White Paper:

Kinetic Model of Stabilized PAN Fiber Mass Loss During Carbonization

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Abstract

The carbonization process converts stabilized precursor (i.e. stabilized PAN) fiber into carbon fiber and takes place within two high temperature furnaces, namely the LT (Low Temperature) and HT (High Temperature) furnaces. The largest fiber mass loss occurs within the LT furnace which typically operates with a temperature between 500 and 800°C. The volatiles released from the fiber during the carbonization are generally not uniform throughout the process and are strongly dependent on operating conditions such as temperature, heating rate, residence time, and even extent of oxidation from the previous step. Since its inherent complex nature, little research works has focused on the mass loss kinetics within the carbonization process in spite of significant impacts on the quality of the final product. We have developed a continuous model for the carbonization process including mass loss rate as a lumped kinetic using two-zone model for the fiber and pseudo-pure off-gas. The kinetic coefficients used in this model have been estimated by reviewing existing literature data and extending it to real operating conditions. Fiber conversion (i.e. linear density change) predictions over the fiber travel direction are obtained from the model by applying realistic operating conditions. A parametric study on fiber conversion with different time and temperature conditions was also performed.

1. Introduction

Carbon dioxide emission reduction is major challenge for automotive industry. Many developed and developing countries already enacted or drafted legislation on their carbon emission. The bottom-line is identical: carbon emission reduction for environmental sustainability for the future generation. There are several viable ways to achieve this environmental friendly objective. Among them, one of promising solutions is weight-reduction design without sacrifices on safety and performance of the vehicle. Aluminum, magnesium and their alloy are used to replace steel not only for automotive structural body, but also powertrain components for this purpose. Carbon-fiber-reinforced polymer (CFRP) is known for higher strength-to-weight ratio than other light weight metal or alloys. Nevertheless, its high manufacturing cost impedes the automotive industry from adapting CFRP in their products. Therefore, cost-efficient lightweight automotive design would be viable by low cost carbon fibers, which will eventually lead to energy saving as well as a sustainable future.

Achieving consistent fiber quality across the width of the system is one of the major scale-up challenges for reducing the manufacturing cost and large-volume production. With increasing capacity requirements, the system widths have been steadily increasing. For example, 15~20 years ago a typical width for carbon fiber manufacturing furnaces was 1 to 2m wide. For new systems a production scale is often 3 to 4m wide. Considering the height of the system is minimal, achieving uniform conditions across these increasing widths is challenging. Regarding this aspect, we have been conducted series of Computational Fluid Dynamics (CFD) works [1]. Unfortunately, this computational model cannot predict the relation between product quality and surrounding conditions. However, maintaining consistent temperature and process gas conditions to the fiber should result in consistent fiber properties. There are technical difficulties on both computational power limitation and unknown physical properties and intrinsic kinetics for fiber carbonization process. In this work, we have set up the simplified one-dimensional mathematical model including mass loss rate during carbonization process in carbon fiber manufacturing from the fitting of literature data. This is one of the steps to the goal of an integrated system model.

2. Mathematical Models

To investigate uniformity of product fiber, fiber mass loss should be incorporated in the mathematical model. It is manifested in a 2D model for both longitudinal (fiber moving direction) and transversal (furnace width direction) changes inside the furnace. However, transversal change is nonessential to incorporate into the model if the transversal change is caused by interaction with surroundings rather than internal-gradient. Fiber bands passing through the furnace consisted of bundle of tows. In this rationale, 1D model with appropriate surrounding conditions might be enough to study transversal uniformity of product fibers. In this study, a 1D model has been developed for this purpose. This model is not limited to a circular cross-sectional area but an extruded shape is essential for this 1D model.

2.1 Mass and Energy Balances

Two distinct phases exist inside the carbon fiber manufacturing systems: fiber (solid phase) and a mixture of the evolved gas from the fiber and inert cover gas. All kinds of transport occur between these phases. Among them, the most important one is mass transfer: mass transfer from fiber to gaseous phase, also known as mass loss of the fiber. To investigate changes in fiber phase, the control volume is focused on change of solid fiber.

$$\frac{d\dot{m}}{dz} = -m"L_p = -A_c r_{m,loss} \tag{1}$$

where $\dot{m}$ is fiber mass rate, z is fiver moving direction coordinate, m" is mass transfer flux from solid to gas, L_p is perimeter, A_c is cross-sectional area, $r_{m,loss}$ is mass loss rate per volume.

