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Non-Isothermal Effectiveness Factors in Coal Combustion

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Abstract

Thermo-chemical conversion of porous solids like coal is often modeled using generic approaches capable to reproduce chemical kinetic and mass transfer limitations of the conversion rate. The effectiveness factor (η) is used to describe the intra-particle mass transfer limitations in these models. Since a non-linear second order reaction-diffusion equation has to be solved to obtain the effectiveness factors for exothermic reactions, analytic solutions for the isothermal case are often used instead of solving the reaction-diffusion equation. For highly exothermic reactions, this approach might underestimate the conversion rates. Therefore, this work investigates the influence of non-isothermal effectiveness factors on conversion rates under coal combustion conditions.

The results indicate that non-isothermal effectiveness factors cause a change in the conversion characteristics from progressive core to shrinking particle. Moreover, the conversion rates might be significantly under-estimated by the isothermal effectiveness factors for the investigated conditions.

Introduction

Heterogeneous combustion is a complex phenomenon involving multiple processes. A generic gas-solid reaction may consist of the following sub-processes [1,2]:

- Mass transfer from the bulk gas phase to the external solid surface
  - Mass diffusion of the gaseous reactant towards the reaction site
  - Educt adsorption to an active reaction site
  - Product desorption from the reaction site
  - Mass diffusion towards the external particle surface
- Mass transfer of the product from the particle surface to the bulk gas phase

Gas-solid reactivity can be classified according to the dominating of these sub-processes. Figure 1 shows a generic Arrhenius diagram for heterogeneous combustion indicating the three main conversion regimes: Regime **I**, Regime **II**, and Regime **III** [3-5].

Regime **I** is controlled by the chemical reaction, while at higher temperatures intra-particle mass transport becomes the rate controlling process (Regime **II**). At high temperatures, the mass transport from the bulk gas phase towards the solid surface limits the apparent conversion rates.

Comprehensive gas-solid conversion models have to reproduce these three conversion regimes. Mechanistic conversion models combine the rate limiting steps of the conversion regimes and deduce a closed expression for the effective conversion rate (k_{eff}) [1,3,10]:

$$k_{eff}=\frac{1}{\frac{1}{h_{conv}A_P c_0^{n-1}}+\frac{1}{\eta k_{intrinsic}}}c_0^n \qquad (1)$$

with h_{conv}, A_P, c_0, η, $k_{intrinsic}$, and n being the convective mass transfer coefficient, the external particle surface, the bulk species concentration of the gaseous reactant, the effectiveness factor, the intrinsic reaction rate, and the reaction order. The first term in the denominator represents the mass transfer limitation between the bulk gas phase and the solid surface, while the second term represents the combined kinetic and intra-particle mass transfer limitation. η reduces the intrinsic rate to account for the intra-particle mass transfer. Analytic expressions based on isothermal conversion for η are usually employed in these kind of rate equations.

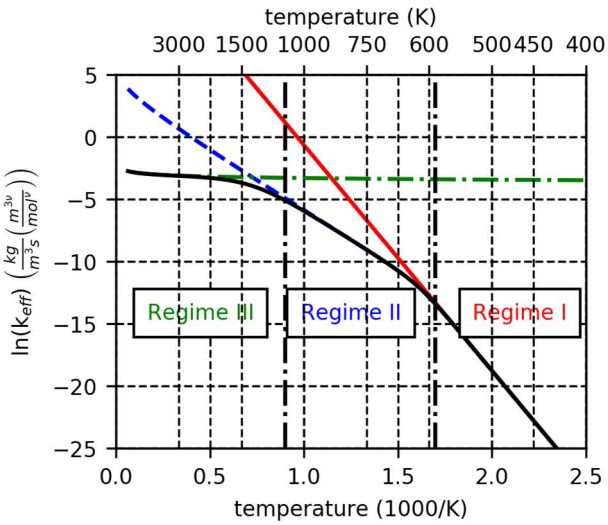

Figure 1: Schematic Arrhenius diagram for heterogeneous combustion.

