specifically the temperature jump at the porous-solid interface has two important effects on the entropy generation rate of the system. The first effect, which is an indirect one, is the consequence of modifications to the temperature field of the system that ultimately impacts the entropy generation rate [13]. The second, is the generation of entropy that occurs within the small gap between the wall and the fluid due to the temperature difference between the wall and fluid [12]. This has a direct influence on the total entropy generation rate of the system. If this condition applies to a channel, the following equation governs the total entropy generation rate:

$$S_t = \int_0^L \dot{S}'' dY + S_L + S_U \quad (13)$$

where the first term on the right hand side integrates the local entropy generation rate over the height of the channel including solid walls, and the two other terms are the entropy generation rate due to the temperature difference between the two adjacent media for the lower and upper interfaces, respectively. This effect on the total entropy generation rate for each interface was recently reported by Torabi *et al.* [12] and can be calculated by the following formulation:

$$S_L = \left| Q_L \left( \frac{1}{T_{L,s}} - \frac{1}{T_{U,p}} \right) \right| \quad (14a)$$

$$S_U = \left| Q_U \left( \frac{1}{T_{U,s}} - \frac{1}{T_{U,p}} \right) \right| \quad (14b)$$

Recently, there have been a number of investigations of the entropy generation in porous channels, in which the velocity slip and temperature jump have been considered. In one recent investigation, Buonomo *et al.* [58] opted in favor of the local and total entropy generation rate in a porous microchannel considering the velocity slip and temperature jump boundary conditions. The LTNE model was employed and a fully analytical solution was used to model the system. However, in this investigation, the wall thicknesses were considered negligible and therefore, the total entropy generation rate did not account for the entropy generation rate at the wall-fluid interfaces [58]. Recently, Torabi and Peterson [13] included the wall thickness in the calculations and the local entropy generation rate for a micro porous channel considering both velocity slip and temperature jump boundary conditions at the interfaces were reported. Consequently, Torabi *et al.* [12] extended their previous investigation [13] to the total entropy generation of the micro porous channels while including the entropy generation at the gap between the interfaces in the total entropy generation rate. In this investigation, it was shown that, depending on the boundary conditions and the exothermicity/endothermicity of the porous medium, the temperature jump boundary condition could reduce the temperature of the system and consequently, the local entropy generation rate of the system [13] (See Fig. 4). This result is of paramount importance to the emerging areas of thermo-electro-chemical systems and flow batteries where the temperature at the porous electrode interface is crucial. However, the entropy generation rate within the interface can compensate for the reduction of the entropy generation rate due to the temperature jump. Eventually, the total entropy generation rate with temperature jump boundary conditions will be higher than that without the temperature jump [12]. This important result is clearly illustrated in Fig. 5. It is important to note that in this figure, the dashed lines are for the cases in which the total entropy generation has been calculated neglecting the entropy generation within the gap of the interfaces, and the solid lines indicate that this effect has been taken into account. It should be also be emphasized that, as shown in Fig. 5, depending on the outer boundary conditions of the micro porous channel, the variation of the total entropy generation versus the temperature jump parameter could be either increasing or decreasing.

As previously discussed, only one second law investigation of filled porous microchannels with temperature jump at the solid-fluid interface has been found [12]. This investigation reflected the significance of the non-continuum effects upon the entropy generation. Extension of this study to other micro-porous configurations and further to nanoporous structures remains an important future task for the research community. Most notably, microchannels have various applications tightly connected to the energy systems such as those in micro heat exchangers [116], micro-reactors [117] and micro-combustors [118], and the emerging area of thermo-electro-chemical systems. This further substantiates the need for developing more realistic second law analyses of these systems.

For the sake of completeness, Table 1 provides a summary of the most important contributions on thermodynamic analyses of thermal porous systems reviewed in this section.

### 3. Entropy generation in porous systems with chemical reactions

Chemically reactive porous media can be found in numerous natural and manmade systems [1,11,119]. The natural characteristics of porous media such as the massive surface area to volume ratio and the highly enhanced transport of heat and mass make them attractive chemical reactors [120,121]. In addition, chemical reactions in porous media can be homogeneous or heterogeneous and occur within either the fluid or solid phases [122]. As a result, a large number of chemical processes take place in porous media with a non-reactive solid phase. None-the-less, there are important cases that do involve solid phase reactions. The former includes those processes, in which homogeneous reactions take place within the fluid phase. Premixed porous burners are a typical example of this class of porous reactors [77,123]. In addition, the recent interest in miniaturization of energy systems has resulted in a significant interest in micro-combustors and micro-porous reactors [119,124–126]. These devices all include micro-porous media. As a result, there have been attempts to analyze heat transfer [118,119] and entropy generation rates in these thermochemical porous systems [42].

Reactive porous solids often include catalytic porous reactors. These are used extensively in chemical and energy industries with classical examples in fuel reformers and exhaust gas treatment [127,128]. Other examples of porous solids that serve as reactants, exist in applications such as biomass in pyrolysis or combustion processes [129]. As was the case for thermo-mechanical systems, a fundamental understanding and thermodynamic optimization of reactive porous systems requires extensive knowledge of the entropy generation in these systems. However, the existence of chemical reactions could invalidate the assumption of local thermodynamic equilibrium and therefore complicate the analysis [122]. In this section the current state of entropy generation modelling in various porous reactors is discussed and the gaps in the literature are identified.

