

White Paper: Computational Fluid Dynamics (CFD) analysis for Off-gas mixing and ventilation inside carbonization furnace during PAN-based carbon fiber manufacturing

By Tae-Seok Lee, Peter Witting, Harper International

Abstract

Ventilation of released gas from stabilized precursor during its carbonization is of importance for high quality carbon fiber manufacturing. Careful consideration of the released gas from stabilized precursor during its carbonization is of importance for design of the carbonization system. The impact of the carbonization reaction on the process energy required, off-gas composition, atmosphere properties are important to the continued scale-up of higher production rate carbon fiber systems. The carbonization of stabilized precursor typically takes place with nitrogen cover gas to protect the carbon fiber from oxidation. Defining the off-gas in carbonization performed in the furnace system is the first step in understanding the mixture of nitrogen and off-gas. The thermodynamic and transport properties of this gas mixture and heat effect of reaction are also defined in terms of the range of possible gas compositions at given thermodynamic variables. Computational fluid dynamics (CFD) analysis was performed on the nitrogen cover gas and process off-gas to determine off-gas concentration differences as well as flow uniformity within the process. For carbon fiber carbonization uniformity of the process is of utmost importance. For economic processing of carbon fiber, the properties of the fiber must be consistent across the width of the tow band. Maintaining consistent temperature and atmosphere conditions result in uniformity of processing carbon fiber. The detailed decomposition mechanism with consideration of temperature, time, and tension is not fully understood. For this CFD work a simplified model of the gas evolution was considered.

1. Introduction

Carbon fibers are defined as anisotropic carbon ranging from 92 to 100 wt%. Carbon fibers generally have excellent tensile property, low density, high thermal and chemical stability, good thermal and electrical conductivity, and excellent creep resistance [1]. These excellent properties make carbon fiber attractive for many industries, aerospace, military, construction, medical, sporting goods as well as automotive industry [2]. Although carbon fibers can be manufactured from variety precursors the most important precursor is polyacrylonitrile (PAN). Global carbon fiber consumption is increasing, while automotive industry has been impeded by high costs and lack of high-speed fabrication techniques [2]. Scale-up challenge for reducing the manufacturing cost and large-volume production requires in-depth understanding of carbon fiber manufacturing process.

The production of carbon fiber from polyacrylonitrile (PAN) is conducted in a carbonization line which includes three distinct process steps: ovens, LT, and HT. Each of these process steps has their unique set of challenges. For this work the focus is on the LT furnace where the bulk of the fiber mass loss occurs. Within the LT furnace typical temperature ranges are between 400 and 800°C with mass loss of 30 to 40%. The LT furnace has a single tow band with typical residence time between 60 and 90 seconds. Achieving consistent fiber quality across the width of the system is of utmost importance. With increasing capacity requirements, the system widths have been steadily increasing. A few years ago a typical width for LT 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. Maintaining consistent temperature and process gas conditions to the fiber result in consistent fiber properties. This work is conducted in two parts: (1) definition of the properties of the off-gas; (2) CFD analysis of a unit cell along the length of an LT furnace system focusing on temperature and gas composition. It is planned to continue this work for full, across the width models for uniformity considerations.

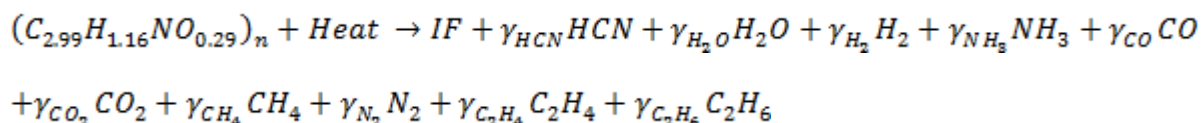
2. CFD simulation setup

2.1 Off-gas Constituents and Concentration

Off-gas is released from stabilized PAN fiber (SPF) during carbonization inside the LT furnace. Several papers show off-gas constituents as a function of operating temperature [3-5]. The common chemical species are HCN, H₂O, H₂, NH₃,

CO, CO₂ and CH₄ in this step of the carbonization process. It is noticeable that the amount of each species is strongly dependent on parameters in stabilization process (e.g. temperature, heating rate, residence time and oxygen amount). There are many differences within the industry for the oxidation process, depending on the final properties of the fiber targeted. To form a basis, the Stabilized PAN is assumed as based on the analysis of Stabilized PAN fiber from Griffing and Overcash [6].

In this simulation, the off-gas (also known as evolved gas and volatiles) are assigned as composing from 10 chemical species: 7 common components and N₂, C₂H₄, and C₂H₆. Therefore, overall chemical reaction for carbonization of stabilized PAN (C_{2.99}H_{1.16}NO_{0.29})_n can be written as follow,



where *IF* denotes intermediate fiber for the LT furnace, and γ_i denotes the stoichiometric coefficient for *i*th chemical species. Unfortunately, the composition of intermediate fibers at the exit of the LT is unknown. Chemical composition of the intermediate fiber is a complex function of LT furnace operating conditions (temperature, residence time and etc) and stabilized precursor as well. The bulk of the mass loss is within the LT furnace system. For the purposes of off-gas compositional analysis a simplifying assumption was made that the mass loss within the HT furnace is much smaller than in the LT furnace. Assuming the entire mass loss is within the LT furnace the intermediate fiber is assumed to have an identical composition to the final product (containing 95wt% carbon and 5wt% nitrogen). This assumption is applied in the current study.