Typically, gas-solid reactions or combustion processes take place in the intermediate temperature range, where intra-particle mass transfer is dominant. Heterogeneous catalysis is probably the prime example. Damköhler [6], Thiele [6], Weehler [7], and Zeldovic [8] independently investigated heterogeneous catalysis and proposed a dimensionless relation which is today known as Thiele modulus [9]:

$$\Phi=\frac{V_P}{A_P}\sqrt{\frac{n+1}{2}\frac{k_{intrinsic}c_0^{n-1}}{D}} \qquad (2)$$

where V_p and D denote the particle volume and the effective diffusion coefficient in the particle pores. Furthermore, they proposed a number which quantifies the extent of the heterogeneous reaction (k) compared to the reaction at ambient conditions (k_0). This ratio is known as effectiveness factor (η) and is used to correct intrinsic conversion rates in the intra-particle mass transfer limited region [1,6,11]:

$$\eta=\frac{k}{k_0} \qquad (3)$$

The effectiveness factor is only a function of Φ for a given

reaction and particle shape and can be calculated by solving the reaction-diffusion equation for the corresponding reaction and ambient conditions analytically or numerically [11,14-16].

The reaction-diffusion equation and its application for the calculation of isothermal and non-isothermal effectiveness factors is discussed subsequently. The discussed theory is then applied to compare isothermal and non-isothermal effectiveness factors occurring during coal combustion.

Reaction-Diffusion Equation

The reaction-diffusion equation for spherical particles is given by [6,14]:

$$D\left[\frac{d^2c}{dr^2}+\frac{2}{r}\frac{dc}{dr}\right]-k_{intrinsic}c^n\cdot F(c)=0 \tag{4}$$

where D, c, r, and n are the effective diffusion coefficient, the species concentration, the radial position, and the reaction order. F(c) is a disturbance function and depends on the assumptions for the reaction, e.g. isothermal, non-isothermal, isochoric. This equation can be rewritten in a non-dimensional form by using the following identities [7, 12, 15-17]:

$$Y=\frac{c}{c_0},\qquad X=\frac{r}{R},\qquad \Phi=R\sqrt{\frac{k_{intrinsic}c_0^{n-1}}{D}} \tag{5}$$

with R being the bulk species concentration and the particle radius. The non-dimensional form is then given by:

$$\frac{d^2Y}{dX^2}+\frac{2}{X}\frac{dY}{dX}-\Phi^2Y^n\cdot F(Y)=0 \tag{6}$$

The boundary conditions for the dimensionless reaction-diffusion equation are as follows:

$$Y=1|_{X=1},\qquad \frac{dY}{dX}=0|_{X=0} \tag{7}$$

Analytic solutions for the concentration profile within the solid particle exist for isothermal conditions and integer reaction orders [2,6,11,14,16]. In these cases, the dimensionless intra-particle concentration profiles correlate with the Thiele modulus and particle shape.

Combustion reactions are highly exothermic, thus, introducing significant temperature gradients within the solid. A coupled system consisting of the reaction-diffusion and the solid energy equation has to be solved for non-isothermal particle conversion. The equations are coupled by the chemical source terms [11,14]:

$$F(c)=k_{intrinsic}(T)\cdot c_0^n \tag{8}$$

$$F(h)=\frac{\Delta H}{c_p\rho}\cdot k_{intrinsic}(T)\cdot c_0^n \tag{9}$$

with T, ΔH, c_p, and ρ being the temperature, the heat of reaction, the specific solid heat capacity, and the solid density. Damköhler and Prater derived a uniquely defined relationship between the concentration and temperature in solid fuels [12,13]:

$$\Delta T=T-T_0=\frac{\Delta H\,D}{\lambda}(c_0-c) \tag{10}$$

where T_0 and λ denote the temperature of the bulk gas phase and the thermal conductivity of the solid. This expression can be introduced into the reaction-diffusion equation instead of solving the energy equation. In this case, the non-dimensional disturbance function for the reaction-diffusion equation is given by [14]:

$$F(Y)=\exp\left[\frac{\beta\gamma(1-Y)}{1+\beta(1-Y)}\right] \tag{11}$$

The parameters β and γ represent the normalized temperature variation and the reaction rate sensitivity on temperature [14]:

$$\beta=\frac{c_0\Delta H\,D}{\lambda T_0},\qquad \gamma=\frac{E_a}{RT_0} \tag{12}$$

where E_a and R denote the activation energy and the ideal gas constant.

