Effects of Radiation on a Chemically Reacting Flow with Hydrolysis

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Abstract — This study focuses on modeling of heat and fluid flow with a chemical reaction in the hydrolysis step of the Copper-Chlorine (Cu-Cl) cycle. The thermochemical Cu-Cl cycle has been established as a promising method of sustainable hydrogen production because of its low heat requirement relative to the other hydrogen production cycles. There have been several studies on the heat and mass transfer of hydrolysis reactors to better understand their relative roles and optimize the overall cycle efficiency. Few or no past studies have examined the effect of radiation during the process. This study presents a semi-analytical model to study the effects of thermal radiation on the laminar boundary layer with a similarity solution in the presence of a chemical reaction. A similarity transformation is used to convert the governing partial differential equations to ordinary differential equations. The numerical method of solution is based on the shooting method with a Runge-Kutta iteration scheme. A Rosseland approximation is utilized to study thermal radiation and numerical simulations are conducted for cases with and without radiation. Past studies indicate that the presence of thermal radiation thickens the boundary layer and broaden the temperature distribution. This concept is studied and extended to the hydrolysis step of thermochemical hydrogen production in this paper. The model is first validated by a previously established system of equations and then extended to report the effects of radiation on the temperature gradient and concentration gradient in the boundary layer during the hydrolysis process. Sensitivity analysis is performed to report the influence of radiation and chemical reaction parameter in detail. A better understanding of the effects of thermal radiation in the flow with chemical reaction will be useful to improve the design of the hydrolysis reactor in the thermochemical cycle of hydrogen production and improve the overall cycle efficiency.

Keywords - Heat Transfer, Thermal Radiation, Copper-Chlorine Cycle, Hydrolysis, Hydrogen Production

I. INTRODUCTION

A thermochemical hydrogen production cycle involves a sequence of chemical processes that separate water into hydrogen and oxygen. The copper-chlorine (Cu-Cl) cycle of thermochemical water splitting is a promising method to produce hydrogen at a large-scale from either nuclear, solar or other thermal energy sources [1]. With lower operating temperatures (below 550°C) and the capacity to efficiently use low-grade waste heat for endothermic reactions, it has several advantages over other thermochemical cycles. There are four main steps in the Cu-Cl cycle, namely: 1) hydrolysis, 2) thermolysis, 3) electrolysis, and 4) water separation (e.g., crystallization). The hydrolysis reaction is an endothermic non-catalytic gas-solid reaction at a temperature around 400°C where CuCl₂ particles from the crystallization process are reacted with superheated steam to produce copper oxychloride solid (Cu₂OCl₂) and hydrogen chloride in gaseous form (HCl). The non-catalytic gas-solid reaction and the hydrolysis reaction may be represented respectively as [2]:

\[
A(g) + bB(s) \rightarrow cC(g) + dD(s) \quad (1)
\]

\[
H_2O(g) + 2CuCl_2(s) \rightarrow Cu_2OCl_2(s) + 2HCl(g) \quad (2)
\]

The rate of conversion of cupric chloride particles to copper oxychloride is highly dependent on heat transfer that occurs between the fluid and the solid CuCl₂ particles. Considerable significance is attached to the study of heat and mass transfer in chemical reactions. It is established that the overall reactant conversion rates can be substantially affected by transport phenomena and the mass and/or heat transfer rates is influenced in the presence of chemical reaction processes [8]. The significance of thermal boundary-layers for two-dimensional steady and incompressible laminar flow past a wedge has been examined previously [4]. Two-dimensional laminar boundary layer-flow and convective heat transfer have been studied by other investigators; however, the cases when thermal radiation becomes an additional factor are limited [3,5]. Past studies by Howe, Kadanoff, Ruminski [3,6] have shown thermal radiation to affect heat transfer both directly and indirectly. Radiative heat transfer can either be directly absorbed or emitted by a surface. This can alter its heat-transfer characteristics or thermal radiation may be indirectly and partially absorbed in the boundary layer, changing the temperature distribution, and impacting the properties of convection and conduction [3].

The purpose of this paper is to study the effects of thermal radiation on the temperature distribution and heat transfer during
flow of an absorbing / emitting and chemically reacting medium. Steam flow along a CuCl₂ surface is studied so that a better understanding of combined radiation and convection is obtained.

