Exploring Chemical and Thermal Non-equilibrium in Nitrogen Arcs

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Abstract Plasma torches operating with nitrogen are of special importance as they can operate with usual tungsten based refractory electrodes and offer radical rich non-oxidizing high temperature environment for plasma chemistry. Strong gradients in temperature as well as species densities and huge convective fluxes lead to varying degrees of chemical non-equilibrium in associated regions. An axi-symmetric two-temperature chemical non-equilibrium model of a nitrogen plasma torch has been developed to understand the effects of thermal and chemical non-equilibrium in arcs. A 2-D finite volume CFD code in association with a non-equilibrium property routine enabled extraction of steady state self-consistent distributions of various plasma quantities inside the torch under various thermal and chemical non-equilibrium conditions. Chemical non-equilibrium has been incorporated through computation of diffusive and convective fluxes in each finite volume cell in every iteration and associating corresponding thermodynamic and transport properties through the scheme of 'chemical non-equilibrium parameter' introduced by Ghorui et.al. Recombination coefficient data from Nahar et. al. and radiation data from Krey and Morris have been used in the simulation. Results are presented for distributions of temperature, pressure, velocity, current density, electric potential, species densities and chemical non-equilibrium effects. Obtained results are compared with similar results under LTE.

Introduction

Industrial plasma torches operating with nitrogen have the advantages of operating with usual tungsten based refractory electrodes and radical rich non-oxidizing high temperature environment for plasma chemistry and processing. Strong gradients in temperature as well as species densities and huge convective fluxes are very common in such devices. While the regions away from the core are most affected by thermal non-equilibrium, convective and diffusive fluxes results in varying degrees of chemical non-equilibrium in the associated regions. Existence of steep gradients in plasma quantities, extremely high temperature at the core, high fluid dynamic flow fields, highly nonlinear variation of plasma properties and mutual interactions among thermal, chemical, electric, magnetic and fluid dynamic fields make the region difficult to be modelled numerically. The species densities computed under the assumption of chemical equilibrium deviate significantly from the actual densities due to presence of huge diffusive and convective fluxes. As a consequence, thermodynamic and transport properties of associated regions also get affected and final distribution of plasma quantities differ significantly from that under equilibrium. Several modeling works on nitrogen plasma under LTE considerations have been reported. Efforts have been made to model such phenomenon in oxygen cutting torches using two-temperature non-equilibrium model [1]. However, no effort has been made...
to explore the thermal and chemical non-equilibrium in dc nitrogen arcs to the best of the authors’
knowledge.
The paper considers an axi-symmetric two-temperature chemical non-equilibrium model of a
nitrogen plasma torch to understand the effects of thermal and chemical non-equilibrium. A 2-D finite
volume CFD code in association with a non-equilibrium property routine enables extraction of steady
state self-consistent distributions of various plasma quantities inside the torch for different thermal and
chemical non-equilibrium conditions.
Chemical non-equilibrium has been incorporated by computing diffusive and convective
fluxes in each finite volume cell in every iteration and associating corresponding thermodynamic and
transport properties through the scheme of ‘chemical non-equilibrium parameter’ [2]. Recombination
coefficient data from Nahar et. al. [3] and radiation data from Krey and Morris [4] have been used in
the simulation. Results are presented for distributions of temperature, pressure, velocity, current
density, electric potential, species densities and chemical non-equilibrium effects. Obtained results are
compared with similar results under LTE.

**Computational Model**

The plasma torch, computational domain and the finite volume grid considered in the present study are
shown in Fig.1. The cathode is made of copper with a hafnium insert and the anode is made of copper.
Both the electrodes are appropriately water-cooled to maintain the system integrity under intense heat
flux. Pure nitrogen is considered as the plasma gas. Under two-fluid model, the plasma is considered
to be composed of two interpenetrating fluids: one formed of the electrons and the other formed of all
other heavy particles including ions, atoms and molecules. Locally, the electrons are in thermal
equilibrium among themselves at a temperature $T_e$ while the rests are in similar equilibrium at
different temperature $T_h$. In general, $T_e$ and $T_h$ are not equal for most of the regions inside the plasma.

