Molybdenum oxide reduction using syngas and heat from an inert porous media reactor

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ABSTRACT

A method of molybdenum oxide (MoO_3) reduction using both the heat released and gaseous products from hydrocarbon fuels partial oxidation (H_2 and CO) in a novel inert porous media reactor is studied. The numerical approach considered a two-temperature model for filtration combustion of methane with a four-step reaction mechanism to solve temperature, H_2 and CO production, and MoO_3 reduction through shrinking core model. A maximum for molybdenum oxide reduction was found with an increasing equivalence ratio (ϕ). Use of propane resulted in a low reduction degree and a maximum temperature of 641 K for the molybdenum oxide powder. SEM and XRD analysis were conducted on the tested powders. Empirical data predicts a favorable reduction degree for the new reactor proposed.

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Introduction

Starting from the extraction of the molybdenite mineral (MoS_2) and its corresponding sulphide roasting process, the molybdenum oxide (MoO_3) reduction to pure metal (Mo) is the final stage to obtain refractory metal, and one of the main methods to obtain high purity molybdenum [1]. The process to obtain Molybdenum (Mo) from molybdenum trioxide requires two reduction steps ($MoO_3 \rightarrow MoO_2$ and $MoO_2 \rightarrow Mo$), using hydrogen as reducing agent.

MoO_3 reduction is an exothermic process and, at low temperatures (723—823 K), an intermediate oxide (Mo_4O_{11}) is generated [2,3]. The growth of the intermediate phase occurs on the surface of MoO_3 with a constant grain size, which develops into the inner layers of MoO_2 as it enters the reducing gas and thus coexist the three stages during this process [2]. The reduction process decelerate when the conversion rate exceeds 90%. It has been reported that besides hydrogen, carbon-containing gases can successfully reduce MoO_3 powder [3].

The second reduction step is the molybdenum dioxide reduction (MoO_2). For this reaction, the conversion rate takes place starting from 900 to 1050 K. It was possible to identify two different conversion paths that powders took depending on the hydrogen dew point: Pseudomorphic and grain transformation due to chemical vapor transport, were both governed by H_2 dew point. The path taken influences the nucleation and growth of the Mo phase [2].

The constant search for clean and efficient combustion processes as well as lowering their emissions has promoted the creation of new technologies such as the filtration combustion in inert porous media (IPM). The operation principle behind these reactors is based on a self-sustaining combustion wave sustained within a porous packed bed [4,5]. Due to a highly developed interstitial area between the gas and solid phases, along with an increase in the diffusion of species, the porous bed acts as a heat accumulator and therefore allows for the recirculation of thermal energy inside the reactor. This arrangement results in an enthalpy excess in the process: rising the free flame temperature over its adiabatic value and extending the flammable range for gaseous fuels. Most studies report that the propagation rate in IPM combustion corresponds to a low-velocity regime (LVR). Therefore, temperature profiles display an evident maximum in the combustion zone. The transient process allows the combustion wave to move ways either in an upstream or downstream fashion along the porous bed. Through an array of thermocouples, it is possible to calculate the wave's position and in consequence estimate its propagation rate. In ultra-lean combustion conditions is possible to support a stable and high thermal efficiency combustion wave with low pollutants emissions (CO, NO$_x$). Another special application of the IPM technology is observed when operating under ultra-rich conditions, generating syngas (H$_2$, CO) as a result from partial oxidation.