Ordinary differential equation for temperature can be obtained from taking appropriate energy balance. Equation 2 shows the fiber energy balance with sensible heat effect, enthalpy change for evolved gas, and heat transfer with surroundings.

$$\frac{dT}{dz} = \frac{-A_c r_{m,loss}\left(h_{gas} - h_{fiber}\right) + q_s L_p}{\dot{m} C_p} \tag{2}$$

where T is temperature of the fiber, h_{gas} and h_{fiber} are enthalpy for volatiles and fiber, respectively. q_s is heat flux at the fiber surface, L_p is perimeter, and C_p denotes heat capacity of fiber. Mass and energy balances are closely linked each other and thus they need to solve simultaneously.

2.2 Off-gas Constituents and Concentrations

The main focus of this computation is fiber not volatiles but, nonetheless, defining gaseous phase is important on this study. Off-gas is released from stabilized PAN fiber (SPF) during carbonization inside the carbon fiber manufacturing furnace. Several papers show off-gas constituents as a function of operating temperature [2-4]. Volatiles released from carbonization process might depend on many parameters: such as extent of carbonization, temperature, oxidation state of the SPF and other conditions. Those variations of constituents and concentrations are beyond scope of this work. Off-gas constituents and concentrations for this work are assigned as overall average value over the furnace based on our previous work [1] and the literature [5].

Enthalpy of the volatiles is referred to fiber energy balance as endothermic reaction heat of carbonization. Therefore, it is of importance to evaluate enthalpy of the evolved gas precisely. Critical temperature and pressure and its reduced temperature and pressure (@ 1bar and 300°C) were evaluated for all off-gas constituents. From these calculations, it verifies the reasonable assumption that the off-gas is in ideal gas state inside LT furnace [1]. The NASA gas property data [6] was used for to calculate the specific heat of the off-gas.

$$h_{gas} = {}^{1}\!/_{\overline{M_w}} \left[\sum_i x_i h_{\Delta f,i} + \int_{T_R}^{T} \sum_i x_i C_{p,i}\, dT \right] \tag{3}$$

2.3 2-Zone Model for Fiber

Unlike gaseous phase, physical properties of the fiber are more complex since properties are dependent on not only temperature but also conversion. Furthermore, carbonization might be continuous series of chemical reactions rather than clearly distinct single process. A 2-discretized-zone model has been developed for the sake of simplicity and an illustrative conceptual depiction of this model is given in Figure 1.

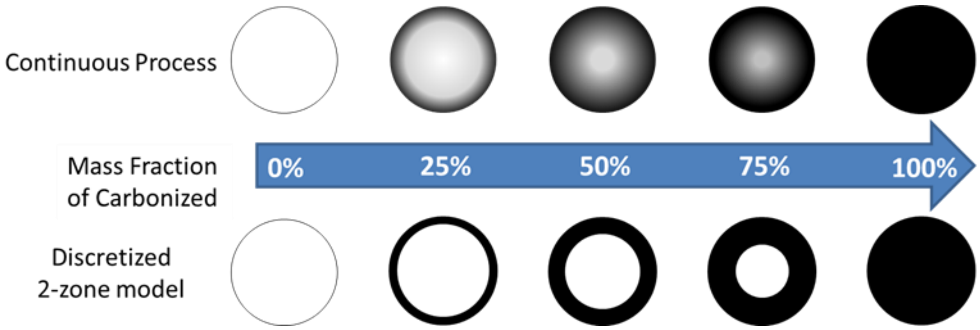

Figure 1. Schematics of discretized 2-zome model for carbonization process

In this 2-zone model, the physical property at any extent of carbonization is expressed using two pure states of fibers: SPF (white region in Fig. 1) and carbonized fiber (black region in Fig. 1) and its mathematical expression is given as follow

$$h(\alpha, T) = \sum_i Y_i(\alpha) h_i(T) = Y_I(\alpha) h_I(T) + \big(1 - Y_I(\alpha)\big) h_S(T) \tag{4}$$