#### 3.1. Entropy generation in multicomponent, chemically reactive flows

A chemically reactive, multicomponent flow includes a number of irreversibilities arising from the heat of reaction and the diffusion of chemical species in diffusive fluid flow. Teng *et al.* [130] provide a comprehensive derivation of the fundamental equations in reactive flows. In this analysis, the transport of entropy is written as

$$r \frac{ds}{dt} = \frac{1}{T} \mathbf{R} \cdot \mathbf{A} - \frac{1}{T} \nabla \cdot \left( \mathbf{q} + \sum_{i=1}^N T s_i \mathbf{J}_i^D \right) + \frac{1}{T} \Pi : E + \sum_{i=1}^N \frac{1}{T} \left( \mathbf{V}_i' \cdot \nabla p_i + \Pi_i : E_i' - \mathbf{J}_i^D \cdot \nabla m_i \right) \quad (15)$$

In Eq. (15)  $T s_i \equiv h_i - \mu_i$ , in which  $\mu_i$  is the chemical potential of species  $i$ .  $\mathbf{R} \cdot \mathbf{A} = \sum_{r=1}^N \mathbf{R}_r \cdot \mathbf{A}_r$  where  $\mathbf{R}_r$  is the reaction rate of the  $r^{th}$  reaction and  $\mathbf{A}_r$  is the corresponding affinity. Further,  $\mathbf{J}_i^D$ ,  $\Pi$ ,  $E$ ,  $E_i'$  and  $\mathbf{V}_i'$  are respectively the

diffusion flux of species  $i$ , shear stress tensor, mean flow strain rate tensor, diffusive flow strain rate and diffusion velocity of species  $i$ . Eq. (15) can be manipulated to a standard transport equation [131]. That is

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}^s + \dot{S}''' \quad (16)$$

where  $\mathbf{J}^s$  is the flux of entropy and, similar to the previously discussed entropy generation formula,  $\dot{S}'''$  shows the volumetric entropy generation rate. These are given by

$$\mathbf{J}^s = \frac{q}{T} + \sum_{i=1}^N s_i \mathbf{J}_i^D \quad (17)$$

$$\begin{aligned} \dot{S}''' = & \frac{1}{T} \mathbf{R} \cdot \mathbf{A} - \frac{1}{T^2} \mathbf{q} \cdot \nabla T - \frac{1}{T} \sum_{i=1}^N s_i \mathbf{J}_i^D \cdot \nabla T + \frac{1}{T} \Pi : E \\ & + \sum_{i=1}^N \left( \frac{1}{T} \mathbf{V}_i' \cdot \nabla p_i + \frac{1}{T} \Pi_i : E_i' - \frac{1}{T} \mathbf{J}_i^D \cdot \nabla \mu_i \right) \end{aligned} \quad (18)$$

These formulations lead to the identification of the irreversibilities listed in Table 2. The existence of a porous medium can affect all these sources of irreversibilities through the influence of the heat conduction, effective viscosity and mass diffusivity. It can also further introduce new sources of irreversibility due to interphase heat and mass transfer at local non-equilibrium state.

### 3.2. Modeling of entropy generation in reactive porous media

Modelling of chemical reactions in porous media, generally, requires releasing the assumption of local chemical equilibrium and using chemical kinetic schemes to represent chemical activities [78,79]. Further, fast reactions and high levels of exothermicity or endothermicity may influence the local thermal equilibrium and push the system towards local thermal non-equilibrium [132]. Thus, porous chemical reactors can be far from the state of local thermodynamic equilibrium [122]. Furthermore, many thermo-electro-chemical systems are not in local chemical equilibrium and bulk charge concentration polarization can drastically affect the efficiency of these systems [133]. The local non-equilibria are a major contributor to entropy generation in porous reactors and are essential for inclusion in the second law analyses of these systems. Inclusion of chemical and thermal non-equilibrium, however, adds significant complexity to the investigation. This is because each kinetic step is represented by a stiff ordinary differential equation and non-equilibria adds more partial differential equations to the mathematical model [11,122]. More importantly, the implementation of non-local equilibria utilizes ‘interface models’ [19,20]. These are the boundary conditions at the porous-fluid and porous–solid interfaces and finding the optimal and realistic form of these models continues to be a challenge [1]. Consequently, entropic analyses of chemically reactive porous media involve various layers of simplification. In the first and most simple layer, chemical reactions are represented solely by their thermal effects through adding thermal energy source terms to transport of energy. In this level, full local thermodynamic equilibrium is assumed and irreversibility of chemical reactions and mass transfer are ignored [134].



In the second layer of complexity, the effects of chemical reactions are still replaced by simple heat sources in the transport of energy, and chemical and mass diffusion irreversibilities, are ignored. However, the porous system is assumed to be under local thermal non-equilibrium. Recent theoretical studies of forced convection in porous media showed that the existence of the energy source term in the system can cause significant deviations from local thermal equilibrium [14,132]. This necessitates the use of a two-equation model of the transport of thermal energy. Hence, the calculated entropy generation takes into account the irreversibility of interphase heat transfer set by exothermicity or endothermicity of the chemical reaction. This level of modelling remains amenable to analytical approaches and has attracted some attention in recent years [14,16,20]. The obvious shortcoming of this method is an omission of the irreversibility of mass transfer and chemical reactions. Nevertheless, existing studies show that for highly exothermic (and endothermic) processes, thermal irreversibilities could be the dominant source of entropy generation [135]. Hence, at this limit the method becomes an acceptable approximation.

The third level of modelling takes into account the chemical reactions, but ignores the local chemical and thermal non-equilibria. Modelling at this level includes (i) momentum transport, often in the form of a Darcy flow, (ii) a one-equation model of the transport of thermal energy, (iii) a model of transport of chemical species, and (iv) a single or multi-steps chemical reactions. Due to the consideration of thermodynamic local equilibrium, chemical kinetics are often ignored and the porous system is then modelled in a manner similar to that used for conventional reactive flows, and irreversibilities due to viscous effects, intra-phase heat and mass transfer and chemical reactions are considered. This modelling approach has been applied to the problems of exergetic efficiency of chemical reactors and fuel cells. In the analytical investigations of Azoumah *et al.* [136,137] the solid-gas porous reactors were optimized through the minimization of entropy generation. This work included the modelling of fluid flow as well as heat conduction and convection, in a single phase medium and a chemical reaction under equilibrium [136,137]. Irreversible thermodynamics were employed to develop functional form of the local and total entropy generation [138]. Exergy optimization of the porous reactor was then conducted by applying the Lagrangian multiplier method. In another application the analysis of heat storage systems have been investigated. Solar thermal energy could be stored in a way that provides energy to a reversible endothermic reaction [139]. The heat can be directed to water thermolysis, which is a highly endothermic process [40,140]. To do so, a porous matrix was used as a volumetric solar thermochemical reactor that receives energy from the sun. Hence, to analyse the system heat transfer equations should be solved within the porous matrix [141]. These investigations have been conducted using both well-known VAT models in porous media, *i.e.*, LTE [142] and LTNE [140,141] models. The exergetic optimisation technique developed in [136,137] has been applied to porous heat storage systems with thermochemical effects.