**Fig.1.** The plasma torch, the computational domain and the computational grid

**Fig.2.** Assumed distribution of current density over the Cathode surface

To extract electro-fluid dynamic and thermal behaviour, the plasma is considered to be continuum
with varying degree of electrical and thermal conductivity under the framework of two-fluid model.
Usual Navier-Stokes equation appropriately modified by additional source terms originating from electromagnetic interaction with conducting fluid describes the system with appreciable accuracy. Sets of equations and associated boundary conditions are similar to those used in Ref. [1]. The study does not include any turbulence. Plasma being a viscous medium, flow inside the torch is mostly laminar and inclusion of turbulence does not significantly change the scenario [1]. The set of differential equations representing conservation of mass, momentum and energy are solved under finite volume formulation with SIMPLE [5] like algorithm. Separate energy equations are considered for electrons and heavy particles. Ohmic heating and radiation are considered to be part of electron energy equation alone. Inter-fluid exchange of energy is implemented through the inclusion of appropriate exchange terms involving volumetric collision coefficient.

For the considered torch the simulation is carried out for a current of 200A distributed over the cathode surface with a current density profile as shown in Fig2. Gas injection port, located on the top of the torch near the edge of the annular channel, makes an angle such that the gas enters with no radial velocity but with an axial velocity of 20.60 m/s and an azimuthal velocity of 6.77 m/s. The torch operates in transferred arc mode so that no current transfer happens with the nozzle. While the cathode stays at negative potential, the nozzle and the plasma at the location of exit from the nozzle are assumed to be at ground potential.

3. Thermodynamic and Transport Properties of Nitrogen Plasma for CFD Modelling Under Chemical and Thermal Non-equilibrium

Chemically, the generated plasma is modeled with four simultaneous reactions:
(I) \( \text{N}_2 = \text{N} + \text{N} \), (II) \( \text{N}^+ = \text{N}^- + e \), (III) \( \text{N}^{++} = \text{N}^- + 2e \) and (IV) \( \text{N}^{+++} = \text{N}^- + 3e \)

The system involves six species: molecules (M), atoms (A), ions (I), double ions (D), triple ions (τ) and electrons (e). While, electron dynamics, electronic excitations and ionization of atoms and ions are governed by electron temperature \( T_e \), the heavy particle dynamics, molecular dissociation, rotational and vibrational level populations are governed by heavy particle temperature \( T_h \). Under two temperature formalism, number densities for a given \( T_e \) and \( T_h \) are determined by solving associated two temperature Saha equations [2,6] together with the equations for total pressure, charge and mass conservation. Once the number densities are computed, associated thermodynamic properties are determined from standard thermodynamic relations.

Transport properties are determined following the first order perturbation theory of Chapmann and Enskog. The properties appear as ratios of infinite determinants, elements of which are functions of collision integrals [6]. Required collision integrals for the present computation are taken from ref [7]. While the details of the computation of associated thermodynamic and transport properties are being published elsewhere, a comparison of the computed properties with those published in literature under thermal equilibrium is presented in Fig.3. The properties are computed for \( T_e \) ranging from 0K to 50,000K, \( T_e/T_h \) ranging from 1 to 20 and pressure ranging from 0.1 atm to 7 atm. It may be noted from Fig.3 that the computed properties matches quite well with those published in literature under thermal equilibrium.

4. Scheme for Handling Chemical Non-equilibrium

Regions inside the plasma torches are exposed to extremely high gradients in velocity, temperature and species densities. Depending on realized temperature, specific reactions take place at specific spatial zones and localized generation of newer species starts playing dominant role in determining the thermo-physical properties. The process in association with sharp gradients in temperature results in spatial spiking of species densities. Convection and diffusion start playing significant role in
determining the number densities in the nearby regions. The phenomenon, termed as chemical non-equilibrium, quantifies itself through the following equation [8] for the $k^{th}$ species:

$$\frac{\partial n_k}{\partial t} + \nabla .(n_k \vec{u}) + \nabla . \vec{g}_k = \dot{n}_k$$

(1)

$n_k \vec{u}$ is the convective flux and $\vec{g}_k$ is the diffusive flux for species $k$.

Fig.3. Comparison of computed properties of nitrogen plasma with those published in literature under thermal equilibrium ($T_e=T_h$): (a) electrical conductivity (b) thermal conductivity (c) specific heat (d) viscosity.

