MATHEMATICAL MODELING AND EXPERIMENTAL STUDIES OF CONDENSED-PHASE REACTION IN Ti-Mo-Si SYSTEM IN THE PRESENCE OF GAS PRESSURE GRADIENT

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Abstract

A mathematical model describing propagation of a combustion front in the presence of axial pressure gradients has been developed. The results of mathematical modeling of Ti-Mo-Si system are accompanied by experimental studies in a specially designed pressure cell allowing laser ignition of a reacting system under the external gas pressure gradient. Ti-Mo-Si reacting system is considered as a potential environmentally benign replacement of ignition delay systems, currently used in various military and civilian applications. The effect of uni-axial gas pressure gradient on the combustion front propagation velocity in Ti-Mo-Si reacting system was studied using mathematical modeling and experimental technique. Both experimental and modeling results are compared and discussed.

Introduction

Mathematical modeling of combustion synthesis phenomena has been the interest to many researchers for the last several decades. This area of research has proven to be very challenging due to the complexity of combustion processes, especially those involving condensed phases. One example of such class of reactions is a numerical simulation of temperature and conversion profiles in the self-propagation high-temperature synthesis (SHS), also known as combustion synthesis. Despite the significant progress, the mathematical modeling has not been thoroughly conducted; especially when partial vaporization or combustion-induced gas flows take place [1]. There exist a significant number of condensed-phase reacting mixtures (e.g. B-$BaCrO_4$, Mn-$PbCrO_4$-$BaCrO_4$, and W-$BaCrO_4$-$KClO_4$). Many of currently used condensed mixtures are not environmentally friendly due to the toxicity of individual components. Recently it was found that Ti-Mo-Si, Al-Si-Fe_2O_3, and Si-Al-Fe_3O_4 could be considered as potential replacements of commercial formulations. These mixtures appear to be very safe when tested by impact or friction and they are rather insensitive to electrostatic discharge.

The objectives of this paper were: i) mathematical modeling of combustion front propagation in the presence of uniaxial gas pressure gradients; ii) measurements of the combustion front propagation velocities in the presence of uniaxial gas pressure gradients ; and iii) measurements and testing of permeability of Ti-Si-Mo delay system.

Mathematical Modeling

The main focus of mathematical modeling was to simulate the combustion wave propagation in condensed reacting systems, both with and without the presence of uni-axial gas pressure gradient. In mathematical modeling same composition of (5Ti+3Si) and (Mo+2Si)

was used as for experimental study. These models assume gasless and elementary character of the combustion process. This reaction can be represented as:

$$\text{A (solid)} + \text{B (solid)} \rightarrow \text{P (solid)}. \tag{1}$$

The governing equations describing the condensed-phase reacting system for the semi-finite cylindrical body in dimensionless form are [1-7]:

Mass Balance

The mass balance for Ti-Si and Mo-Si reactions can be written as follows:

$$\frac{\partial \eta_p}{\partial \tau} = t^{**} f_p(\eta_p) \Re_p^{(\Theta-1)} \tag{2}$$

where *p* stands for the number of reactions, Ti-Si and Mo-Si systems and f_p may take the following forms:

$$f_1 = k_1 C_{Ti,0,1}(1-\eta_1) \tag{3}$$

$$f_2 = 3\lambda(1-\eta_2) \tag{4}$$

$C_{Ti,0}$ is the initial concentrations of titanium described as follows:

$$C_{Ti,0} = \frac{WF_{Ti}(1-\Phi)}{WF_{Ti}\left[\frac{1}{\rho_{Ti}} + \frac{3M_{Si}}{5\rho_{Si}M_{Ti}}\right] + \frac{WF_{Ti_5Si_3}}{\rho_{Ti_5Si_3}}} \tag{5}$$

and

$$\lambda = 3\frac{k_{0,p}M_{LR}C_{LR,0}}{aM_B\rho_B R_p} \tag{6}$$

Energy Balance

The dimensionless energy balance for semi-finite cylindrical body is written as:

$$\frac{\partial \Theta}{\partial \tau} + \Gamma\frac{\partial \Theta}{\partial \xi} = \frac{\partial^2 \Theta}{\partial \xi^2} + \Im Q_r^{\bullet} - \mathrm{H}^*(\Theta - \Theta_0) \tag{7}$$