This non-linear second order boundary value problem requires special numerical treatment, since a Neumann condition is imposed at X=0 and a Dirichlet boundary condition is imposed at X=1. Moreover, multiple solutions of the equation exist for certain combinations of β and γ and the center concentration might be zero for large values of Φ.

Different algorithms have been proposed in literature to solve the reaction-diffusion equation, the most common one might be the shooting method. This numerical method presumes a value for Y at X=0 and solves the equation as an initial value problem. The Y value for X=0 is then adjusted until the calculated Y value at X=1 satisfies the boundary condition. This method is reliable as long as a single solution exists and the Y at X=0 is positive [15,16].

Calculation of Effectiveness Factors

Effectiveness factors can be determined by analytic solutions of the reaction-diffusion equation. The analytic solution of the effectiveness factor for a first order reaction in a spherical particle is given by [9]:

$$\eta=\frac{3}{\Phi^2}(\Phi\cdot\coth(\Phi)-1) \tag{13}$$

However, for non-integer reaction orders the concentration profiles within the solid have to be calculated numerically and the following definition is used to determine the effectiveness factor [9,14-16]:

$$\eta=\frac{k}{k_0}=\frac{1}{X}\int_0^1 Y(X)dX \tag{14}$$

Since the conversion rate is a function of temperature, the temperature profile needs to be incorporated to the definition of the effectiveness factor in non-isothermal solid fuel conversion. Using equation (10) and expressing the ratio of the kinetic rate as a function of temperature, the non-isothermal effectiveness factor can be calculated by [21]:

$$\eta=\frac{k}{k_0}=\frac{1}{X}\int_0^1 Y(X)\cdot e^{-\Theta}dX \tag{15}$$

where θ is ratio of the kinetic rates:

$$\Theta=\gamma\left[\frac{1}{\beta\left(1-Y(X)\right)+1}-1\right] \qquad (16)$$

Figure 2 shows a comparison of the isothermal and non-isothermal effectiveness factor for β = 3 and γ = 5 versus the Thiele modulus. Both effectiveness factors are similar for small Thiele moduli. The differences between them start at Φ ~ 0.2, where the effectiveness factors for the non-isothermal case start to rise and reach values above unity. The initial onset might be regarded as an ignition point of the solid at which conversion rates increase significantly [1,3,4,7,14]. The regions including multiple solutions for the intra-particle concentration profiles are unstable and the actual conversion rate is forced to either of the two stable boundaries. The heat release and heat transport rates determine which boundary is the stable one.

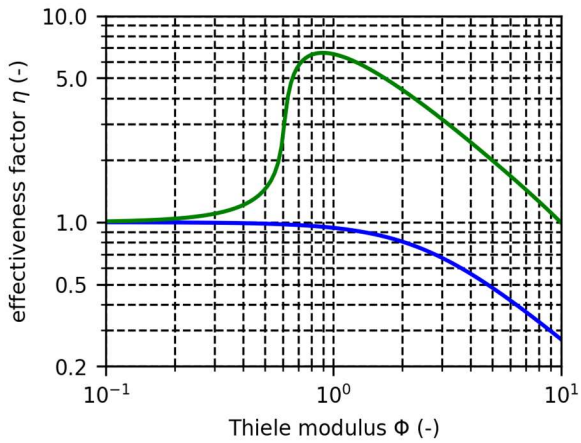

Figure 2: Isothermal (blue) and non-isothermal (green) effectiveness factor versus Thiele modulus. Parameters pairs for the non-isothermal cases are: γ = 5, β = 3.

Effectiveness Factors in Coal Combustion

The effectiveness factor for isothermal coal combustion is calculated according to the analytic solution for a first order reaction in a spherical particle given equation (13).

The non-isothermal effectiveness factor needs additional parameters to be specified to calculate β and γ. Average values for the thermal conductivity, effective diffusion coefficient and heat of reaction are employed with global kinetic parameters for coal char oxidation. The employed values are summarized in Table *1*.