In a system containing $\nu$ different species, the expression for $\vec{g}_k$ in terms of overall pressure gradient $(\nabla p)$, individual species gradient $(\nabla x_j)$, species temperature gradient $(\nabla T_k)$ and external electric field $(E^X)$ can be written as:

$$g_k = \frac{n^2}{\rho} \sum_{j=1}^{\nu} m_j D_{xj} \left[ \nabla x_j + \left( x_j - \frac{\rho_j}{\rho} \right) \nabla \ln p \right] - \frac{n}{\rho} \sum_{j=1}^{\nu} \left( \frac{n_j Z_j e D_{xj}}{kT} \right) E^X - \frac{D_{kf}}{m_k} \nabla \ln T_k$$

(2)
Where, \( \rho \) is the total mass density, \( k_B \) is the Boltzmann constant, \( x_j \) and \( \rho_j \) are, respectively the mole fraction and the mass density of species \( j \), \( D_{ij}, D_{kj}, D_{jk}^{\text{aT}} \) are respectively the general diffusion coefficient, the general ambipolar diffusion coefficient and the thermal ambipolar diffusion coefficients for the \( k \)th species \([6]\).

Fig. 4. Effect of chemical non-equilibrium on transport properties under different thermal non-equilibrium. \( r=0.5 \) corresponds to \( r_1=r_2=r_3=r_4=0.5 \) and so on. (a)-(c): total thermal conductivity; (d)-(f): Electrical conductivity; (g)-(i): viscosity.
In terms of recombination coefficients and equilibrium rate constants, the right hand side of equation (1) can be expressed as following for the second reaction [8]:

\[ \dot{n}_f = \alpha_n n_a \left( S_2 - \frac{n_e n_I}{n_a} \right) \]  

(3)

where, \( \alpha_2 \) and \( S_2 \) are the recombination coefficient and equilibrium rate constant for reaction-2. \( n_e \), \( n_I \), and \( n_a \) are the actual steady state densities of electron, ion and atom including non-equilibrium. Combining equation (1) and (3) it is possible to write the revised rate equation as following for steady state under chemical non-equilibrium:

\[ \frac{n_e n_I}{n_a} = R_2 \]  

(4)

with \( R_2 = S_2 - \Delta S_2 \), and \( \Delta S_2 = \frac{1}{\alpha_n n_a} [\nabla (n_e \mu_e) + \nabla \cdot \vec{g}_f] \)  

(5)

In similar way, the revised rate constant \( R_i \) for any \( i^{th} \) reaction can be written down. The effect of chemical non-equilibrium can thus be incorporated in a thermal plasma system just by modifying the equilibrium rate constant in an appropriate manner. From simulation point of view, in every iteration the associated convective and diffusive fluxes in a control volume are computed by associated CFD routine and utilized by corresponding thermodynamic and transport property routine (TTP) to determine the actual number density of species through equations (4) and (5). Once the updated number densities are obtained associated thermodynamic and transport properties are recomputed by TTP routine and fed back to the CFD routine for recalculating the fluid dynamic fields based on the updated property values. The cycle goes on and on. The CFD and the TTP routine communicate sequentially with each other until a final self-consistent converged solution is obtained.

The degree of chemical non-equilibrium for the \( i^{th} \) reaction is quantified by chemical non-equilibrium parameter \( \left( r_i \right) \) as following [2]:

\[ r_i = \frac{S_i - \Delta S_i}{S_i} \]  

(6)

Figure 4 presents the effect of chemical non-equilibrium on various transport properties under different thermal non-equilibrium. For ease of presentations, the graphs are presented with identical \( r_i \) for all reactions. It is noted that the effect depends on temperature and may cause a deviation from equilibrium value by as high as 30%.

4. Results and Conclusions

Results of simulation under thermal and chemical non-equilibrium and the way it differs from the results under thermal equilibrium are presented in Fig.5. Inclusion of non-equilibrium results in lower potential drop, lower exit velocity but higher exit temperature compared to the LTE case. Under non-LTE the heavy particle temperature near the exit is lower compared to LTE temperature but the electron temperature is much higher than LTE temperature and heavy particle temperature. Exit velocity is more realistic when non-equilibrium is included. Distribution of chemical non-equilibrium parameter, electron, single ion and double ion densities are presented in Fig.6. Significant variation of chemical non-equilibrium parameter is observed near the core region [Fig.6a] where sharp gradients in particle densities occur and sudden increase in velocity takes place [Fig.6(b)-(d)].
Fig. 5 Temperature, velocity and potential distribution under LTE [(a), (b) and (c)], non-LTE [(d), (e) and (f)] and axial variation of them [(g), (h) and (i)]. [X and Y dimensions are in mm]
Fig. 6. Distribution of (a) chemical non-equilibrium parameter for single ions ($r_2$), (b) electron density, (c) ion density and (d) double ion density. [X and Y dimensions are in mm]

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