Where Q_r^*, Γ, $\Im$, and H^* are defined as follows:

$$Q_r^{\bullet} = \sum_{p=1}^{n}\left(\left(-\Delta \mathrm{H}_{Rp}\right) f_p(\eta_p)\Re_p^{(\Theta-1)}\right) \tag{8}$$

$$\Gamma = \frac{v_0 L \rho_{g,0} \upsilon^* \rho^* C p_g}{\lambda} \qquad \Im = \frac{L^2}{\lambda T_c} \qquad \mathrm{H}^* = \frac{4hL^2}{D\lambda} \tag{9}$$

Continuity Equation

$$\frac{\partial(\rho^* \Phi)}{\partial \tau} + \frac{t^{**} v_0}{L} \frac{\partial(\rho^* \Phi \upsilon^*)}{\partial \xi} = 0 \tag{10}$$

Ideal Gas Law

$$\rho^* = \frac{T_0}{T_c}\left(\frac{P^*}{\Theta + 1}\right) \tag{11}$$

Ergun Equation

It was decided that the pressure drop in the cylindrical specimen can be calculated by Ergun equation [7]:

$$\frac{\partial P^*}{\partial \xi} + \alpha \upsilon^* + \beta \upsilon^{*2} = 0 \tag{12}$$

where α and β are described by the following expressions:

$$\alpha = 150 \frac{L v_0 \mu}{P_0 g_c D_p^2}\left(\frac{(1-\Phi)^2}{\Phi^2}\right) \qquad \beta = 1.75 \frac{L \rho_{g,0} v_0^2 \rho^*}{P_0 g_c D_p}\left(\frac{1-\Phi}{\Phi}\right) \tag{13}$$

The initial and boundary condition are as follows:

$$\tau \le 0, \quad 0 \le \xi \le 1, \quad \Theta = \frac{T_0 - T_c}{T_c}, \quad P^* = 1, \quad \upsilon^* = 0, \quad \eta_p = 0 \tag{14}$$

$$\tau > 0, \qquad \xi = 0, \qquad \Theta = 0, \quad P^* = \frac{P_h}{P_0} \tag{15}$$

$$\xi = 1, \qquad \frac{d\Theta}{d\xi} = -Bi[\Theta(1) - \Theta_0], \quad \frac{dP^*}{d\xi} = 0 \tag{16}$$

The dimensionless variables and parameters used in Equations 2 through 16 are defined in nomenclature. In order to perform numerical simulation, the first and second order spatial derivates were approximated by an upwind and a central finite different scheme, respectively [1, 8, 9].

Numerical Results and Discussion

The numerically calculated dynamic profiles of dimensionless velocity, temperature, pressure, density, and conversion profiles are presented in Figures 1 through 6. The kinetic and physico-chemical data for Ti-Si were taken from [10, 11]. A good qualitative agreement between the experimental results and numerical calculations was found regarding the effect of gas pressure gradient on the propagation velocity. It was observed that as the gas pressure increases the propagation become faster. This could be due to the fact that an increase in gas pressure during the combustion allows the gas to preheat the unreacted mixture ahead of a combustion front [1].