With the input fiber and output fiber defined the stoichiometric coefficients, γ_i , for all species needs definition for off-gas composition estimates. There are 11 stoichiometric coefficients, product fiber and 10 off-gas species and 5 equations are available: total mass balance and 4 atomic (C, H, O, N) balances. 6 more independent mathematical relationships are required for mathematical unique solution of 11 stoichiometric coefficients. As mentioned previous, off-gas compositions are function of operating conditions mainly temperature of local fiber, residence time and fiber composition. Therefore, temperature, residence time and local fiber composition effects should be considered in additional to the 6 independent mathematical equations. Usually, these relationships are defined chemical reaction kinetics equations. These chemical kinetic relationships for carbonization of stabilized PAN are not readily available through a literature search on the subject. Some reference tackled this difficult subject and the results were used to form the basis of the composition.

The literature of off-gas composition shows significant variation of potential composition. This is no surprise considering the composition is a function of the exact composition of the PAN, stabilization process, time, temperature, and even tension to some extent. With all these variables and different product types targeted, off-gas variations are bound to exist. For this analysis the released amount of off-gas constituents are taken from Griffing and Overcash [6] and are presented in Table 1. These values are generated by using the conditions from Chung [4] to drive their analytical model.

Table 1. Chemical composition of Stabilized PAN, product fiber and off-gas

	Species	Mw [g/mol]	100g STB PAN basis [g/100gPAN]	mol basis [mol/PAN]
input	C(2.99)H(1.16)O(0.29)N	55.71133	100	1
(solid) outlet	CF (95wt% C 5%N)	12.09689	56.766	2.614316
(gas) outlet	H ₂	2.01588	0.013	0.003593
	N ₂	28.0134	13.8	0.274446
	CO	28.0101	2.06	0.040973
	CH ₄	16.0425	2.36	0.081957
	CO ₂	44.0095	3.24	0.041015
	NH ₃	17.0305	1.317	0.043083
	H ₂ O	18.0153	5.29	0.16359
	HCN	27.0253	14.3	0.294788
	C ₂ H ₄	28.0532	0.412	0.008182
	C ₂ H ₆	30.069	0.442	0.008189

2.2 Physical Properties of Off-Gas

The physical properties of the off-gas including specific heat, diffusivity, viscosity, and thermal conductivity, are importance parameters in the modeling of the system.

Pure gaseous substances are divided into two categories, namely ideal gas and real gas. With ideal gas, many physical properties for pure substances are function of temperature only. In general, ideal gas is typical when it is not close to a saturated condition (which is under equilibrium condition with its liquid phase) and/or is a low density gas. So gases at high temperature and low pressure condition typically satisfy these conditions. Two different criteria are used for determining ideal gas state using Reduced Pressure $P_r = P/P_c$ and Reduced Temperature $T_r = T/T_c$ as follow,

$$P_r \ll 1$$

$$P_r < 1 \text{ and } T_r \geq 2$$

Critical data (temperature and pressure) and its reduced temperature and pressure (@ 1bar and 300°C) are evaluated for all off-gas constituents. From these calculations, it is reasonable assumption that the off-gas is in ideal gas state inside LT furnace. The NASA gas property data [7-8] was used for specific heat, thermal conductivity, and viscosity for this work.

2.2.1 Mixing Law (Mixture properties)

There are several mixing laws available for mixture property from its constituents: Wilke's method, Brokaw's method and kinetic theory of gases. Also, more simple methods exist such as mole fraction weighted average, and mass fraction weighted average. In this calculation, the mole fraction weighted average method was applied to calculate the physical properties for a mixture from its constituents. Therefore, the physical properties are a function of mole fraction and temperature. However, the current solver (Autodesk CFD package) allows only one independent parameter per variable gas physical property [9], so each effect (variations due to temperature or mixing) was evaluated in full span for its contribution toward property change. The physical properties percent changes with temperature for several fixed mol fractions as well as the changes associated with mixing with at fixed temperatures (400, 600, and 800C) are presented in Table 1. For viscosity and thermal conductivity, the temperature contribution is larger than the mixing effect. So temperature was picked as the independent variable for the CFD code. The mixing had the greatest impact on the specific heat, so mixing was used as the independent variable for this case.

Table 2. Gas Property Dependency due to temperature and mixing

		Temperature Effect	Mixing Effect	Dominant independent variable
Full span		400 ~ 800 °C	0 ~ 1 [mole fraction of off-gas]	
difference	Viscosity	37.28% (@ $x_{\text{off-gas}} = 0.8$) 34.56% (@ $x_{\text{off-gas}} = 0.5$) 32.13% (@ $x_{\text{off-gas}} = 0.2$)	23.64% (@ T=400°C) 18.62% (@ T=600°C) 14.82% (@ T=800°C)	Temperature
	Thermal Cond.	51.44% (@ $x_{\text{off-gas}} = 0.8$) 46.11% (@ $x_{\text{off-gas}} = 0.5$) 39.30% (@ $x_{\text{off-gas}} = 0.2$)	14.13% (@ T=400°C) 25.33% (@ T=600°C) 33.84% (@ T=800°C)	Temperature
	Specific heat	13.42% (@ $x_{\text{off-gas}} = 0.8$) 11.69% (@ $x_{\text{off-gas}} = 0.5$) 9.59% (@ $x_{\text{off-gas}} = 0.2$)	29.01% (@ T=400°C) 32.69% (@ T=600°C) 35.40% (@ T=800°C)	Mixing

2.2.2 Density of gas

Since it satisfies ideal gas assumption from its reduces temperature and pressure, density of gas is evaluated from ideal gas law,

$$\rho = \frac{pM_{mix}}{RT}$$

where M_{mix} denotes averaged molecular weight for mixture and it is function of mole fraction of its constituents.