where a is conversion defined below in equation 5. Y_i *is mass fraction of i-th component,* h_I *and* h_S *are enthalpy for intermediate fiber and stabilized PAN fiber, respectively.*

$$\alpha = \frac{m_o - m}{m_o - m_f} \qquad (0 \le \alpha \le 1) \tag{5}$$

Mass fraction and linear density, ρ_L *, are also changing over the carbonization furnace. And those are definitely related with conversion and their relationships are given below.*

$$Y_I = \frac{m_f}{m_o - m_f} \left[\frac{\alpha\left(1 - \frac{m_f}{m_o}\right)}{1 - \alpha\left(1 - \frac{m_f}{m_o}\right)} \right] \qquad (0 \le Y_I \le 1) \tag{6}$$

$$\rho_L = \rho_{L,o} \left[1 - \alpha\left(1 - \frac{m_f}{m_o}\right) \right] \tag{7}$$

where m is mass of fiber, subscript f denotes final state and subscript o denotes initial state. In the following figures, carbonized fiber mass fraction, Y_I, *and linear density of fiber,* ρ_L *, are plotted as a function of conversion for reasonable mass ratio,* m_f/m_o *(=0.5 ~ 0.8).*

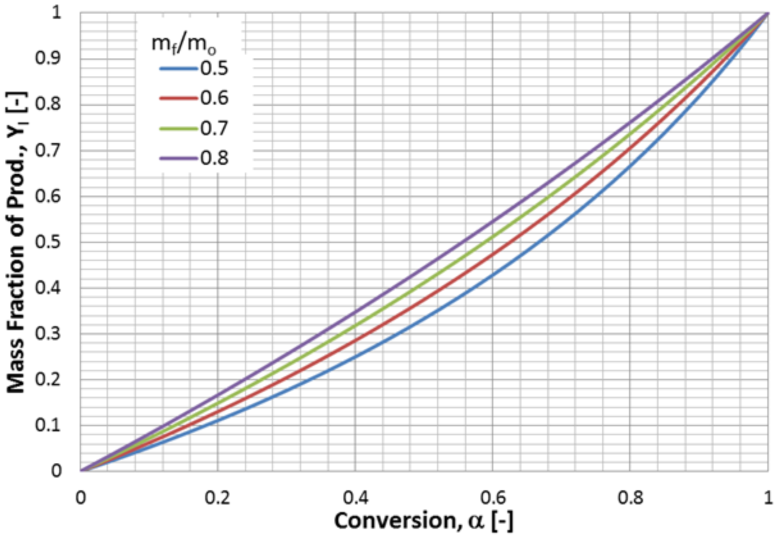

Figure 2. Mass fraction of carbonized fiber as a function of its conversion for various stoichiometric conditions

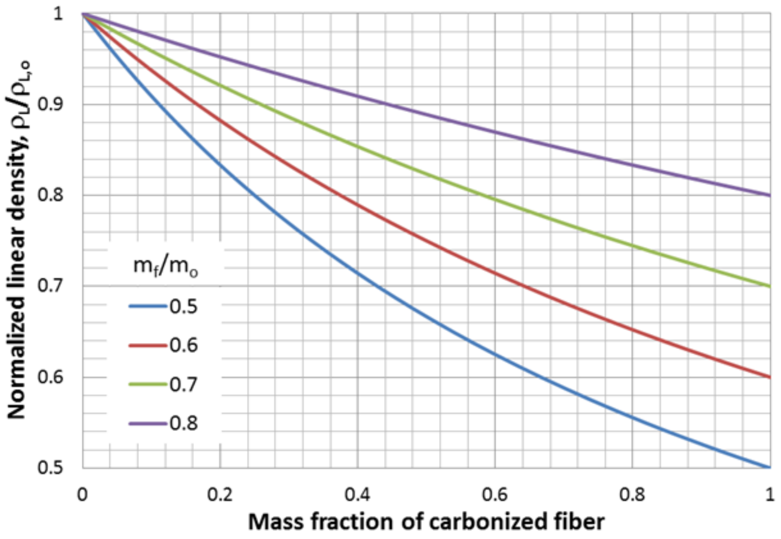

Figure 3. Normalized linear density of the fiber as a function of mass fraction of carbonized fiber for various stoichiometric conditions

Even though it is a simplified model, evaluation of physical properties using this model is still challenging since their properties at a homogeneous state are not fully known.