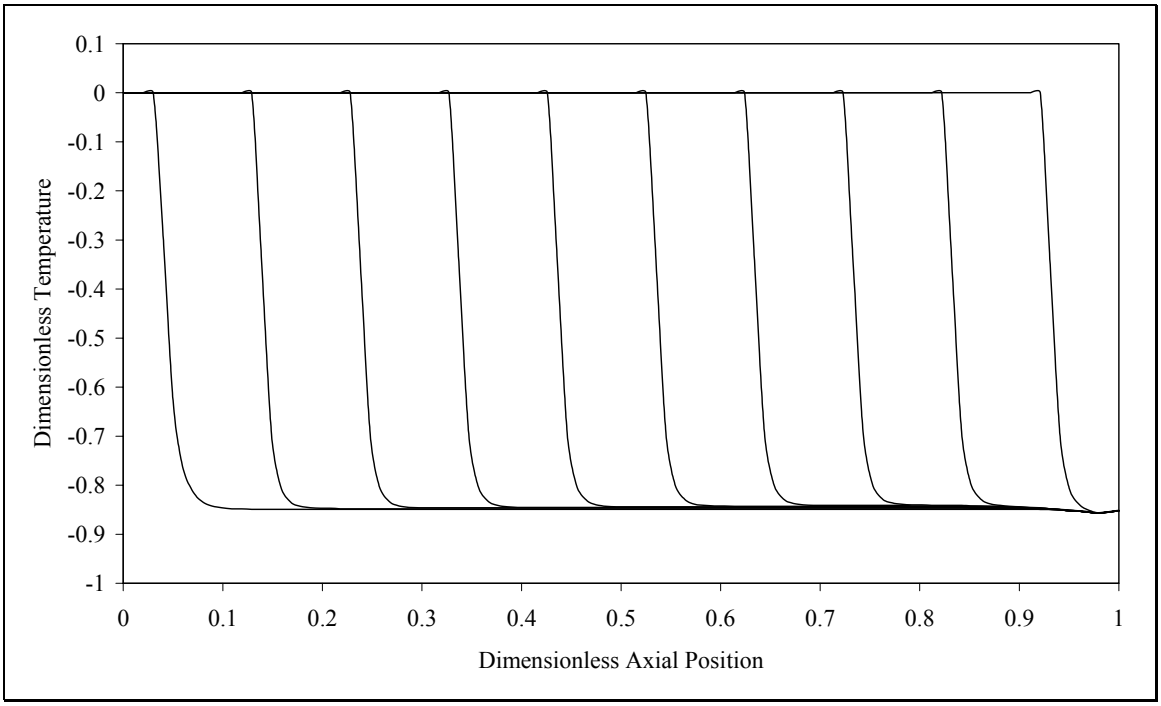

Figure 1. Temperature profiles with ΔP = 140 bar, Φ = 0.4, and $\Delta\tau = 1.0 \times 10^{-3}$.

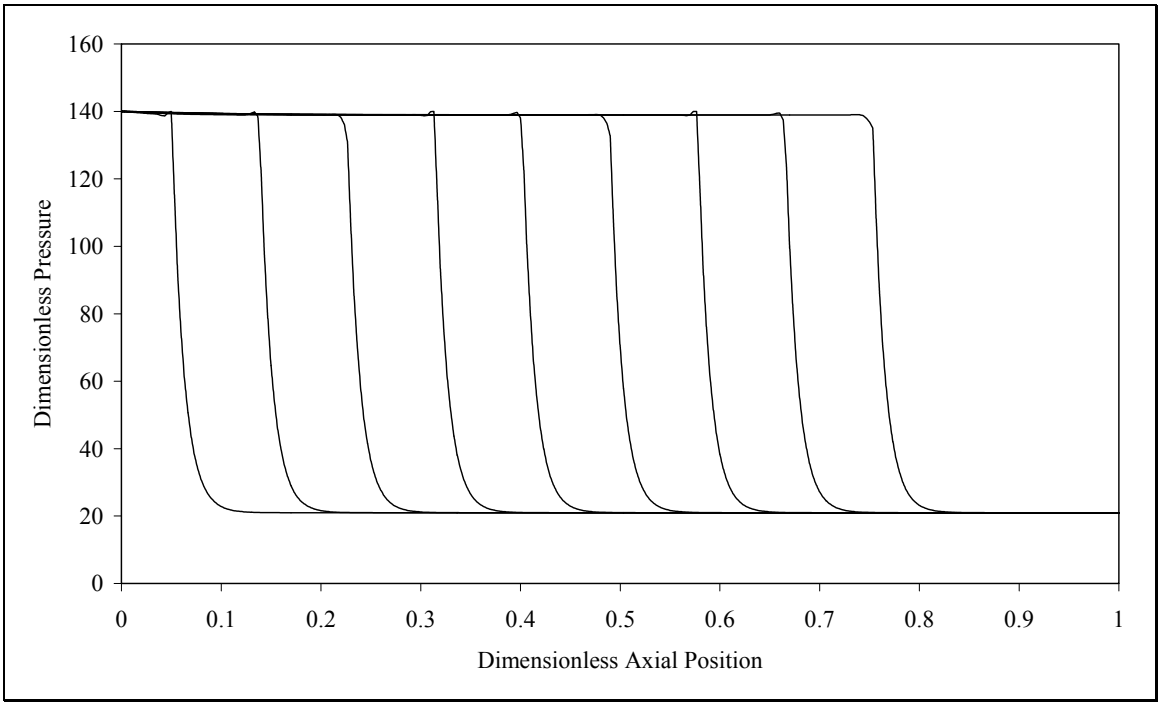

Figure 2. Pressure profiles for constant porosity ($\Phi = 0.4$) and $\Delta\tau = 1.0 \times 10^{-3}$.