2.2.3 Diffusion coefficient

In Autodesk CFD solver, diffusion and/or mixing of fluids are limited into binary mixing [9]. Therefore, it model consists of binary mixing between purge-gas (nitrogen) and pseudo-pure gas (off-gas composing 10 chemical species). There might be several approximation techniques available for evaluating binary diffusion coefficients involving pseudo-pure chemical species but here the mixture averaged method for all 10 chemical species was applied. Therefore, instead of A-B binary diffusion coefficient with imaginary B species, it is evaluated that diffusion coefficient for A diffusing into mixture of 10 chemical species including A-species itself. This process requires evaluating 9 binary diffusion coefficients among 10 chemical species and application of the mixing rule. For 9 binary diffusion coefficients, the kinetic theory of gases is applied and Wilke's method is applied for mixing rule.

$$D_{AB} = 0.0018583 \frac{\sqrt{T^3 M_{AB}}}{p \sigma_{AB}^2 \Omega_{D,AB}}$$

where D_{AB} is binary diffusion coefficients between A and B chemical species, T is absolute temperature, p is pressure, M_{AB} and σ_{AB} are defined as follow

$$M_{AB} = \frac{M_A M_B}{M_A + M_B}$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

And $\Omega_{D,AB}$ is collisional integral as a function of dimensionless temperature, $\frac{\kappa T}{\sqrt{\epsilon_A \epsilon_B}}$, where k is Boltzmann constant, e and s are Lennard-Jones potential parameters. Two different forms of collisional integral are available, but in this calculation the following formula is applied [10].

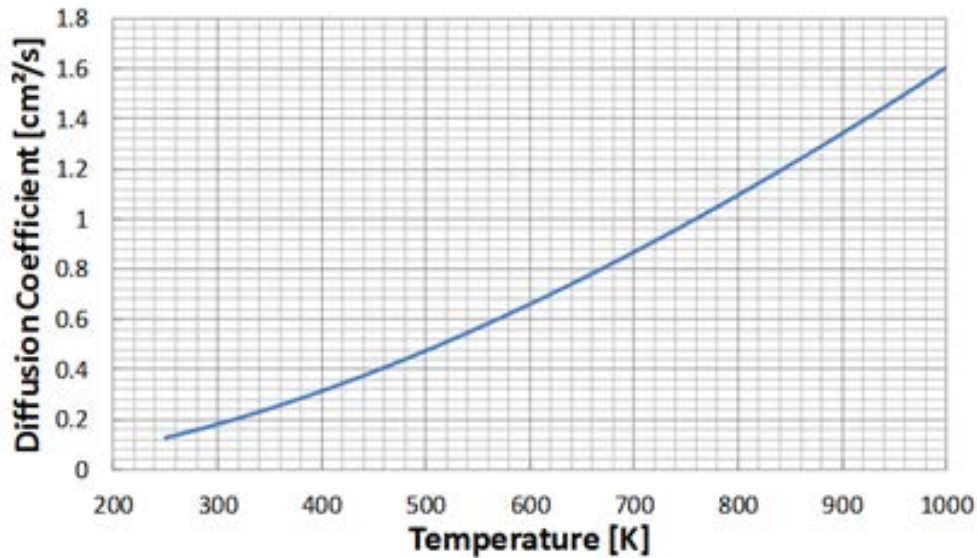
$$\Omega_{D,AB} = (44.54T^{0-4.909} + 1.9117T^{0-1.575})^{0.10}$$

After evaluating 9 binary diffusion coefficients involving nitrogen, the nitrogen diffusion coefficient through the mixture is evaluated using Wilke's method shown below,

$$D_{N_2,og} = \frac{1 - x_{N_2}}{\left(\sum_{j,j \neq i} \frac{x_j}{D_{N_2,j}} \right)}$$

Where $D_{N_2,og}$ denotes binary diffusion coefficient for nitrogen and pseudo-pure-off gas binary mixture, x_i denotes mol fraction of i-th species, and $D_{N_2,j}$ is binary diffusion coefficient for nitrogen and j-th species. Figure 1 presents the diffusion coefficient with temperature for the mixture of the nitrogen and off-gas. Unfortunately, the current AutoDesk CFD solver only allows a single number for binary diffusion coefficient [9]. So the averaged-mixture diffusion coefficient ($\sim 1.28 \text{ cm}^2/\text{sec}$) was selected for this fixed at arithmetic average temperature (600°C) of LT furnace operating range ($400 \sim 800^\circ\text{C}$).

Figure 1. Binary diffusion coefficient between nitrogen and pseudo-pure off gas as a function of temperature



2.2.4 Heat of Reaction

Heat of reaction (a.k.a. standard enthalpy of reaction) is defined as enthalpy change occurring chemical reaction under standard condition based on one mole of limiting reactant. It is calculated using standard enthalpy formation and stoichiometric coefficients for all involved chemical species. However, it is very challenging to evaluate heat of reaction for carbonization since enthalpies of formation for the intermediate fiber (product from LT furnace) and stabilized PAN fiber (reactant for LT furnace) are unknown. Intermediate fiber exiting from LT furnace could be assumed as carbon fiber like previously by assuming mass loss is negligible inside the HT furnace. A further approximation is required to evaluate standard enthalpy of formation for intermediate fiber product because it is also unknown. By assuming carbon fiber consists of only carbon atom in spite of 5 wt% of nitrogen, the enthalpy can be calculated. From these two assumptions, standard enthalpy of formation for intermediate fiber product from LT furnace is approximated as identical to that of solid carbon, graphite.