In the fourth level of modelling, the assumption of local thermal non-equilibrium is maintained. Yet, chemical equilibrium does not necessarily hold and chemical kinetics are considered. Second law analyses of fuel cells with local thermal equilibrium assumption and inclusion of electro-chemical reactions do exist. Solid oxide fuel cells have been investigated from the viewpoint of entropy generation minimisation (EGM) by Sciacovelli and Verda [143,144]. Heat and fluid flow in porous electrodes using the Darcy-Brinkman equation was modelled and a one-equation thermal energy transport model with Joule heating effects was included [143]. To represent the mass diffusion and chemistry

of the fuel cell, a diffusion-reaction equation was further considered. Additionally, electro-chemical effects lead to the appearance of the corresponding irreversibility in the balance of entropy. These authors [143] expressed the transport of entropy as

$$\rho \frac{Ds}{Dt} = -\nabla \cdot \mathbf{J}^s + \dot{S}''' \quad (19)$$

Sciacovelli and Verda [143] utilized the Gibbs relationship and developed the following formulation for the entropy flux.

$$\dot{S}''' = \dot{S}'''_{\mu} + \dot{S}'''_h + \dot{S}'''_m + \dot{S}'''_c + \dot{S}'''_{ohm} \quad (20)$$

The first term in Eq. (20) represents the contribution of viscous irreversibility, the second term denotes the entropy generation by heat transfer, the third term represents the irreversibility associated with mass transfer, and the fourth term arises from the coupling between heat and mass transfer. The last term in Eq. (20) represents the entropy generation through Ohmic losses. This relation was then expanded in the following form

$$\dot{S}''' = \underbrace{\frac{1}{T} \Pi : E}_{\text{entropy generation due to viscous dissipation}} + \underbrace{\frac{1}{T^2} (-\vec{J}_q \cdot \nabla T)}_{\text{entropy generation due to heat transfer}} + \underbrace{\frac{1}{T} \left( \sum_i -\vec{J}_i \cdot \nabla \mu_i \right)}_{\text{entropy generation due to mass transfer}} + \underbrace{\frac{1}{T} \left( \sum_i -s_i \vec{J}_i \cdot \nabla T \right)}_{\text{entropy generation due to coupling between heat and mass transfer}} + \underbrace{\frac{1}{T} \sigma \nabla \phi \cdot \nabla \phi}_{\text{entropy generation due to Ohmic losses}} \quad (21)$$

In Eq. (21)  $J_q$  is the heat flux ( $J_q = -k \cdot \nabla T$ ),  $\phi$  and  $\sigma$  are the electrical potential and conductivity, respectively. The analyses conducted by Sciacovelli and Verda [143,144] showed that in solid oxide fuel cells the irreversibility of mass transfer and that due to the coupling of heat and mass transfer are the main sources of entropy generation. It has been shown that by decreasing the entropy generation, the optimized configuration of the solid oxide fuel cell generated much higher power density [144].

Entropy generation in proton exchange membrane fuel cells was investigated by Hernandez *et al.* [145]. These authors modelled the interface between the gas flow channel and the gas diffusion layer as a porous medium with prescribed porosity and permeability. Hernandez *et al.* [145] evaluated the local and total entropy generation in the system in an analogous way to Sciacovelli and Verda [143]. These authors found that the main source of irreversibility is the concentration losses and the heat transfer irreversibility in fuel cells is negligible [145]. In general, validation of this statement requires conduction of local thermal non-equilibrium analysis. However, the non-equilibrium investigation of Zheng *et al.* [146] showed that the assumption of local thermal equilibrium in fuel cell analysis is correct. Li and Faghri [147] performed numerical exergetic analysis of direct methanol fuel cell through modelling the fluid flow by a simple Darcy equation and a one-equation model of thermal energy transport in porous media. Advection-diffusion-reaction equations within the porous media were used to model transport of different species [147]. The subsequent exergy analysis revealed that irreversibilities in electrochemical reactions is the main source of entropy generation in the direct methanol fuel cells. Other numerical studies on entropy generation in porous parts of fuel cells have been summarised in Table 3. Level four of modelling has been also applied to fuel reformer; Chen *et*

*al.* [148] investigated the generation of entropy in a catalytic partial oxidation of methane in a Swiss-roll reactor with a porous core. Authors used a reduced kinetics scheme to represent catalytic reactions in the porous component of the reactor and considered local thermal equilibrium [148]. Calculation of the local and total entropy generation by viscous dissipation, heat transfer, and chemical reactions showed that the chemical and thermal irreversibilities are much stronger than that of fluid friction [148].

The last and most comprehensive level of modelling of chemically reactive porous media considers full local thermodynamic non-equilibrium and chemical kinetics. Examples of this type of modelling are infrequent. In numerical work, Bidi *et al.* [91] investigated entropy generation in a premixed, porous burner. The authors modelled fluid flow through a modified version of steady Navier-Stokes equations and used a two-equation model of heat transfer considering radiative effects. Their two-dimensional analysis further included a chemical kinetics scheme consisting of fifteen reactions and nineteen species [91]. Bidi *et al.* then calculated the local and total entropy generation from fluid friction, heat transfer, and chemical reactions [91]. In Keeping with findings of level 3 and 4 of modelling, it was found that viscous irreversibilities are an insignificant part of the overall entropy generation, see Fig. 6. Looking through the values of local entropy generation rates for dissipation friction and porous media friction, it is apparent that these types of entropy generations are negligible compare with the other three types presented in this figure. The non-equilibrium approach in this investigation [91] explored the influence of chemical kinetics on irreversibilities. The method of EGM for optimising the porous burner and finding the flame stabilisation limits was also used in this study. Their work is a successful demonstration of the capacities of local non-equilibrium EGM for the analysis and optimisation of porous reactive systems.