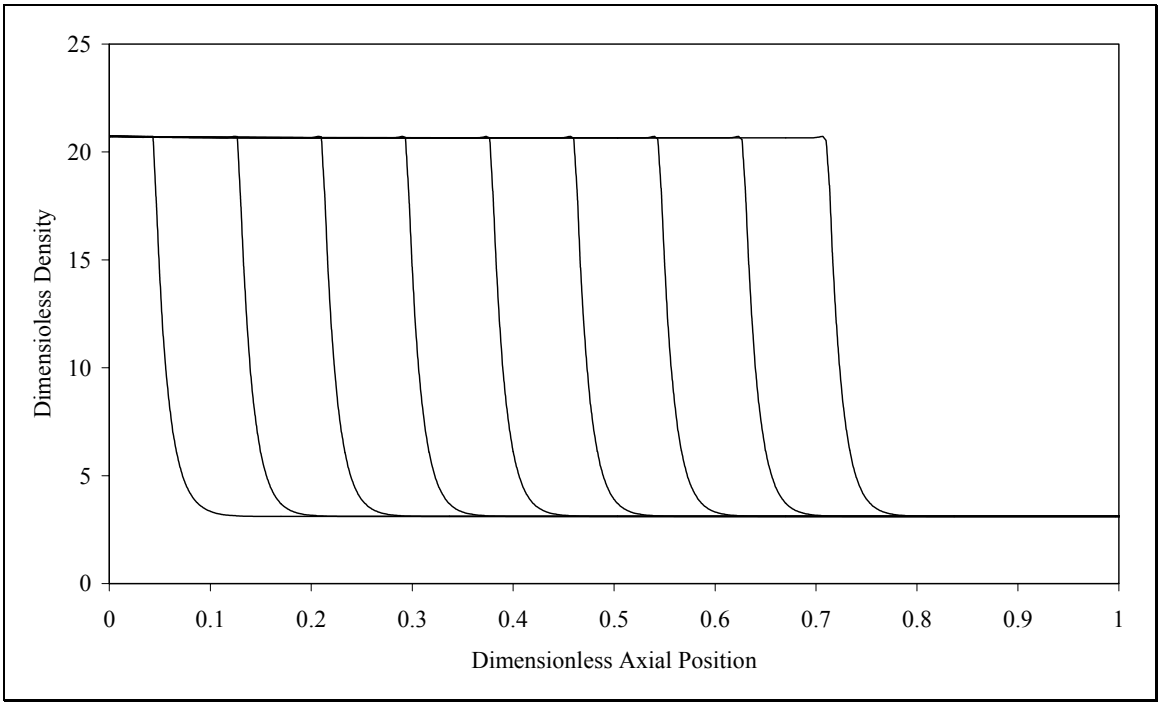

Figure 3. Density profiles with $\Delta P = 140$ bar, $\Phi = 0.4$, and $\Delta\tau = 1.0 \times 10^{-3}$.