For stabilized PAN fiber, it is more complicated. It requires successive evaluations from a well-defined state. The standard enthalpy of formation for acrylonitrile is known for both liquid and gaseous states [11]. So estimation of standard enthalpy of formation for stabilized PAN fiber should be started from acrylonitrile. Liquid acrylonitrile undergoes polymerization forming solid PAN (polyacrylonitrile) and the heat effect of this polymerization reaction is reported by Roberts as -17.3 kcal/(mol of monomer) @ 76.8°C [12]. Technically, it is not standard heat of formation since it was not measured at standard temperature, but here the assumption is made of negligible change in heat of polymerization. Therefore, the standard enthalpy of formation for solid PAN fiber is 72.38 kJ/mol lower than liquid acrylonitrile since it is exothermic reaction. Heat of formation for liquid acrylonitrile is 140 kJ/mol [11], therefore heat of formation for solid PAN fiber could be evaluated as 67.62 kJ/mol (of monomer). Precursor PAN is stabilized when passing through oxidation ovens. This process consists of several reactions: Cyclization, Dehydrogenation and Oxidation [13]. Those reactions inside the oven are known to be exothermic reactions so thermal management inside the oven is very critical. There might be several different approaches to evaluate thermal effect on stabilization. In this study, we took the value reported by Dunham and Edie.

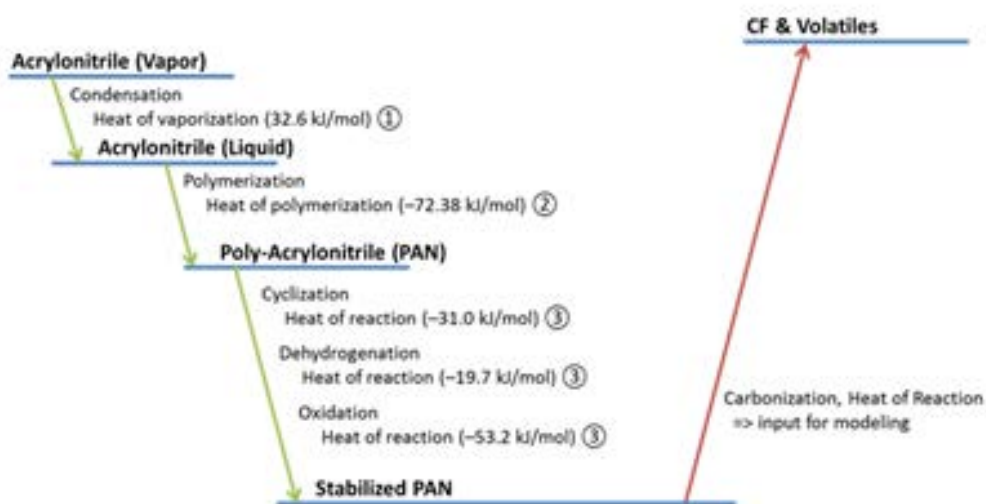
Dunham and Edie [14] focused on well-defined reactions occurring in series and parallel and heat effects of each reaction. From Dunham and Edie [14], heat effect of PAN stabilization could be expressed as follow

$$\Delta H_{StbPAN} = \Delta H_{cyc} + \Delta H_{dehydro} + \epsilon_{oxi} \Delta H_{oxi}$$

where ΔH_{StbPAN} is standard heat of reaction for stabilization reaction, ΔH_{cyc} , $\Delta H_{dehydro}$, ΔH_{oxi} are heat of reactions for cyclization, dehydrogenation and oxidation, respectively. And ϵ_{oxi} is extent of oxidation reaction. From the

structure reported by Gupta [15], extent of oxidation can be obtained as 0.45~0.5 and taking 0.5 extent of oxidation total heat effect based on Dunham and Edie's method could be obtained as -77.3 kJ/mol (of monomer). The standard heat of formation of stabilized PAN is 77.3 kJ lower than that of PAN per mole of monomer. This process is illustrated in Figure 2. To evaluate, standard heat of reaction, one needs standard heat of formations for products exiting from LT furnace. The off-gas products of LT furnace are well-defined. All standard heat of formations for 10 gaseous chemical species is taken from NASA database [8]. In this study, intermediate fiber is assumed as 95wt% carbon and 5wt% nitrogen but standard heat of formation is taken for pure solid carbon (graphite).

Figure 2. Estimation of heat of carbonization reaction of stabilized PAN fiber



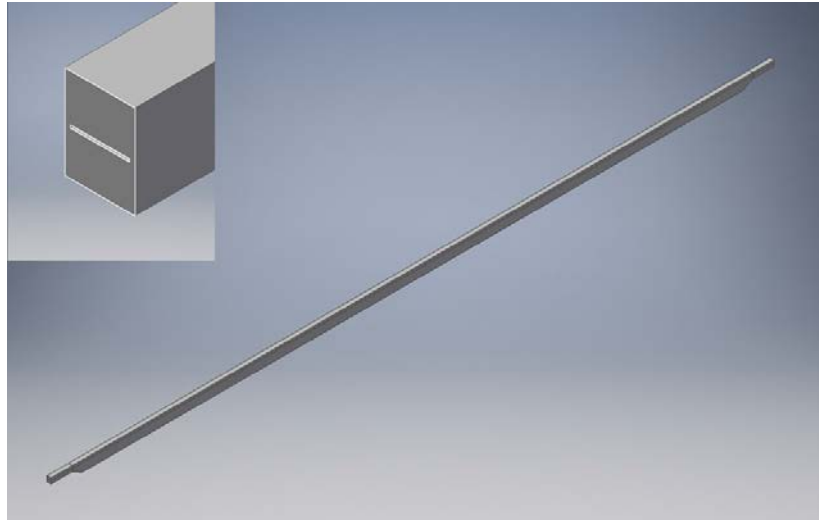
Heat effect of actual chemical reaction is deviated from the standard heat of reaction discussed previously. Standard enthalpy of reaction is usually measured (or calculated) based on standard state, though actual reaction does not occur at that temperature. Sensible heat effects for both reactants and products should be taken into account for actual heat effect of the chemical reaction. Actual heat effect consists of 3 independent heat effects: sensible heat effect for reactant, heat of reaction, and sensible heat effect for product (and unreacted reactant). Heat capacities for products species to evaluate sensible heat effect for product are taken from NASA database [8]. The main difficulty is specific heat for stabilized PAN fiber. Zoltek's whitepaper [16] has some thermal properties of their products (oxidized polyacrylonitrile fiber). Heat capacity for Panex® 35 is provided in whitepaper from Zolteck. Actually it (Panex® 35) is more like carbon fiber rather than oxidized PAN. Zoltek's whitepaper has specific heat @ 2 different temperatures (23 and 550 °C) and linearized specific heat is applied to heat capacity for stabilized PAN. Those properties are very limited in publications. Calculated standard heat of reaction is 124 kJ/kg of StbPAN @ 25°C and heat effect converting stabilized PAN from 240°C into 500°C products would require 867.9 kJ/kg of StbPAN.