The conservation of energy transforms into a nonlinear integrodifferential equation when energy transfer via radiation and convection is included. It is challenging to accurately analyze how a radiation field interacts with absorbing and emitting substances in the laminar boundary layer. The radiant-energy flux vector is approximated using the Rosseland approximation. The method of solution is based on a similarity transformation utilizing the Runge-Kutta method together with a shooting method [7,8]. This paper attempts to apply the study to heat and mass transfer in the hydrolysis step of thermochemical hydrogen production by analyzing the effects of chemical reaction and thermal radiation on the surface boundary layer flow.

II. GOVERNING EQUATIONS

A. Boundary Layer Equations

The flow is assumed to be an incompressible viscous fluid over a flat plate. The temperature of the surface or wall represented by T_w is uniform, constant and lower than the free stream temperature of the fluid, T_infinity. It is assumed that the free stream velocity, U_infinity, is also uniform and constant. Further, assuming that the flow in the laminar boundary layer is two-dimensional, the continuity equation and the boundary-layer equations may be expressed as:

Conservation of mass
\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \]  
\[ (3) \]

Conservation of momentum
\[ u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{\partial p}{\partial y} + \frac{1}{\rho} \frac{\partial}{\partial y} \left( \rho \frac{\partial u}{\partial y} \right) \]  
\[ (4) \]

where \( u \) and \( v \) are the velocity components in the \( x \) and \( y \) directions, respectively, and \( v \) is the kinematic viscosity.

Conservation of energy:
\[ u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial y^2} - \frac{1}{\rho C_p} \frac{\partial q_r}{\partial y} \]  
\[ (5) \]

where \( T \) and \( C_p \) is fluid temperature in the boundary layer and specific heat respectively.

Similarly, \( q_r = \frac{4\sigma^* T^4}{k^*} \) is the radiative heat flux simplified form the Rosseland approximation for radiation [9], \( \sigma^* \) and \( k^* \) are the Stefan–Boltzmann constant and the mean absorption coefficient, respectively. The temperature differences within the flow are expressed as a linear function of temperature. Hence, expanding \( T^4 \) in a Taylor series about \( T_{\infty} \) and neglecting higher-order terms provides
\[ T^4 \approx 4T_{\infty}^3 - 3T_{\infty}^4 \]  
\[ (6) \]
The energy equation can then be represented by

\[ \frac{\partial T}{\partial x} + \frac{\partial T}{\partial y} = \left( \alpha + \frac{16\sigma^* T_{\infty}}{3\rho C_p k^*} \right) \frac{\partial^2 T}{\partial y^2} \]  
\[ (7) \]

The variable \( \alpha \) is the thermal diffusivity. The above equation shows that the effect of radiation is to enhance the thermal diffusivity. Taking \( N_R \) as the radiation parameter given by
\[ \frac{\partial T}{\partial x} + \frac{\partial T}{\partial y} = k_0 \frac{\partial^2 T}{\partial y^2} \]  
\[ (8) \]
where \( k_0 = \frac{3N_R}{3N_R+4} \).

Species Conservation:
The conservation of species can be represented by
\[ \frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} - b \gamma \left( C_{\infty} - C \right) \]  
\[ (9) \]
where \( b \) is the stoichiometric reaction coefficient, \( k_i \) is the chemical reaction reaction constant, \( C \) is solute concentration and \( D \) is the effective diffusion coefficient.

The associated boundary conditions for this system of equations are assumed to be:
\[ u = v = 0, T = T_{\infty}, C = C_{\infty} \text{ at } y = 0 \]  
\[ (10) \]
\[ u = U_{\infty}, T = T_{\infty}, C = C_{\infty} \text{ at } y \to \infty \]  
\[ (11) \]

\( T_w \) is the constant temperature of the wall, \( T_{\infty} \) is a constant temperature of the ambient fluid (\( T_{\infty} > T_w \)) and \( U_{\infty} \) is a constant free stream velocity and \( C_{\infty} > C_w \).