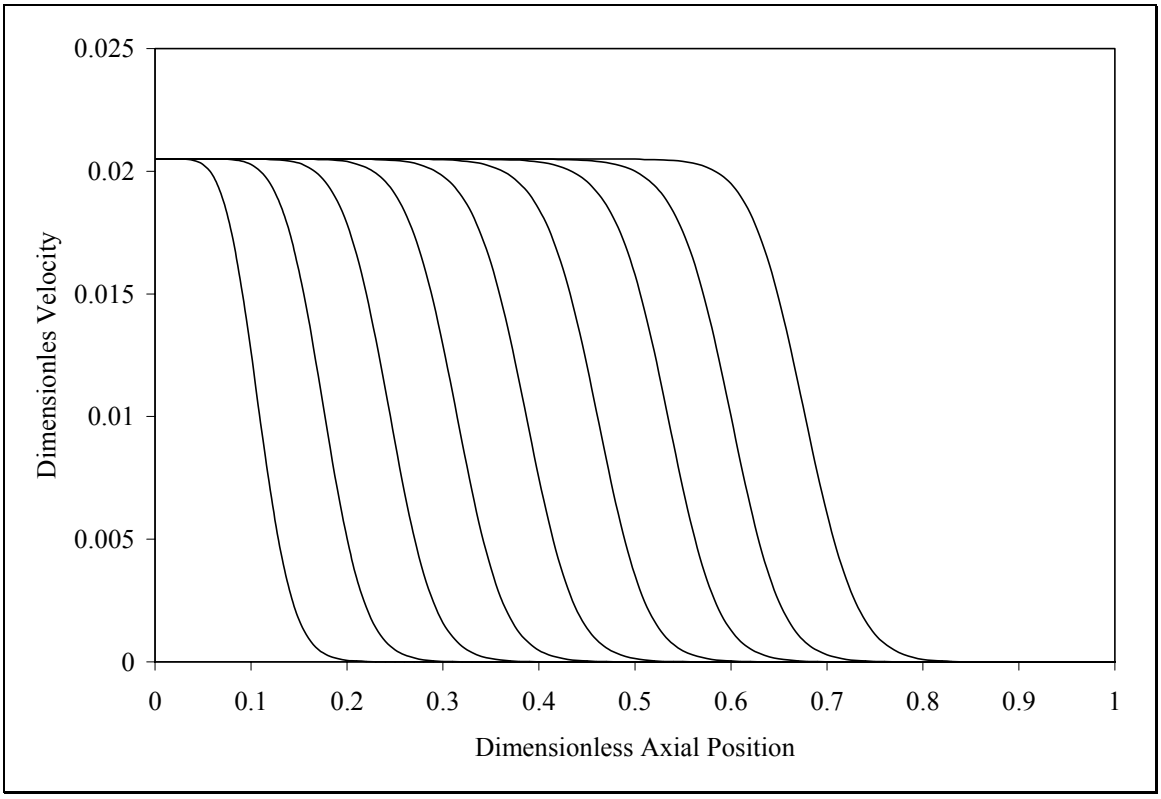

Figure 4. Velocity profiles with ΔP = 140 bar, Φ = 0.4, and $\Delta\tau = 1.0 \times 10^{-3}$.

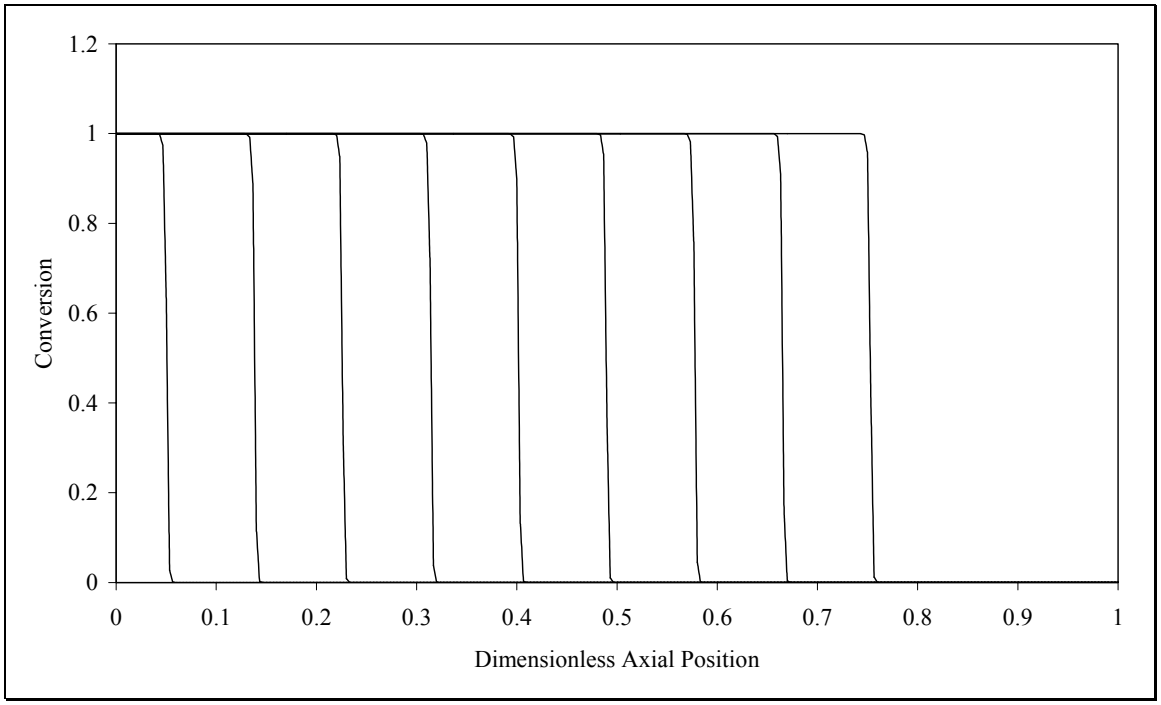

Figure 5. Conversion profiles with ΔP = 140 bar, Φ = 0.4, and $\Delta\tau = 1.0 \times 10^{-3}$.