### 3.3. Research challenges and opportunities on modelling of entropy generation in reactive porous media

A comparison of the existing works on entropy generation in porous media and the wider literature on entropy generation in reactive systems reveals a few points. First, so far, the subject of entropy generation in chemically reactive porous media has received very limited attention. This is regardless of the level of modelling and can be easily verified by comparing the size of literature in this area to the corresponding body of works on the general problem of entropy generation in reactive systems [149–153]. Most of the existing studies belong to level two and four of modelling; that is LTNE with no chemistry or LTE with reduced chemistry. Although these levels of modelling offer analytical and numerical convenience, they neglect some potentially important contributions. Level two of modelling, in which only heat of reaction is considered in an LTNE analysis of porous media, is a fair approximation of reactors under chemical equilibrium. Level four, which ignores inter-phase heat transfer, applies to those reactors with insignificant heat generation or consumption. However, a large fraction of chemical reactors operate far from chemical equilibrium and under highly exothermic/endothermic conditions [154,155]. In such cases, utilisation of level five modelling is the only acceptable approach to the modelling entropy generation. There currently exists a major shortage of studies at this level of modelling. In fact, with the exception of the work of Bidi *et al.* [91] there is currently no other study on full non-equilibrium entropy generation in reactive porous media. Furthermore, the area of entropy generation in catalytic porous media has remained almost entirely unexplored. Given the significance of catalytic

porous media in a chemical and energy technologies, the lack of studies in this area is surprising. It is finally emphasized that PSM of entropy generation [22] is yet to be extended to chemically reactive flows.

#### 4. Analysis methods

Analysis methodology can be categorized into four groups, namely analytical, analytical-numerical, semi-analytical, and numerical. These four solution methods have been comprehensively reviewed in our previous review of entropy generation investigations in solid media [156]. The above mentioned methods can be similarly applied to thermal or chemical porous systems, depending on their suitability for a specific situation. Hence, for the sake of brevity, only one example will be provided here regarding the application of each method on a specific system. Needless to say that almost all of these simulations have used the direct approach for calculating the entropy generation rate [48].

A number of investigations of the entropy generation analysis in porous media have utilized an analytical method [15,58,89,157]. In these systems, due to the simple differential [15,58,89] or empirical [157] equations, the solution is an analytically exact procedure without any approximation or discretization of the equation. As an example, LTNE model has been considered by Buonomo *et al.* [58], and the two coupled differential energy equations have been decoupled by straightforward mathematical manipulations. Then, the two decoupled energy equations have been solved analytically together with the available boundary conditions. In a relatively different approach, many investigations employed combined analytical-numerical solution procedures [19,20,31]. In this methodology, first the governing differential equations are first solved analytically. Then a numerical method is used to find the particular solution. For instance, Torabi and Zhang [31] solved the momentum equation using an exact analytical procedure, although a combined analytical-numerical solution method was considered for the temperature visualization. Another approach is using a special transformation technique to decompose the nonlinear differential equation into many simpler linear differential equations, which can be solved analytically [158]. Hence, semi-analytical methods such as homotopy analysis have been also applied to porous thermal systems [62,95]. The last category, using purely numerical approaches, such as those used in computational fluid dynamics finite volume method, finite element method and finite difference method are employed [159,160]. This approach is the most powerful of all techniques and has been repeatedly used by many scholars to solve the continuity, momentum, energy, and species conservation equations and to consequently investigate the entropy generation in porous systems [21,32,91,161]. An interesting example of the application of this method is the investigation of Bidi *et al.* [91] on the entropy generation in a chemically reactive porous medium discussed in Section 3.2. Another category of numerical approaches belongs to lattice Boltzmann based methods [162]. While in more conventional computational methods nonlinear partial differential equations are converted into a set of nonlinear algebraic equations, in this method the fluid is replaced by fractious particles. Readers may refer to a readily understandable textbook by Mohamad on this topic [162]. As this method is much simpler than conventional computational methods, there has been a surge of interest in applying lattice Boltzmann method (LBM) or its branches for simulation of thermofluid systems [35,88,110,163]. In a classical thermofluid system, the problem requires two different distribution functions, where the first one is for the flow field and the second one is for the temperature field [162]. By considering  $D_2Q_9$  model and introducing BGK approximation

[164], the general forms of lattice Boltzmann equation for each of velocity or temperature fields are written as [165,166]:

$$f_i(x + c_i \Delta t, t + \Delta t) = f_i(x, t) + \frac{\Delta t}{\tau_f} [f_i^{eq}(x, t) - f_i(x, t)] + \Delta t c_i F_k \quad (22)$$

$$g_i(x + c_i \Delta t, t + \Delta t) = g_i(x, t) + \frac{\Delta t}{\tau_g} [g_i^{eq}(x, t) - f_i(x, t)] \quad (23)$$

where the local equilibrium distribution functions  $f_i^{eq}$  and  $g_i^{eq}$  determine the type of the problem under investigation.

For example, if a system with a fluid phase is considered, the distribution functions are governed by the following equations:

$$f_i^{eq} = w_i \rho \left[ 1 + \frac{c_i \cdot \mathbf{u}}{c_s^2} + \frac{1}{2} \frac{(c_i \cdot \mathbf{u})^2}{c_s^4} - \frac{1}{2} \frac{\mathbf{u}^2}{c_s^2} \right] \quad (24)$$

$$g_i^{eq} = w_i T \left[ 1 + \frac{c_i \cdot \mathbf{u}}{c_s^2} \right] \quad (25)$$

For the solid phase of the system that needs to be simulated when the PSM approach is used, the velocity of the particles should be set to zero. A bounce back at the fluid-solid interfaces is applied to confirm the no-slip velocity boundary condition. To obtain the macroscopic specifications of the system such as fluid density, velocity and temperature, each of these characteristics should be specifically added as follow:

$$\rho = \sum_{i=0}^8 f_i \quad (26)$$

$$\rho \mathbf{u} = \sum_{i=0}^8 c_i f_i \quad (27)$$

$$T = \sum_{i=0}^8 g_i \quad (28)$$

It should be noted that to simulate other specifications of the system, such as concentration, another distribution function would be needed in addition to Eqs. (22) and (23). Since this method can provide accurate result for thermofluid systems as well as reducing the complicity of the numerical simulations, this method and its branches such as finite difference lattice Boltzmann may lead the future simulation strategy in thermal systems [162].