Table 1: Parameters used in the non-isothermal effectiveness factor calculation.

property	value	source
λ	1.241 W/m/K	[17,18]
D	$5\cdot10^{-6}$ m²/s	[19]
ΔH	31.38 MJ/kg	[20]
E_a	135.92 kJ/mol	[20]

The bulk gas phase is assumed to be at temperatures ranging from 700 to 2000 °C. Using these parameters gives values between 0.65 and 0.1 or 23 and 8 for β and γ. Table *2* summarizes these parameter pairs arising for the aforementioned coal combustion conditions. The calculated values indicate that significant differences between the isothermal and non-isothermal effectiveness factors might arise for low ambient temperatures, since β and γ are large.

Table 2: Reaction rate sensitivity on temperature (γ) and normalized temperature variation (β) for typical coal combustion conditions.

T_0 (K)	γ (-)	β (-)
710	23	0.63
905	18	0.39
1250	13	0.20
2025	8	0.08

Figure 3 shows the calculated effectiveness factors for typical coal combustion conditions. The unstable regions where the reaction-diffusion equation has multiple solutions are excluded. Furthermore, the regions with changing slopes at Φ > 1 are removed from the plot, since the currently employed mathematical method fails to give correct results for Y(0) = 0, which occurs in this region.

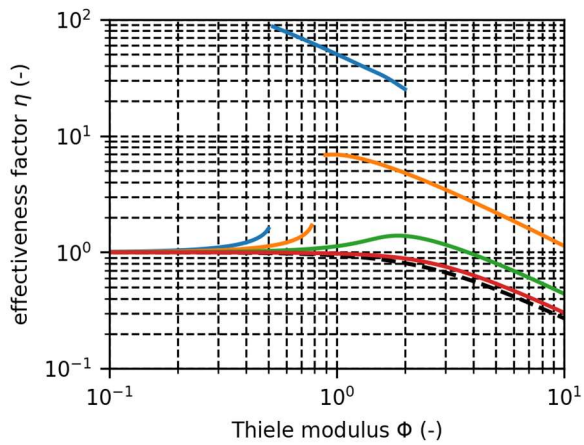

Figure 3: Isothermal (dashed) and non-isothermal effectiveness factor versus Thiele modulus for typical coal combustion conditions. Parameters pairs for the non-isothermal cases are: γ = 23, β = 0.63 (blue), γ = 18, β = 0.39 (orange), γ = 13, β = 0.0.20 (green), γ = 8, β = 0.08 (red).

Non-isothermal effectiveness factors start to exceed unity at Φ > 0.3. The ignition onset correlates with γ and β; higher γ and β result in an earlier ignition point. This behavior is expected, since high γ and β values occur at low ambient temperatures. Furthermore, the severity of the discontinuity in non-isothermal effectiveness factors caused by the ignition region increases for low ambient temperatures. Heat generation and removal rates determine if the solid fuel ignites. Particle temperatures significantly exceed ambient temperatures in case ignition occurs.

Comparing the isothermal effectiveness factor with the non-isothermal ones reveals significant higher solid conversion rates if heat release effects are considered. For low T_0, the conversion rates can be more than hundred times higher than predicted for isothermal conditions.

Effectiveness factors of unity characterize uniform reacting fuel particles. The consequences of η > 1 might be evaluated by investigating intra-particle temperature and reactant concentration profiles. The normalized temperature and concentration profiles for selected conditions are shown in Figure 4 and Figure 5. As indicated by the correlation of Damköhler and Prater [12,13], temperature and concentration profiles are inversely proportional to each other. Peak temperatures and concentration minima migrate towards the particle surface in case of non-isothermal combustion. The concentration profiles reveal that the gaseous reactant is depleted in significant particle portions. As a result, solid combustion starts to confine towards the particle surface region for non-isothermal effectiveness factors above unity.