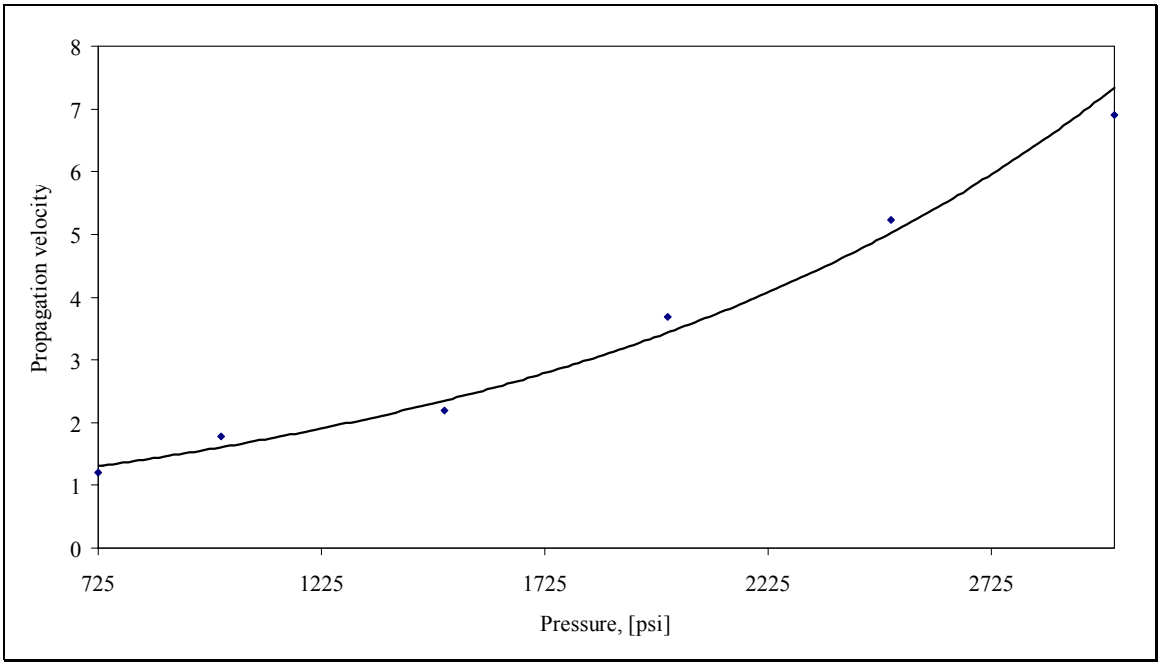

Figure 6. Propagation front velocity profiles at various gas pressure gradients with constant porosity (Φ = 0.4).

As can be seen from Figure 6, when the gas pressure gradient increases the propagation become faster. This may be due to the fact that an increase in gas pressure during the combustion allows the gas to preheat the unreacted mixture ahead of a combustion front, which makes the system faster.

Measurement of Propagation Velocity Under Uniaxial Pressure Gradients

In an actual close column cartridge, pressure is rapidly built up in the ignition cavity, which causes hot gases to flow through the porous reactant mixture. These hot gases preheat reactants leading to faster combustion front propagation velocities. The source of the pressure may be gas output from the ignition source, temperature increase, or desorption of volatile species [12]. In an attempt to better understand the effect of pressure on the burning time, experiments were conducted under uniaxial gas pressure gradients in Ti-Mo-Si system consisting of 58 wt % (5Ti+3Si) and 42 wt % (Mo+2Si).

Experimental Set-up

Propagation velocities under uniaxial gas pressure gradients were measured using the setup shown in Figure 7. A laser source (Nd: YAG Pulse Laser) provides a pulse to ignite a delay mixture. For these experiments the delay mixture was pressed into a cylindrical steel capsule (dia= 0.203 inch, height=1 inch). One side of the delay column is pressurized through a gas inlet using argon gas, when another side is exposed to ambient pressure. The laser beam passes through the glass window, and ignites the A1A mixture, initiating the reaction and sends the first signal to the data acquisition through photodiode 1. The mixture burns and upon

completion a second signal is sent to the data acquisition as a response from photodiode 2. The time difference between two signals allows calculation of the burn rate.