## 5. Conclusions

In recent years, the interest in second law analyses of porous thermal and thermochemical systems has increased. A great deal of attention has been paid to the LTNE model of porous media, as this model can more accurately present the energetic and exergetic performances of the system. Although a large number of investigations on entropy generation in porous media under LTNE condition exists, many systems did not receive adequate attention. These

often include those systems that feature extra physicochemical effects. For example, so far, the effects of magnetic field and radiation heat transfer have not been considered in conjunction of LTNE model. Moreover, there is currently only one study that accounts for the effect of temperature jump and its direct effect on the total entropy generation in micro porous channels. There has been also very limited work on entropy generation investigation in chemically reactive porous media. As discussed in Section 3 of this review, although a few published studies have considered LTNE condition to simulate entropy generation in chemically reactive porous systems, only one of them has considered LTNE model together with chemical kinetics.

All of the above mentioned conclusions are related to LTE and LTNE models, which fall within the category of VAT's. Thus far, there have been only two entropy generation analyses using PSM in porous media. This is due to the computationally demanding characteristic of this approach. With the rapid development of computational tools and especially the increased computational power of modern processors, it is perhaps the right time for scholars to shift from a VAT to a PSM approach in the study of porous media, and re-investigate many thermal and/or thermochemical systems which require increased accuracy. Moreover, LBM appears to have potentials to address problems in porous media based on both VAT and PSM approaches.