Until now, research in porous media combustion has been focused on: maximum combustion temperatures; solid phase temperature profiles, the amount of reaction heat released, combustion wave thickness, propagation rates, wave stabilization, and syngas production (H$_2$ and CO) from ultra-rich combustion [4–15]. Moreover, many numerical studies on filtration combustion have been successfully developed [6–8,10–13,16–25]. Most experimental research is focused in a range of lean and ultralean mixtures, aiming to achieve more thermally efficient processes and with less emission. The equivalence ratio (ϕ) is defined as the ratio between the real fuel-to-oxidizer ratio and the stoichiometric fuel-to-oxidizer ratio. For fuel–rich mixtures, $\phi > 1$, and for fuel-lean mixtures, $\phi < 1$. For a stoichiometric mixture, $\phi = 1$. According to the above described case, numerical studies focus their efforts on simulating the performance of a filtration combustion process, thus one-step reaction schemes are often enough to achieve these purposes. Reaction schemes of one-step are inadequate to model the product gases from the partial oxidation of a fuel; therefore, it is necessary to implement three-step schemes at least [10]. As a solution to this issue a four-step global reaction scheme, proposed by Jones and Lindstedt [31], is selected. This approach describes the process of hydrocarbon combustion through four reactions: (i) partial oxidation of fuel, (ii) fuel reforming with steam, (iii) complete oxidation of hydrogen and (iv) water-gas shift reaction.

Given the exothermic nature of an ultrarich combustion wave, its high-energy release rate and its ability to generate H$_2$ and CO, it is envisioned that this combustion process may be coupled to an existing process and offer support in the reduction of metal oxides [13].

The shrinking core model [26] represents the transformation of a spherical solid phase by the action of a gaseous reactant. This model has been used to characterize various heterogeneous reactions mainly involving metal oxides reduction [13,27–30]. The fundamentals of this model involve five stages: (i) Diffusion of gaseous reactant through the gas film surrounding the particle to the surface of the solid particle; (ii) penetration and diffusion of gaseous reactant through the mantle of ash on the surface of the unreacted core; (iii) reaction between the solid reactant gas on the surface of the latter; (iv) diffusion of gaseous reaction products through the ash back to the outer surface of the solid and (v) the diffusion of gaseous reaction products through the gas film back to the main gas flow. Researchers have established that this model fits for simulating the reduction of molybdenum oxides [2,3].

The aim of this work is to successfully implement a numerical model of a syngas generating IPM reactor coupled to a MoO$_3$ reduction process through both heat and syngas releases. Moreover, an experimental assembly featuring a dual combustion system with a porous media reactor and a molybdenum oxide reduction stage was designed and built, according to specifications obtained from numerical data. The numerical model was developed for methane-air mixtures and experimental tests were performed using propane as fuel.

Numerical model

Inert porous media combustion model

The model used for rich and ultrarich combustion of methane was proposed by Refs. [8,20]. The model consists of a set of laws of conservation of energy (solid and gaseous phases), law of continuity and conservation of species (mass) represented as partial differential equations, which describe a full developed steady wave in a one-dimensional coordinates system moving with the reaction zone. The combustion process was modeled using a four-step reaction mechanism for hydrocarbon fuels presented by Jones & Lindstedt [31]. The numerical scheme is shown in Fig. 1.

For this purpose the following assumptions are considered: (i) the gaseous species were consumed and/or generated as the four-step scheme proposed (ii) physical and chemical properties of the involved species are temperature dependent, (iii) an isobaric system is assumed, and (iv) radial dispersion is neglected.

The governing equations for a steady and fully developed combustion wave are now introduced:

- Continuity equation:

$$\frac{\partial \left(\rho_g \varepsilon \right)}{\partial t} + \frac{\partial \left(\rho_g \varepsilon u_f \right)}{\partial x} = 0 \tag{1}$$

- Gas phase energy equation:

$$\varepsilon \left(c_p \rho \right)_g \left(\frac{\partial T_g}{\partial t} + u_f \frac{\partial T_g}{\partial x} \right) + \left(\rho_g \varepsilon \sum_i Y_i V_i c_{p,g,i} \right) \frac{\partial T_g}{\partial x} + \varepsilon \sum_i r_j \Delta H_{c,j}$$
$$= \varepsilon \frac{\partial}{\partial x} \left(\left(k_g + \rho_g C_{p,g} D_{\parallel}^d \right) \frac{\partial T_g}{\partial x} \right) - a_{gs} \left(T_g - T_s \right) \tag{2}$$