It is assumed that the product fiber from the LT furnace is similar in composition to carbon fiber since the mass loss from successor devices (HT furnace) is much lower. In addition carbon fiber composition is also assumed as solid graphite in spite of impurity of the carbon fiber (maximum 5% of non-carbon atom usually N and small amount of H).

$$h_I \cong h_{graphite} = h_{f,g}(T_R) + \int_{T_R}^{T} C_{p,g}\,dT \tag{8}$$

$$h_S = h_{f,S}(T_R) + \int_{T_R}^{T} C_{p,S}\,dT \tag{9}$$

It is very challenging to evaluate the thermodynamic state for Stabilized PAN fiber. The oxidation extent might be a complex function of the following factors, co-monomer, residence time, applied tension, heating rates and temperature. Even in the same index of extent, thermodynamic state might be non-identical due to different molecular structures. In the literature, to the best knowledge of the author of this article, no actual measurement data (heat of formation, specific heat and etc.) is available for stabilized PAN fiber. Standard enthalpy of formation of stabilized PAN is taken from our previous work [1] as a successive evaluation from its monomer as it undergoes polymerization and stabilization.

2.4 Chemical Kinetics for Carbonization

Carbonization process to produce carbon fiber is a chemically similar process to pyrolysis or thermal degradation of a polymer. The main difference is whether the physical properties of the end product have been altered as intended to improve the fiber properties. It is side-group elimination and oxidation of the polymer among several mechanisms for thermal degradation of polymer that makes superior physical properties of carbon fiber such as elastic modulus and tensile strength. The actual process might be very complex and not fully understood but simply controlled oxidation of precursor converts its linear structure into a ring structure and side-group elimination during carbonization releases all other groups except carbon-carbon. In the literature, to the best knowledge of the authors of this article, a general expression of chemical kinetic of carbonization of stabilized PAN is not available. Many research works [7-9] were published for the kinetic expression of thermal degradation of polymer. We borrow the kinetic expression from many available thermal degradation of polymer to apply our mass and energy balances in the previous sections to complete our numerical model. Kinetic parameters are obtained from fitting the experimental results [10]. Among many kinetic expressions available for thermal degradation of polymer [7-9], we found the first order kinetic, equation (10), yields good agreement with experiment. The first order kinetic fitting result along with result for 2nd order is illustrated in Figure 4.

$$r_{m,loss} = -\frac{1}{V}\frac{dm}{dt} = Aexp\left(\frac{-E_A}{RT}\right)(m - m_f) \tag{10}$$

where V is volume of specimen in closed system, A is pre-exponent factor, E_A is activation energy, and R is gas constant.

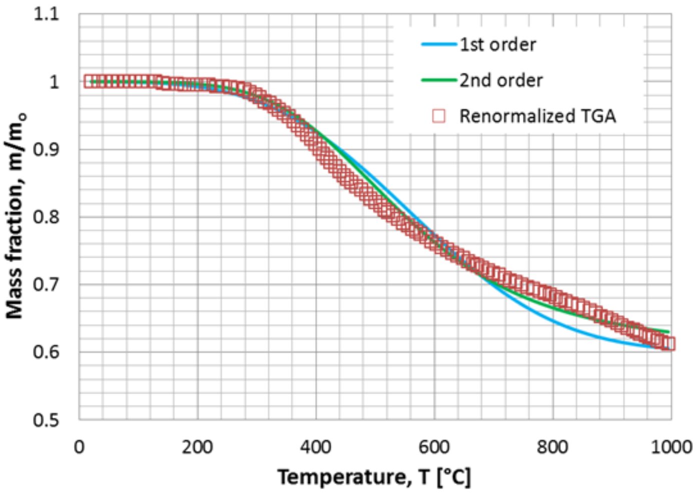

Figure 4. TGA result from literature and first and second order kinetic fitting results

3. Results

Numerical simulation has been conducted by solving systems of non-linear ordinary differential equations given in equations (1) and (2) with kinetic expression (10). Fourth order RK method is applied with step size of 0.001 for dimensionless length scale. All the physical properties and parameters depending on either temperature or conversion are evaluated with internal calculation of fourth order RK method.