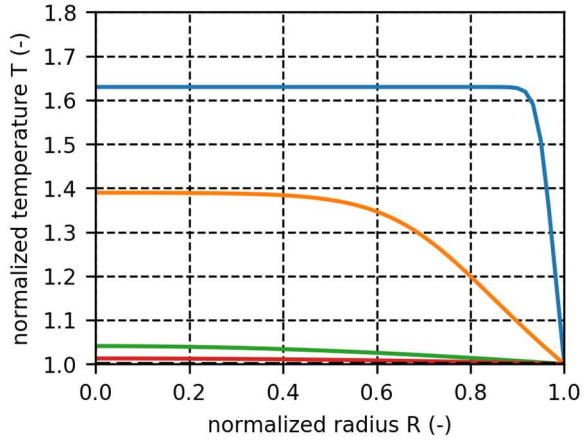

Figure 4: Normalized temperature profiles for isothermal (dashed) and non-isothermal coal conversion at Φ = 1. Parameter pairs for the non-isothermal cases are: γ = 23, β = 0.63 (blue), γ = 18, β = 0.39 (orange), γ = 13, β = 0.0.20 (green), γ = 8, β = 0.08 (red).

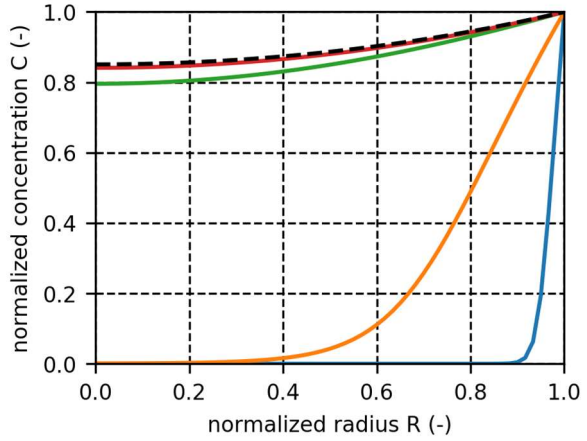

Figure 5: Normalized concentration profiles for isothermal (dashed) and non-isothermal coal conversion at Φ = 1. Parameters pairs for the non-isothermal cases are: γ = 23, β = 0.63 (blue), γ = 18, β = 0.39 (orange), γ = 13, β = 0.0.20 (green), γ = 8, β = 0.08 (red).

This changes the mechanistic combustion regime from progressive core towards shrinking particle [5]. Progressive core combustion is characterized by a decrease in density, while the particle size remains virtually constant. Contrary, particle density stays constant but particle size reduces in shrinking particle combustion. Furthermore, the migration of the reaction zone towards the particle surface might also be interpreted as the transition between conversion Regime **I** and Regime **II** to Regime **III** for high effectiveness factors.

Summary & Conclusion

The theoretical background of the effectiveness factors used in catalysis and thermo-chemical conversion of porous solids has been discussed in this work followed by a discussion of non-isothermal effects occurring in the combustion of porous solids. Subsequently, non-isothermal effectiveness factors were calculated for typical coal combustion conditions.

The investigation of non-isothermal effectiveness factors for coal combustion showed that conversion rates might exceed isothermal conversion rates by a factor of 100. The discrepancy between isothermal and non-isothermal effectiveness factors increases at lower ambient temperatures. Significant ignition effects can occur when heat release exceeds heat transfer. Up to three solutions of the non-isothermal reaction-diffusion equation exist for the ignition region. However, the ignition region is unstable and causes a discontinuity of the effectiveness factor curves [14-16].

Intra-particle temperature and concentration profiles reveal a shift of the conversion zone towards the particle surface leaving a non-reacting particle core for η >> 1. This thermally induced conversion changes might be interpreted as the transition from progressive core (Regime **I** and Regime **II**) to shrinking particle (Regime **III**) characteristics.

The significant deviation between isothermal and non-isothermal effectiveness factors for typical coal combustion conditions suggests that coal combustion rates are significantly under-predicted when employing the analytical expressions for the isothermal effectiveness factors. Moreover, ignition processes cannot be captured by the isothermal approach. The actual deviation depends on the Thiele modulus (Φ), which itself depends on the coal conversion conditions [6, 9]. At small Φ the error introduced by the assumption of isothermal conversion might be small, but significant errors might be introduced starting from the ignition point where η starts to exceed unity.

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