3. Results

3.1 Computational Domain

For the modeling work presented here the temperature and gas compositional analysis focused on the differences along the length of the furnace. The variations along the width are planned for future work. A typical carbonization furnace (540 inch long) is modeled for this study. To reduce computational demand, unit-cell approach is applied to computational domain rather than 2D. The unit-cell is 3 inch wide and carbonization furnace with a 2.52 inch wide tow band. The tow band is model as impervious to flow, leaving the gap between the tow bands for the connection of the upper and lower fluid volumes. This approach is different than a 2D assumption. With the 2D approach, the fiber separates furnace internal upper and lower fluid volumes resulting in no flow or mass transfer between upper and lower section. Computational domain, unit-cell of carbonization furnace, is illustrated in Figure 3.

Figure 3. Computational domain, unit-cell of carbonization furnace



3.2 CFD Setup

The temperature profile of the simulation is a constant boundary condition of 600°C. Typical operation of LT furnaces have a ramped profile starting at ~400° and ending in the 700 to 800°C range.

A new material is created for representing the mixing of two flows (nitrogen and pseudo-pure off-gas). The mean molecular weights are similar for each (nitrogen: 28.0134 g/mol and typical off-gas: 25.0947 g/mol, 12% deviation), so variable density is set as a function of temperature rather than mixing. Therefore, the mean molecular weight is assigned regardless of mixing extent. For this model a value of 0.646 kg of nitrogen purge gas was introduced per 1 kg of carbon fiber. This results in an average molecular weight for 43.18 mol% nitrogen and 56.82% of off-gas of 26.3549 g/mol with a gas constant (mass basis) is 315.4636 m²/(s²K).

There are two purge gas (nitrogen) inlets: front and back. In practice these flows may be different, but for this analysis they are assigned identical flow rates. Baseline nitrogen flow rate is assigned as a boundary condition of 0.5093 g/sec per inlet. The inlet temperature of the process nitrogen purge gas is set 300°C for both the front and back end of the system. The scalar variable (representing mass fraction of off-gas) is set as zero for purge gas inlets. Scaler value of 0 is pure nitrogen, and scaler value of 1 is pure off-gas.

Off-gas release rate is one of the important boundary conditions. As discussed above, the volatiles release rate is a function of many physical quantities and related with chemical kinetics of carbonization reaction. For this analysis two simple cases are considered for simplicity: 1. Uniform release and 2. Tapered release. Volatiles (off-gas) release rate is determined using the ratio of off-gas to feed-rate (or ratio of off-gas to production rate) reported by Griffing and Overcash (off-gas to Stabilized PAN input ratio: 43.234/100) and feed rate for unit-cell (10kg_{SibPAN}/hr). Total off-gas release rate is 1.2 g/sec per unit-cell in consistency with previous condition (Stabilized PAN input rate). And it is assumed only 2 sides (top and bottom) release off-gas, so each side releases 0.6g/sec for uniform release case.

3.3 CFD Results – Uniform Off-gas Release

As mentioned in previous section, uniform off-gas release case was modeled. In this case the off-gas release rate and the endothermic reaction (heat absorbed) was applied as a boundary condition uniformly throughout the length of the furnace heating section. The magnitude of velocity vector at the center plane is illustrated in Figure 4. The lower part of figure is a close up for entrance region. The no-slip boundary condition makes the fiber and gas velocity identical. The velocity of the process gas is much faster than the fiber velocity so for this analysis the fiber velocity was set to zero. The furnace wall is also stationary so the gas velocity at this boundary is zero as well. In real operational condition the fiber would have linear velocity direction from fiber entrance to fiber exit. This fiber linear velocity would be for all practical purposes constant through the furnace.

The fiber may shrink or stretch due to tension, but it is a very small percent compared to the linear velocity of the fiber. The gas velocity appears to accelerate along its direction of progress. This is due to the addition of releases off-gas from the fiber. So total mass flow rate of the gas is increasing along with flow direction until the gas exit (i.e. vent pipe located at the bottom of halfway downstream). This addition of mass can be observed by the change in the scalar variable representing fraction of off-gas in Figure 5. The general scalar transport equation was used to capture volume fraction of off-gas. As you can see in the figure, the top is more quickly saturated with off-gas than the lower part. There are two reasons for this: 1. Vent pipe is located in bottom and 2. Bottom part has an expanded volume, so the purge gas from the fiber inlet tends to flow into the bottom part – resulting in increased gas mass rate in the bottom section. The gas temperature contour is shown in Figure 6. This temperature profile looks very symmetric in this uniform off-gas release case. The symmetric temperature profile is not unexpected due to the constant 600°C boundary condition and symmetric off-gassing. For typical operations of LT where the temperature has a ramped profile, the gas temperature would be non-symmetric.