3.1 Baseline Result

The fitting kinetic parameter obtained from previous section is extensive property, so it depends on the amount of specimen. To apply this fitting result into the system with different size, it should be converted into intensive property. Unfortunately, the author does not have the details to know the size of specimen. Another aspect is the difference on the time scale between TGA and industrial furnace. In TGA experiment it would take around 60min to lose 25% of its mass and 88min to lose 35% of its mass since heating rate was 10K/min. A baseline case was picked representing realistic operating conditions of industrial scale system. The length of the carbonization furnace is assigned as 14 m with equally divided 7 independent heating zones and linear process speed is assigned as 10 m/min. So, fiber residence time is 1.4 min (84 sec). Under these practical conditions, numerical result with kinetic parameters from direct fitting of TGA data shows low conversion due to the size difference as well as residence time difference as mentioned earlier. In this study, the kinetic parameter is increased to match a realistic exit conversion. Results obtained with this condition are illustrated in Figure 5 and Figure 6. Conversion of carbonization looks increasing monotonically, while temperature profile looks stair-wise shape. This represents limiting step is chemical reaction and heat transfer is relatively faster than chemical reaction.

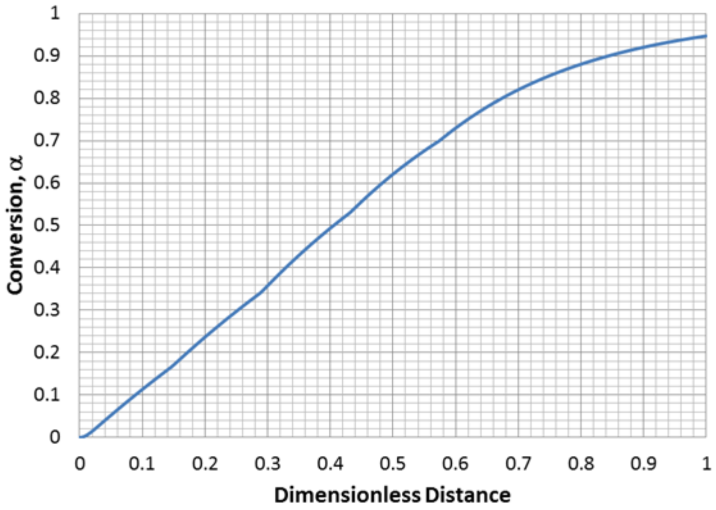

Figure 5. Fiber conversion over the fiber travel direction for baseline case

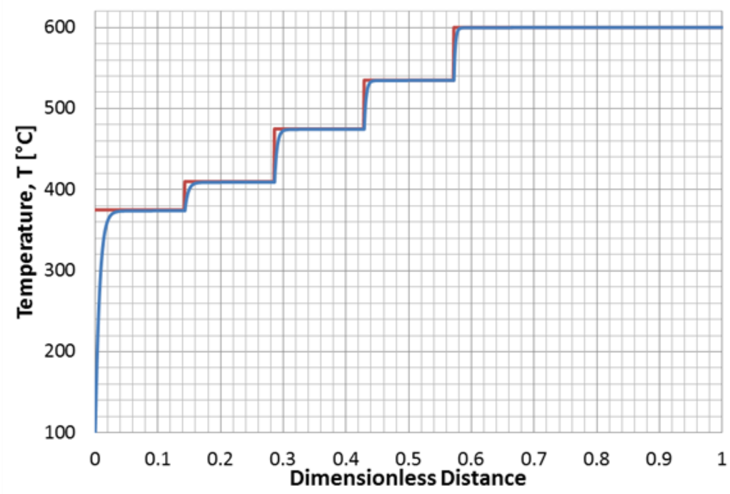

Figure 6. Fiber temperature (blue) and furnace temperature (red) along with length of the furnace

3.2 Parametric Study

3.2.1 Effect of kinetic coefficient

Kinetic parameter (pre-exponent factor) was varied to see how conversion and temperature are sensitive to kinetic parameter. Each conversion profiles are depicted in Figure 7 for 60%, 80%, 100% (baseline) and 120% of pre-exponent factor. Before reaching 600°C isothermal section (around 60% of full length, zone 5 ~ 7), difference in conversion of fibers for various kinetic parameters are getting larger. After this point difference in conversions are diminished. In these condition, final exit conversions are ranging from 82.93% (slowest kinetic) and 97.08% (fastest kinetic). Unlike conversion, temperature profiles are almost identical regardless kinetic parameters.