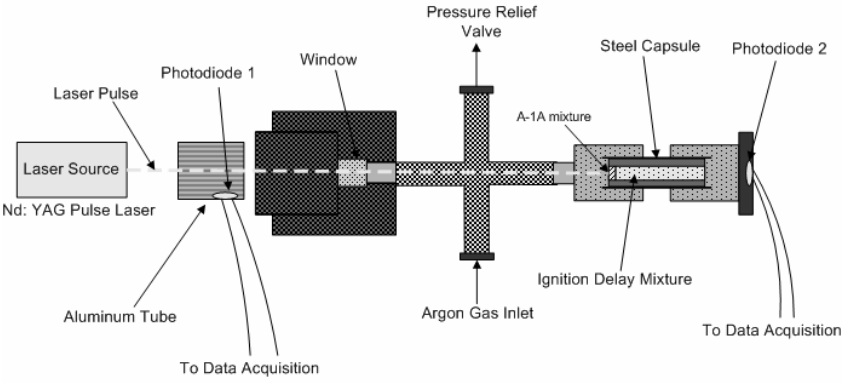

Figure 7. Experimental setup for measurement of propagation velocities under uni-axial gas pressure gradients.

Figure 8 shows the schematic of the experimental set up for the measurement of permeability of unburnt samples. Argon gas flows into the steel casing due to a preset pressure gradient. A valve connected to the T-connector allows the release of high pressure in the system. A flow rate of an argon gas that filters through the pressed powder is measured by using a bubble flow meter.

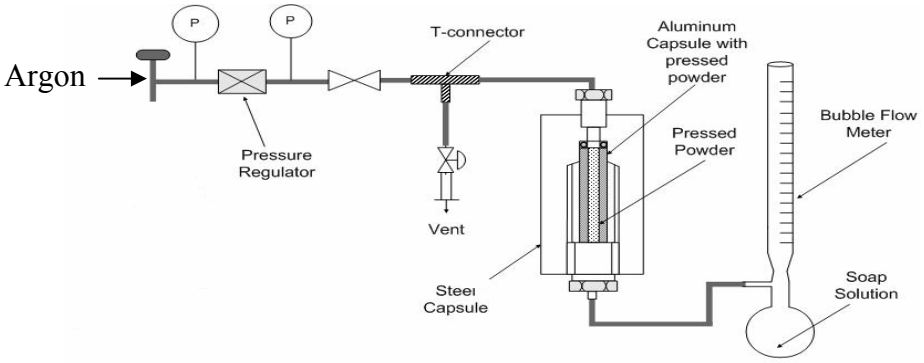

Figure 8. Schematic of the experimental set-up for permeability measurements.

Results and Discussion

A porous medium consists of solid matrix with an interconnected void. The interconnectedness of the void (the pores) allows the flow of the gas through the material. The measured gas flow rates through the unreacted Ti-Mo-Si system are relatively high even at low pressure used in the permeability measurements [13]. At the much higher pressures, during

combustion considerable mass and convective heat transport occurs ahead of the reaction front.