Figure 4. Contour of velocity magnitude for uniform off-gas release.

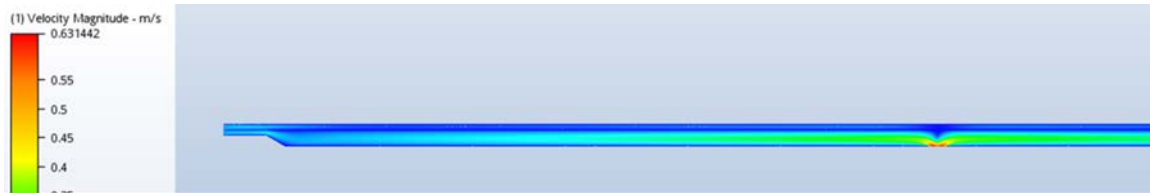


Figure 5. Contour of scalar variable for uniform off-gas release

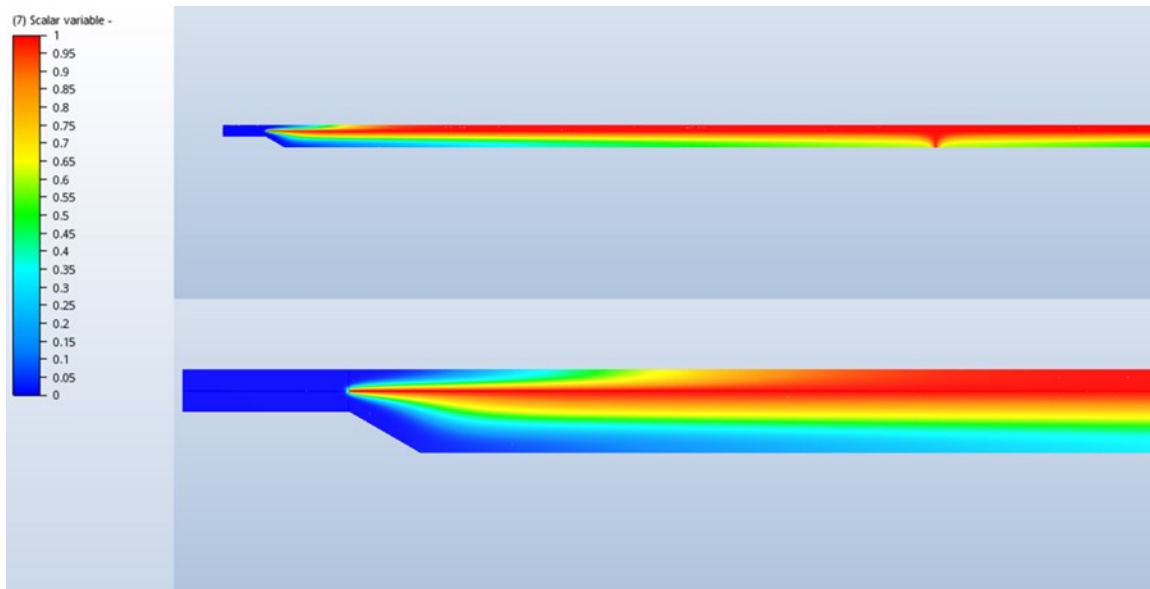
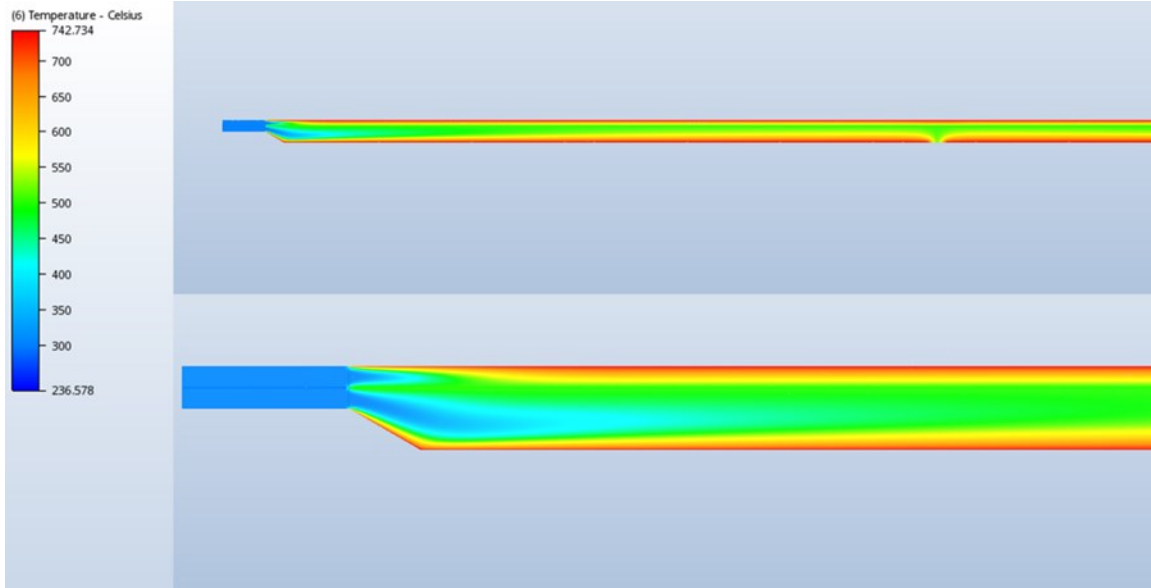


Figure 6. Contour of temperature for uniform off-gas release.