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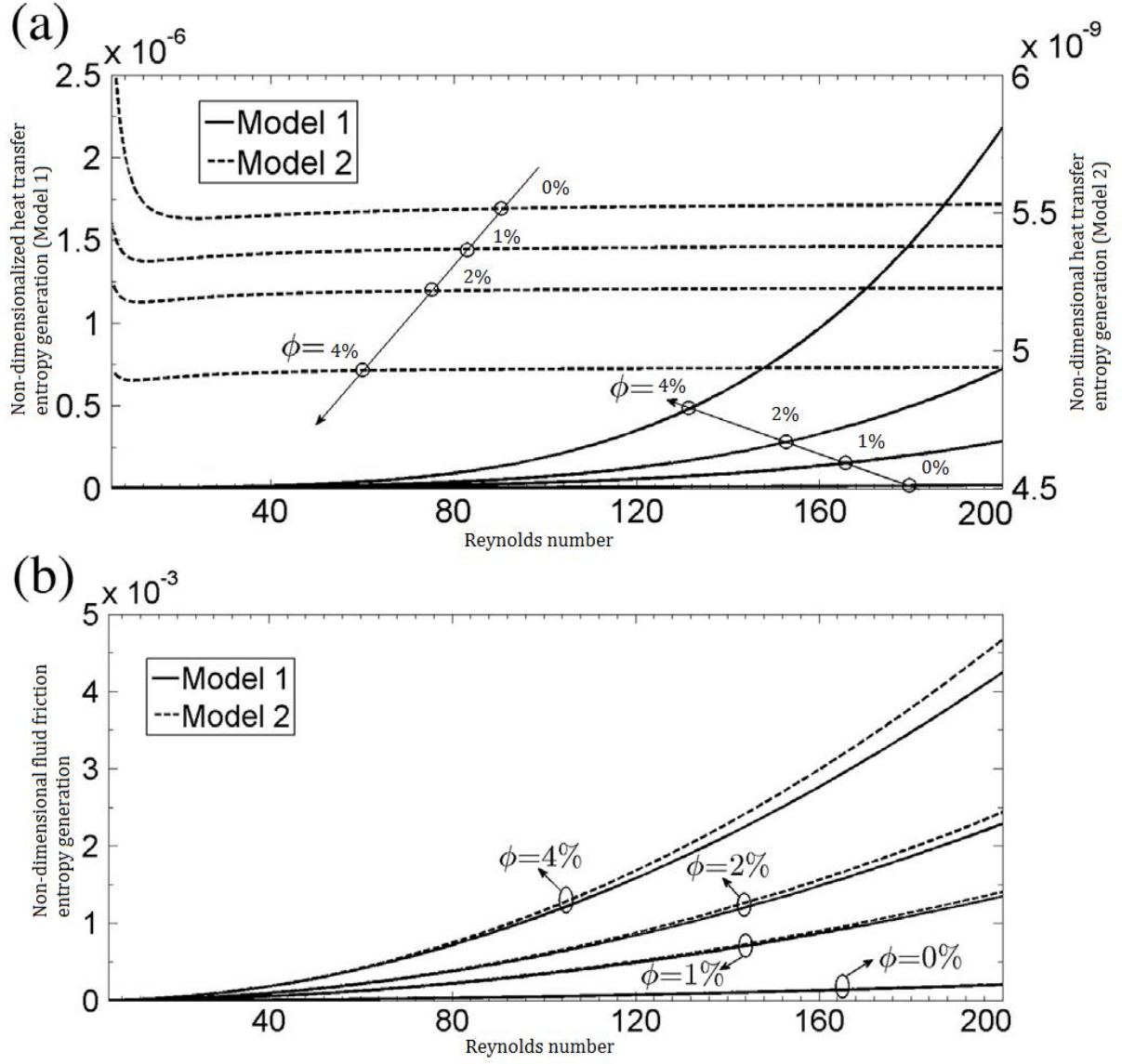
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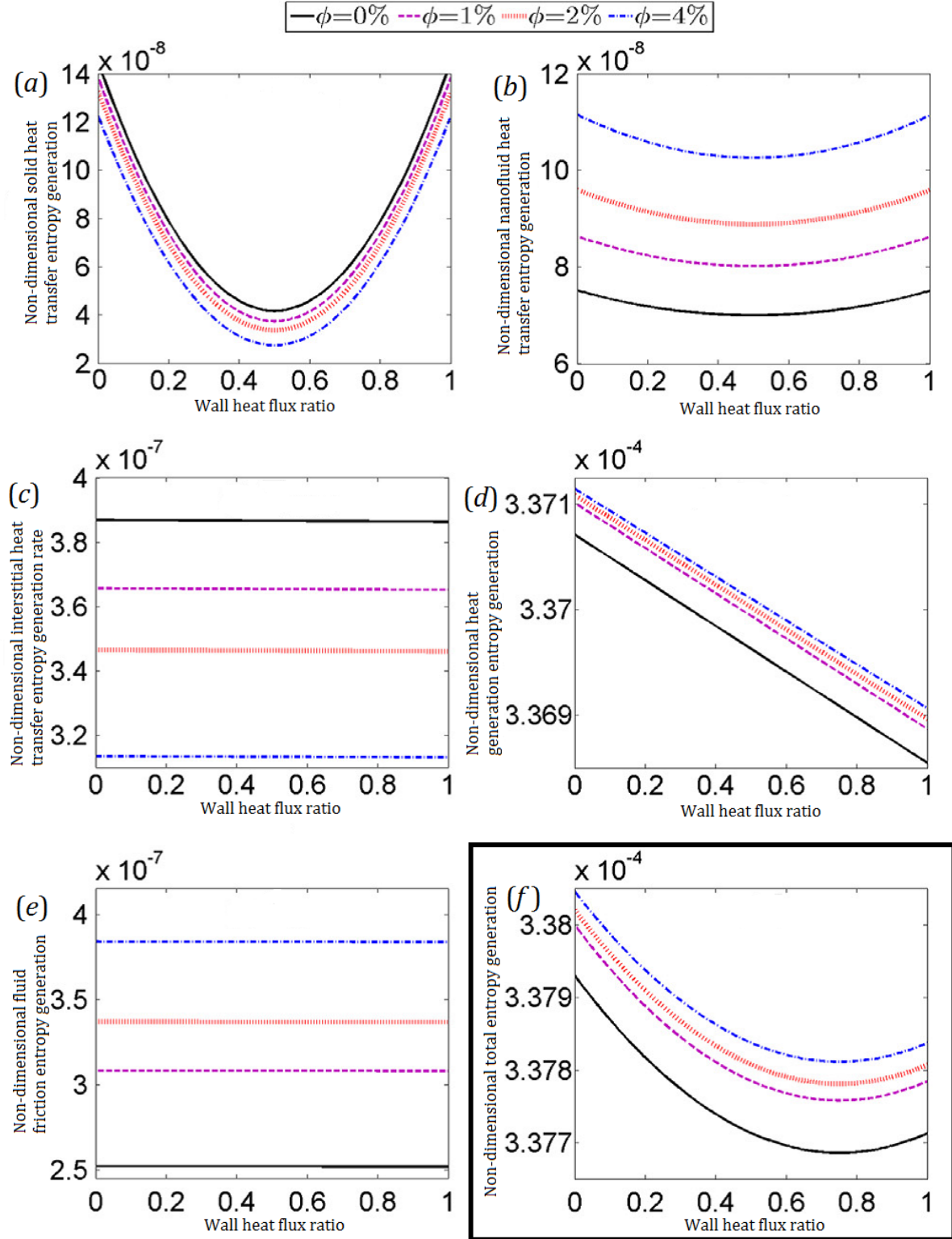
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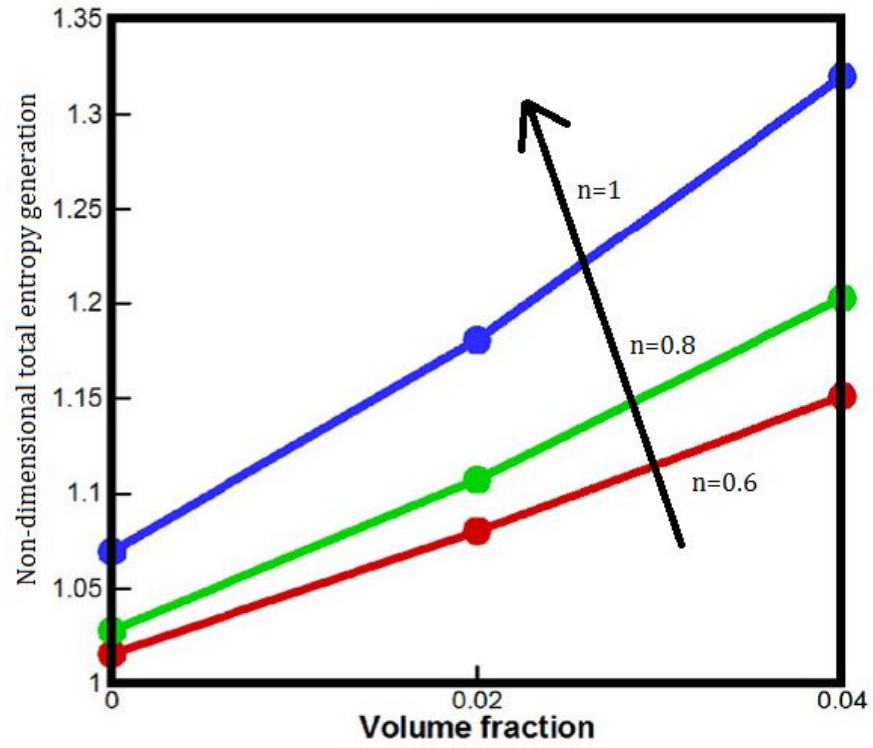


**Fig. 1.** (a) The total heat transfer irreversibility, and (b) the total fluid friction irreversibility versus Reynolds number for a micro porous channel [15].