3.2.2 Effect of linear process speed

Next parametric study is linear process speed (or residence time). Linear process speed is also varied to see how conversion and temperature are sensitive to it for identical range with kinetic parameter. Each conversion profiles are depicted in Figure 8 for 60%, 80%, 100% (baseline) and 120% of line speed. Intuitively slower line speed case shows the highest conversion but its final exit conversion value was not that high due to asymptotic approaching full conversion. In this range of line speed, the window for final exit conversion is 91.37% ~ 99.28%. From the exit conversion comparison, effect of line speed is smaller than that of kinetic parameter. Temperature profiles are almost identical regardless of condition.

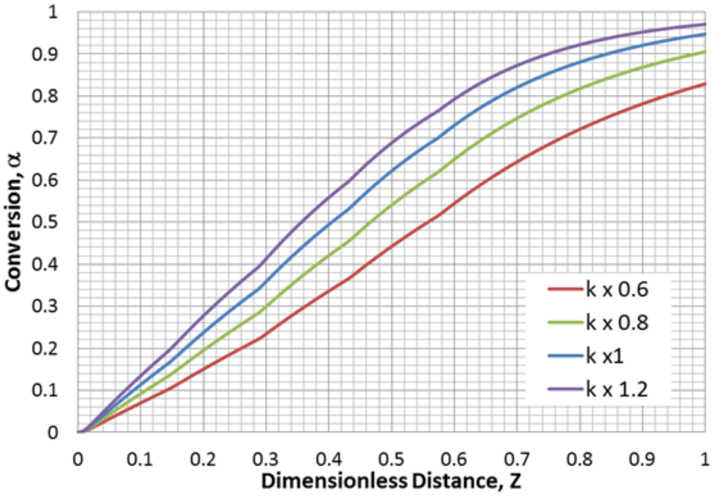

Figure 7. Fiber conversion profiles for various kinetic parameters

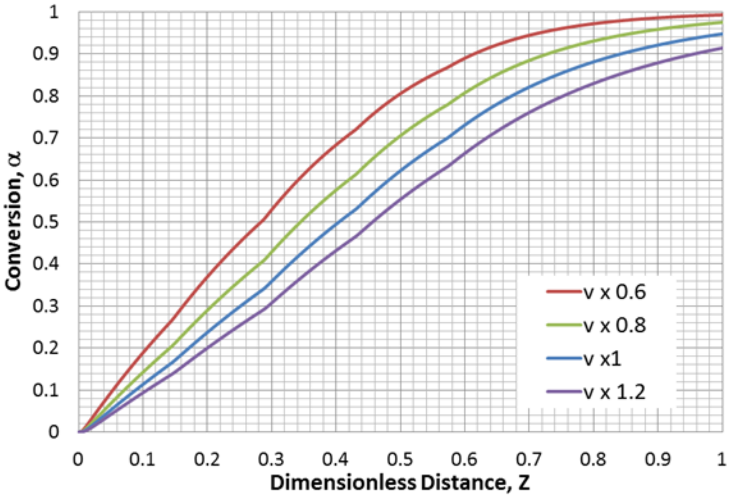

Figure 8. Fiber conversion profiles for various linear process speeds

3.2.3 Effect of temperature profile

Next parametric study is heating temperature profiles. Fiber temperature profiles are illustrated in Figure 9 for 3 different cases. Zone 1 and 7 were kept unchanged and each zone temperature is raised in incremental way: 20°C (Zone 2), 40°C (Zone 3), 60°C (Zone 4), 80°C (Zone 5) and 100°C (Zone 6). Fiber reaches thermal equilibrium quickly so its temperature reaches the heating chamber temperature. Under these conditions, fiber conversions have the least deviation among previous parametric studies. Fiber conversions are shown in Figure 10 and its final exit conversion window is 94.74% ~ 98.59%.