3.4 CFD Results – Tapered Off-gas Release

A tapered off-gas release case was run for comparison. In this case the off-gas release is assigned linear function having maximum at the entrance and tapering to zero off-gassing halfway downstream where gas vent is located. So, carbonization off-gassing is assumed to happen within the first half of the carbonization furnace. It is often the case that most of the off-gas occurs in the first half of the furnace, while a lesser amount within the second half. So the off-gassing of a typical process is something between the uniform release and this tapered case. The magnitude of velocity and scalar variable (Figure 6 and Figure 7 respectively) is much higher in the first half of the model. The gas velocity is increased due to the addition of mass in the first half of the system. All process gasses exit the furnace at the vent located in middle. The second half of the system is filled with only nitrogen purge gas. Notice that the scalar variable in Figure 7 is zero after the vent location verifying only nitrogen gas. Some off-gas is found in the second half near vent pipe due to molecular diffusion. But all the off-gas is exiting from the vent. The tapered off-gas release has impacts the temperature distribution (shown in Figure 8) along the length of the furnace.

Figure 7. Contour of velocity magnitude for asymmetric off-gas release.

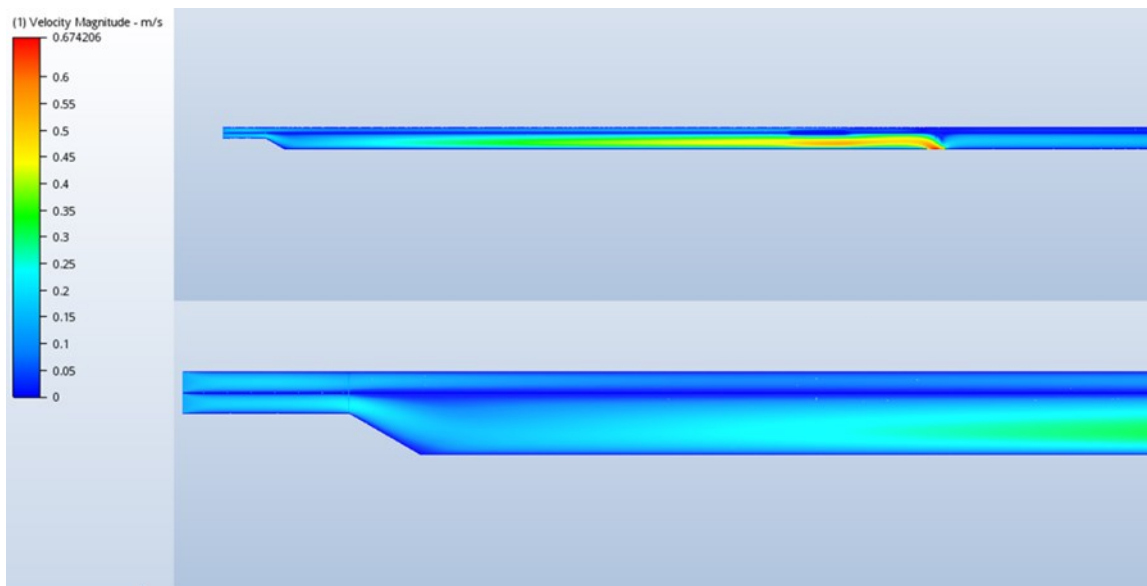


Figure 8. Contour of scalar variable for asymmetric off-gas release.

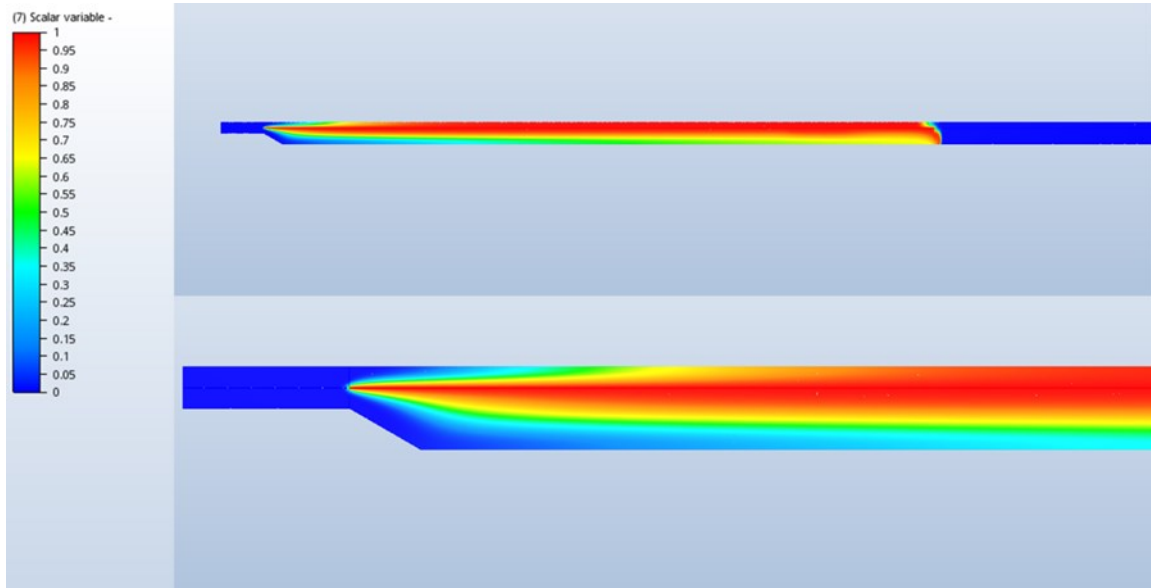
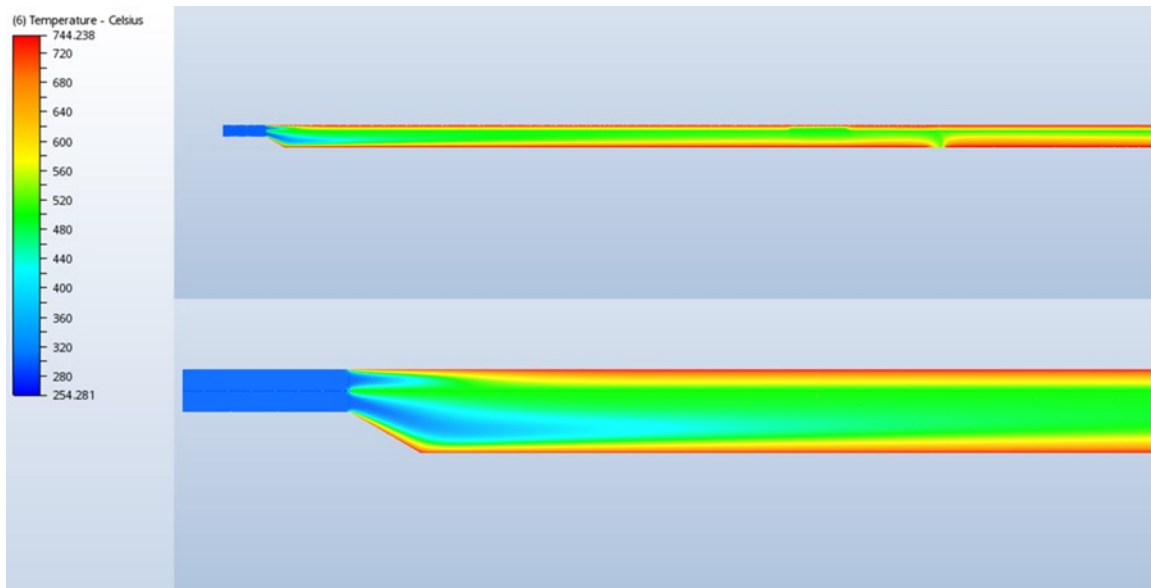