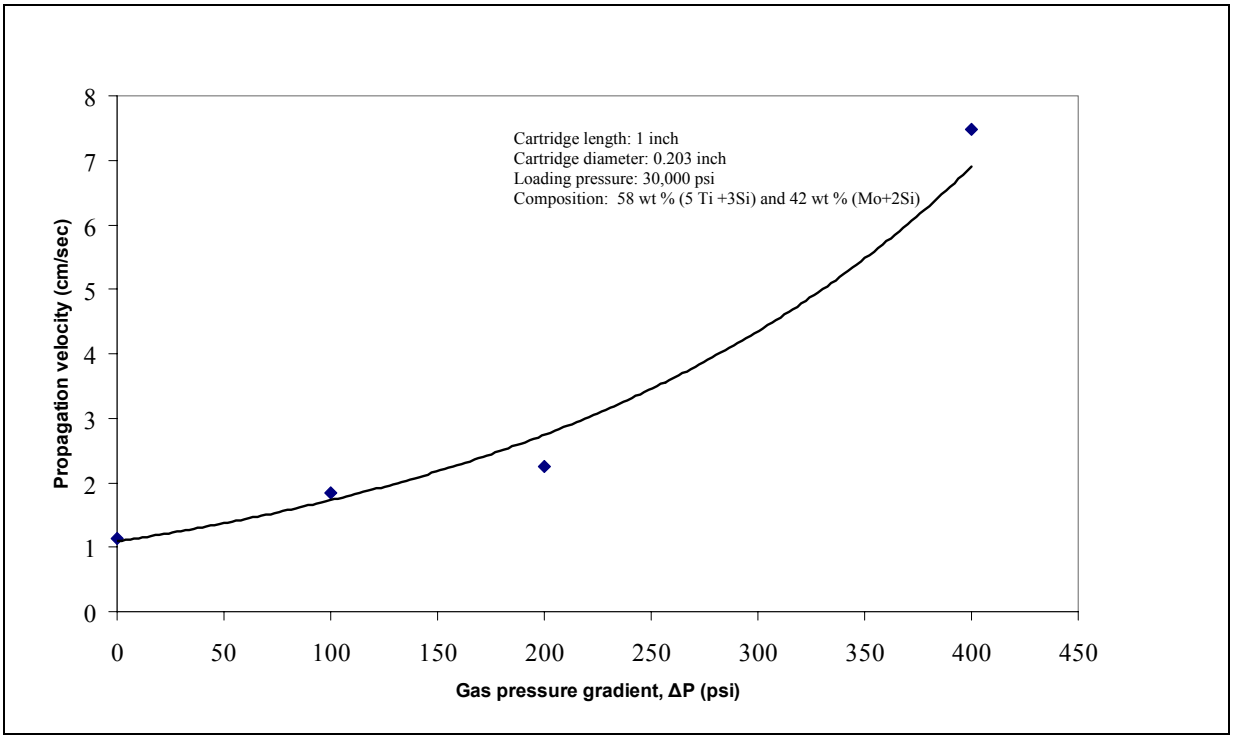

Figure 7. Effect of gas pressure gradient on propagation velocity in Ti-Mo-Si.

It can be seen from Figure 7 that when the gas pressure increases the propagation becomes faster.

Gas permeability in unburnt cartridges were measured by attaching packed aluminum cartridge to the outlet of a gas cylinder (argon) and measuring the volumetric flow rate U of the gas (viscosity η) through the column length L, and the cross-sectional area A, under a pressure gradient ΔP. Permeability coefficients K were then calculated from Darcy's law [14, 15]: $K=L\eta U/\Delta PA$ .The samples were pressed at 22,500 psi and 30,000 psi loading pressure. Gas pressure difference of 600 psi was applied across the cartridge. The permeability coefficients, K of Ti-Si-Mo mixture were measured and the results are listed in Table 1

Table 1. Permeability of the Ti-Si-Mo delay system pressed at different loading pressure and evaluated at uniaxial argon gas pressure gradient of 600 psi

Loading pressure (psi)	Average volumetric flow rate (m^3/sec)	K (m^2)
30,000	($10.38*10^{-4}$)	0.289
22,500	($12.10*10^{-4}$)	0.336

It can be seen from Table 1 that permeability is reduced, as expected, under the greater compaction. In future, experimentally determined K value will be used for mathematical modeling using Darcy's equation instead of Ergun equation.

Conclusions

It was found in this research studies that:

- Gas pressure gradient applied during the combustion has a significant effect on the propagation velocity of the combustion front;
- Very good quantitative agreement between experimental and modeling studies was achieved.

Nomenclature

Bi	Biot number, hL/λ
C	Concentration, kg/m^3
C_p	Heat capacity, J/kgK
D	Pellet diameter, m
D_p	Particle diameter, m
E	Activation energy, J/mol
g_c	Conversion factor, kgm/s^2/N
h	Overall heat transfer, W/m^2K
ΔH_{Rp}	Heat of reaction, J/kmol
L	Length of cylindrical specimen, m
M	Molecular weight of species, kg/kmol
P^*	Dimensionless pressure, P/P_0
P	Pressure, bar
ΔP	Pressure difference, bar
r	Radius of cylindrical specimen, m
T	Temperature, K
T_m	Average temperature, K
t^{**}	Reference time, s, $\overline{\rho C_p} L^2/\lambda$
t	Time, s
v_g	Gas velocity, m/s
v^*	Dimensionless velocity, v_g/v_0

WF	Weight fraction of species, dimensionless
z	Axial position, m
ξ	Dimensionless position, z/L
$\Re_p$	Exponential function, exp (E/R_gT_c)
Θ	Dimensionless temperature, $(T_m - T_c)/T_c$
η_p	Conversion, dimensionless
τ	Dimensionless time, t/t^{**}
ρ^*	Dimensionless density, $\rho_g/\rho_{g,0}$
ρ	Density, kg/m^3
μ	Viscosity, kg/m.s
Φ	Porosity

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