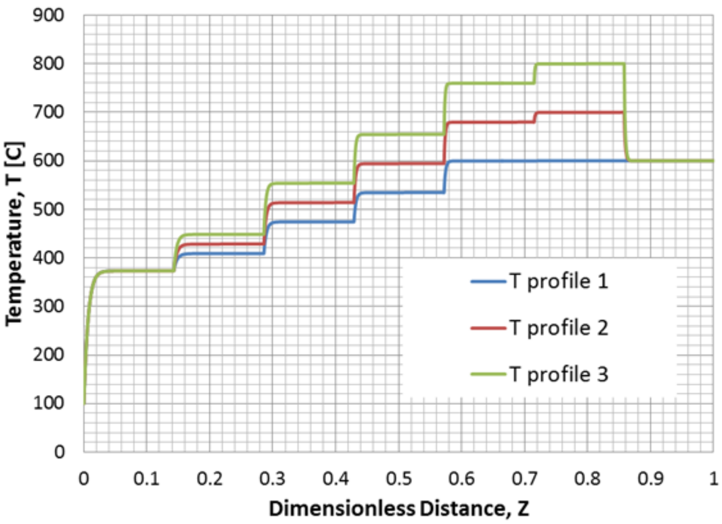

Figure 9. Fiber temperature profiles for different heating temperature profiles

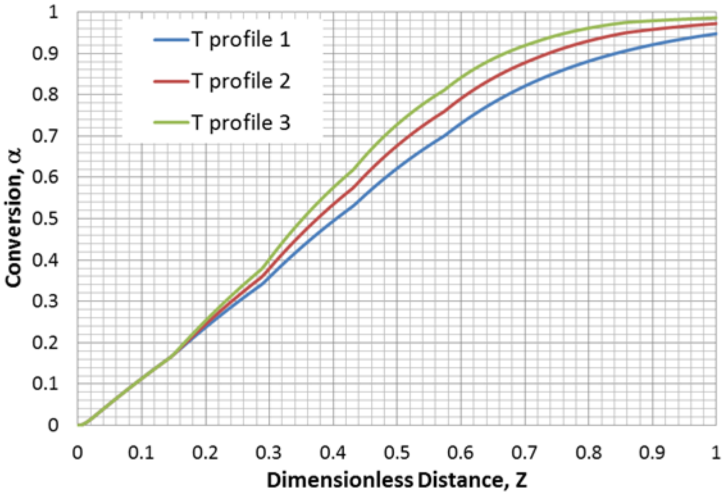

Figure 10. Fiber conversion profiles for different heating temperature profiles

4. CONCLUSIONS

We have developed continuous model for carbonization process for stabilized PAN including mass loss rate as a lumped kinetics using pseudo-pure off-gas and two-zone model for fiber. In this two-zone model for fiber, it was assumed that carbonization occurs from the outer region and penetrates into the center. This change in radial direction inside the fiber is not considered in this model since the main focus of this work is fiber conversion and temperature changes over the fiber moving direction. However, mathematical expressions for mass fraction of carbonized fiber and linear density of fiber are obtained as a function of conversion and overall stoichiometric as derived results. Kinetic fitting was made for literature TGA data for carbonization of stabilized PAN fiber using kinetic expressions from degradation of polymer. Many different expressions were applied but conventional 1st order kinetic also gives good agreement with experimental data and picked for model.

From the baseline result with realistic operating conditions, it is revealed that carbonization reaction is the limiting step, whereas heat transfer is very fast step comparing with carbonization. The results from the parametric study cases were in narrow range since the result of the baseline case was in the asymptotic region so it is not that sensitive. Within our parametric study conditions, the sensitivity toward conversion is in the order of kinetic parameter, line speed and temperature. It is required to have more literature data to improve reliability of the kinetic parameters and expression because our parametric study shows it is the most sensitive parameter. This kind on analysis even with simplification would stimulate and encourage of development of kinetic expression with more data and improve design and performance of industrial furnace. Further works for in-depth analysis is required to look at interaction with fiber and gaseous phase, radial changes inside the fiber tow and variation along the width of the furnace which would affect the system uniformity.

5. REFERENCES

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