Figure 9. Contour of temperature for asymmetric off-gas release.



4. Conclusions

Results of the CFD simulation are shown for the carbonization furnace for PAN-based carbon fiber manufacturing process. Velocity, temperature and volatiles volume fraction are shown as contours. CFD simulation is focused on the gas phase inside the carbonization furnace. To support this work many scientific efforts were carefully considered to determine the physical properties of off-gas at carbonization process of stabilized PAN. Fiber is excluded from the simulation for simplicity. However, many assumptions were made due to the exclusion of fiber, the off-gas release rate and the local fiber temperature etc. This simplified off-gas release rate showed a composition variation from the top to bottom of the system. The off-gas volume fraction increased to a maximum at the vent as expected. The off-gas release also affected the gas temperature as shown differences in temperatures in the tapered and uniform cases. In this simulation, the coupling from the off gas to the temperature and flow is a one-way coupling with no feedback. The off-gas release rate is given rather than evaluated

from the temperature and local mass fraction of fiber. Chemical kinetic of carbonization would provide this two-way coupling. In the literature, to the best knowledge of the author of this article, it is not available for general expression of chemical kinetic of carbonization of stabilized PAN. This kind of CFD simulation even with simplified condition would stimulate and encourage of development of kinetic expression and improve design and performance of industrial furnace. Further work is required to look at variation along the width of the furnace which would affect the system uniformity. To continue to this variation along the width a tow band width model would be required.

5. References

1. Huang, X. "Fabrication and Properties of Carbon Fibers" *Materials* **2** (2009): 2369-403.
2. Frank, E., Hermanutz, F. and Buchmeiser, M. R. "Carbon Fibers: Precursors, Manufacturing, and Properties" *Macromolecular Materials and Engineering* **297** (2015): 493-501.
3. Morgan, P. *Carbon Fibers and Their Composites*. Boca Ration, FL: CRC Press, 2005.
4. Chung, D. D. L. *Carbon Fiber Composites*. Boston, MA: Butterworth-Heinemann, 1994.
5. Rahaman, M. S. A., Ismail, A. F. and Mustafa, A. "A review of heat treatment on polyacrylonitril fiber" *Polymer Degradation and Stability* **92** (2007): 1421-32.
6. Griffing, E. and Overcash, M. Carbon fiber from PAN. 2010.
7. Roger, A. S. Transport Coefficients for the NASA Lewis Chemical Equilibrium Program NASA Technical Memorandum 4647. 1995.
8. Zehe, M. J., Gordon, S. and McBride, B. J. CAP: A Computer Code for Generating Tabular Thermodynamic Functions from NASA Lewis Coefficients. 2002.
9. Autodesk CFD online user manual, <http://help.autodesk.com/view/SCDSE/2016/ENU/>
10. Green, D. W. and Perry, R. H. *Perry's Chemical Engineers' Handbook*. McGraw-Hill, 2008.
11. NIST chemistry WebBook, <http://webbook.nist.gov/chemistry/>
12. Roberts, D. E. "Heats of Polymerization. A Summary of Published Values and Their Relation to Structure" *Journal of Research of the National Bureau of Standards* **44** (1950): 221-32.
13. Fitzer, E., Frohs, W. and Heine, M. "Optimization of Stabilization and Carbonization Treatment of PAN Fibres and Structural Characterization of the Resulting Carbon Fibres" *Carbon* **24** (1985): 287-95.
14. Dunham, M. G. and Edie, D. D. "Model of Stabilization for PAN-based Carbon Fiber Precursor Bundles" *Carbon* **30** (1992): 435-50.
15. Gupta, A. K., Paliwal, D. K. and Bajaj, P. "Effect of an acidic Comonomer on Thermooxidative Stabilization of Polyacrylonitrile" *Journal of Applied Polymer Science* **58** (1995): 1161-74.
16. Handermann, A. Oxidized Polyacrylonitrile Fiber Properties, Products and Applications. Zoltek Corporation, 2013.