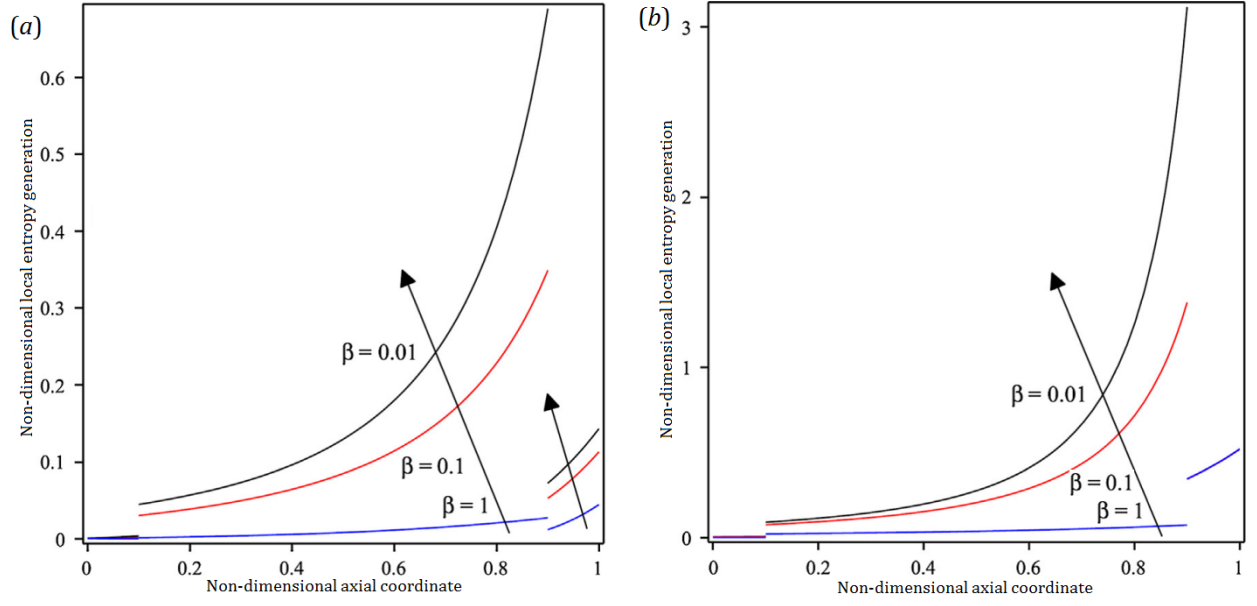




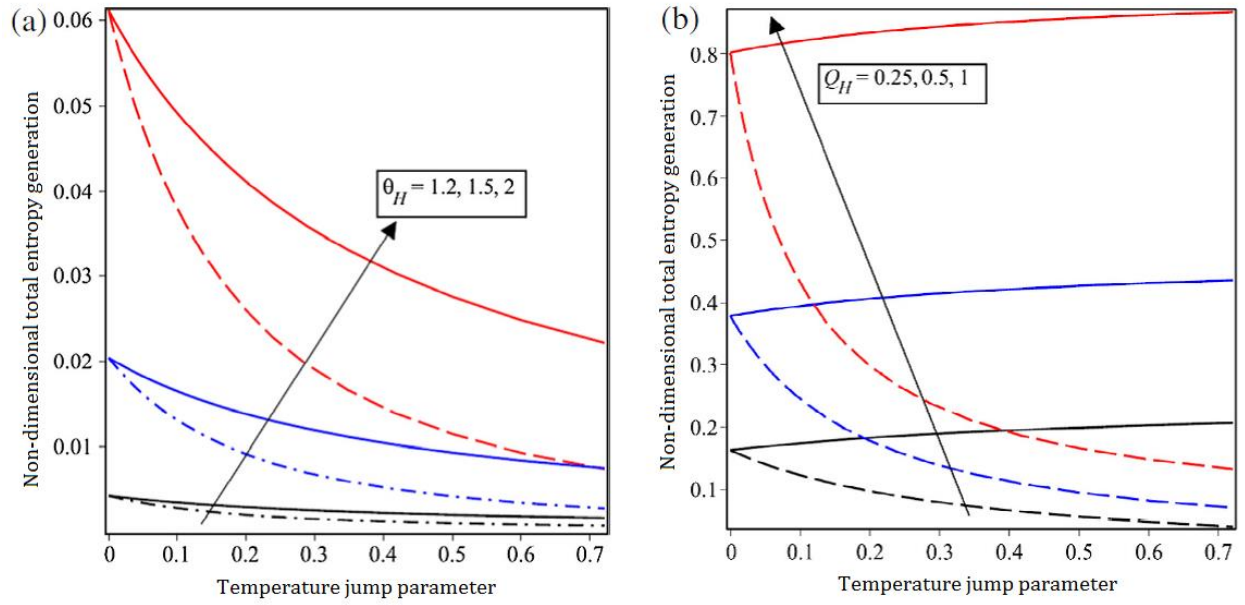
**Fig. 2.** The influence of adding nanoparticles to the base fluid on the entropy generation rate in a micro porous channel [63].



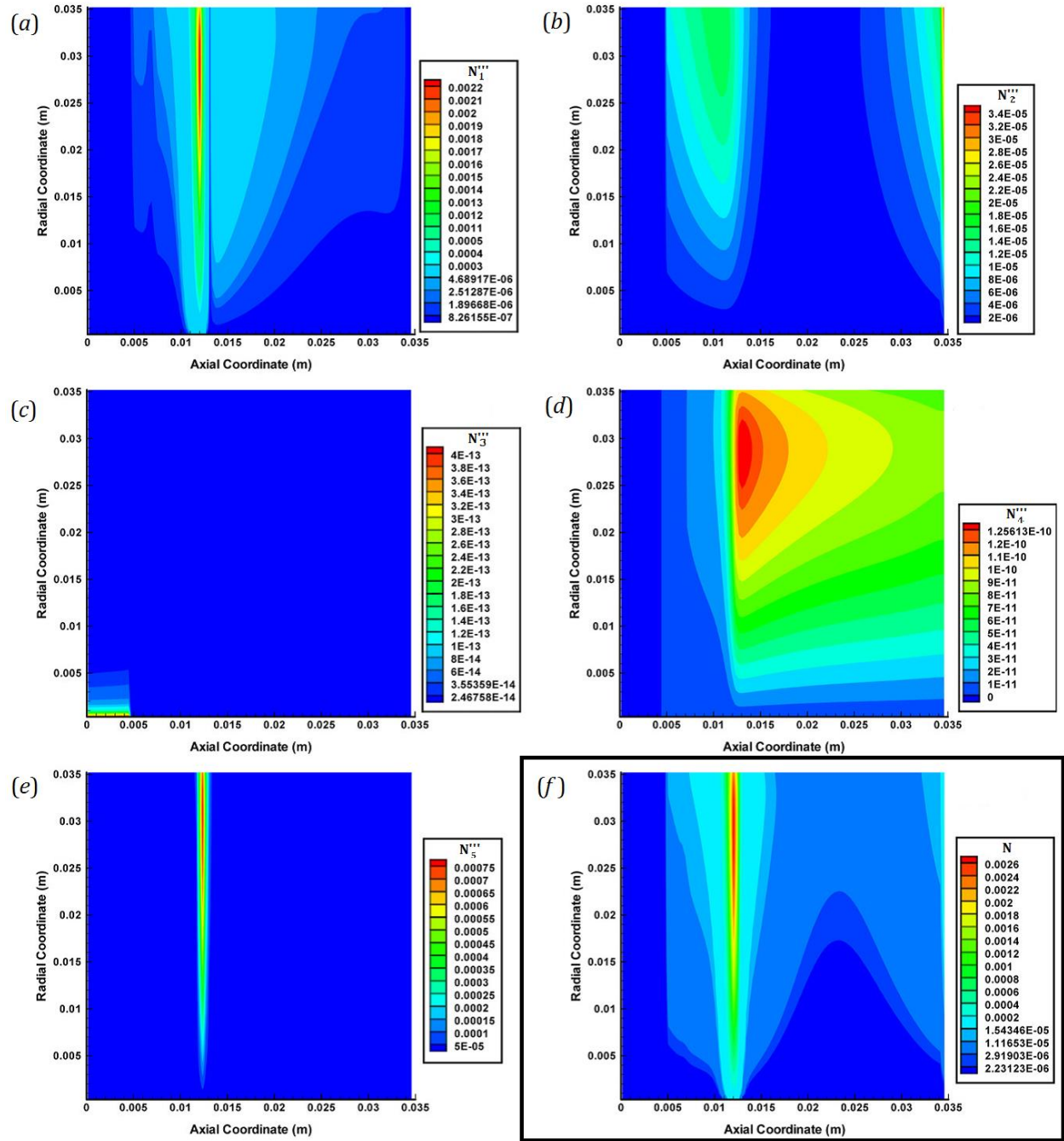
**Fig. 3.** The influence of nanofluid volume fraction on the entropy generation in a porous cavity [35].



**Fig. 4.** Local entropy generation rate for different values of the temperature jump; (a) constant temperature and (b) heat flux, convection heat transfer boundary conditions [13].



**Fig. 5.** Total entropy generation rate versus temperature jump parameter for (a) the first case with different values of lower wall temperature and (b) the second case with different values of heat flux at the lower wall [12].



**Fig. 6.** Local entropy generation contours in a porous burner due to gas heat transfer ( $N_1'''$ ), solid heat transfer ( $N_2'''$ ), dissipation friction ( $N_3'''$ ), porous media friction ( $N_4'''$ ), reaction ( $N_5'''$ ) and total entropy generation rate ( $N$ ) (W/K) [91].

**Table 1.** Summary of entropy generation investigations on thermal porous systems.

Main investigation	Authors	Geometry	Considered model and solution method
Effect of viscous dissipation	Torabi et al. [45]	Horizontal Channel with thick walls	LTNE, analytical-numerical
	Torabi et al. [21][22]	Isotropic porous media with various cross-sections	PSM, numerical
Effect of viscous dissipation and magnetic field	Butt et al. [62]	Horizontal Cylinder embedded in porous medium	LTE, numerical
	Torabi et al. [31]	Horizontal Channel with thick walls	LTE, analytical-numerical
	Nagaraju et al. [75]	Between concentric rotating cylinders with porous lining	LTE, numerical
	Fersadou et al. [74]	Vertical channel	LTE, numerical
	Rashidi and Freidoonimehr [73]	Stagnation-point in porous media	LTE, numerical
Effect of viscous dissipation and radiation	Mahmud and Fraser [89]	Vertical channel	LTE, analytical
	Rashed [72]	Horizontal sheet embedded in porous medium	LTE, numerical
	Dehsara et al. [90]	tilted vertical plate embedded in porous media	LTE, numerical
	Butt and Ali [94]	Vertical plate embedded in porous media	LTE, analytical
	Ellahi et al. [95]	A cone embedded in porous media	LTE, semi-analytical
Effect of viscous dissipation and nanofluid	Ting et al. [15], [63]	Horizontal Channel	LTNE, analytical
	Kefayati [35], Ismael et al. [109]	Cavity	LTE, numerical
	Torabi and co-workers [20][19]	Horizontal Channel with exothermicity/endothermicity	LTNE, analytical-numerical
Effect of velocity slip and temperature jump	Buonomo et al. [58]	Horizontal channel	LTNE, analytical
	Torabi and co-workers [12][13]	Horizontal channel	LTE, analytical-numerical

**Table 2.** Irreversibilities and thermodynamic fluxes and forces [130].

Irreversible process	Flux, $J_k$	Force, $X_k$
Chemical reaction	$R$	$A$
Heat conduction	$q/T$	$-\nabla T$
Thermal diffusion	$s_i J_i^D$	$-\nabla T$
Chemical diffusion	$J_i^D$	$-\nabla \mu_i$
Mechanical diffusion	$-V'_i$	$-\nabla p_i$
Viscous flow	$\Pi$	$\nabla V$
Diffusive-viscous flow	$\Pi_i$	$\nabla V'_i$

**Table 3.** Summary of literature on entropy generation in chemically reactive porous media.

Level of modelling	Assumptions	Application area	References	Approach
1	Local-thermodynamic equilibrium-no chemistry	General chemical reactors	[134]	Analytical
2	Local thermal non-equilibrium-no chemistry	General chemical reactors	[14][16][20]	Analytical/ semi-analytical
3	Local thermodynamic equilibrium- with equilibrium chemistry	Solid-gas reactors & thermal energy storage	[136][137][167]	Semi analytical
4	Local thermal equilibrium- with chemical kinetics	Fuel cell	[143] [144] [145] [147][148][168][169][170]	Numerical
		Fuel reformer	[171]	
5	Local-non-equilibrium-with chemical kinetics	Combustion	[91]	Numerical