B. Similarity Transformation

Similarity solutions are discussed extensively by Schlichting [10]. The system of partial differential equations (3-9) is reduced to three ordinary differential equations by introducing the following similarity transformation variables:
\[ \eta = \sqrt[4]{\frac{U_{\infty}}{\sqrt{\nu}}} \]  
\[ (12) \]
\[ \theta = \frac{T - T_{\infty}}{T_w - T_{\infty}} \]  
\[ (13) \]
\[ \phi = \frac{C - C_{\infty}}{C_w - C_{\infty}} \]  
\[ (14) \]
\[ \Psi = \sqrt{\nu U_{\infty} x f(\eta)} \]  
\[ (15) \]
where \( \eta \) is the similarity variable, \( f \) is the dimensionless stream function, \( \theta \) is the dimensionless temperature, \( \phi \) is the dimensionless concentration and \( \Psi \) is the stream function defined as
\[ u = \frac{\partial \Psi}{\partial y} \]  
\[ (16) \]
\[ v = -\frac{\partial \Psi}{\partial x} \]  
\[ (17) \]
Consequently, the equations (3-9) and the boundary conditions can be expressed in the following dimensionless form:

\[ 2f''' + ff'' = 0 \]  \hspace{1cm} (18)

\[ \theta'' + \frac{Pr k_\infty}{2} f \theta' = 0 \]  \hspace{1cm} (19)

\[ \phi'' = Sc [2 Cr \phi - \frac{\phi f}{2}] \]  \hspace{1cm} (20)

where \( Pr \) is the Prandtl number, \( k_\infty \) is the radiation parameter discussed in (8), and \( f'(\eta) = \frac{u}{u_\infty} \). The Schmidt number is \( Sc = \frac{w}{D} \) and chemical reaction parameter \( Cr = \frac{k_\infty C_\infty x}{u_\infty} \). The boundary conditions reduce to:

\[ f = f' = 0, \theta(0) = 1, \phi(0) = 1 \text{ as } \eta = 0 \]  \hspace{1cm} (21)

\[ f'(\infty) = 1, \theta(\infty) = 0, \phi(\infty) = 0 \text{ as } \eta = \infty \]  \hspace{1cm} (22)

The physical quantities of interest are the first derivative of temperature and concentration.

III. RESULT AND DISCUSSION

The ordinary differential equations (18-20) along with the boundary condition were solved numerically with \( \Delta \eta = 0.01 \) and computational error being less than \( 10^{-5} \) for all considered cases employing a fourth order shooting method. The parameters for the present study are the radiation parameter \( N_R \) and chemical reaction parameter \( Cr \). Since the flow problem is uncoupled from the thermal problem, changes in the values of \( N_R \) will not affect the fluid velocity. Hence, the function \( f(\eta) \) and its derivatives are identical and the physical quantities of interest are \( \theta(0) \) and \( \phi(0) \).

Numerical solutions are presented for a Prandtl number of 1 as selected for steam, Schmidt number selected for water vapor \( (Sc = 0.62) \), and chemical reaction parameter of 3.29, 2.45,1.75 and 1.22 for the temperature of 400°C, 375°C, 350°C and 325°C respectively. Figs. 1-3 show the temperature profiles as a function of the similarity variable, temperature gradients and concentration profile across the boundary layer. The velocity profiles for a constant physical property case are well established and are not studied in detail in this paper. The temperature profiles for the case without radiation \( (k_\infty = 1) \) and for the cases with thermal radiation parameter, \( N_R = 0.7 \) and 1, are considered. Here, \( N_R=0.7 \) is the case when thermal radiation effect dominates and \( N_R=1 \) is the case when the magnitude of radiation is the same order of magnitude as conduction is and \( k_\infty=1 \) is the case without the thermal radiation effect.

The study of temperature distribution concludes that the effect of radiation is to thicken the thermal boundary layer as if to lower the Prandtl number. The dimensionless temperature monotonically varies across the boundary layer from wall to free stream. The deviation of \( N_R=1 \) plot with \( k_\infty=1 \) plot is less compared to the deviation between \( N_R=0.7 \) and \( k_\infty=1 \). It signifies that the thermal radiation effects broaden the temperature distribution. Similarly, it is observed that the values of dimensionless wall temperature gradient \( \theta'(0) \) decreases when the thermal radiation parameter becomes dominant.

Fig. 2 is a plot of the variation of heat transfer across the boundary layer in terms of temperature gradient and is also comparable to the boundary layer temperature gradient study by Viskanta. It is noted that the temperature gradient is maximum some point away from the wall. This trend is observed due to the non-linear dependence of the radiant energy flux on the temperature which is explained by energy equation (19). The effect of radiation is to increase temperature gradient as compared to the case without radiation. Fig. 3 shows the trend of the concentration profile with different values of chemical reaction parameters. The chemical reaction parameter were calculated for different reaction rate constant at the temperatures 400°C, 375°C, 350°C and 325°C. The sensitivity analysis was performed for different values of \( Cr \) for its value changes with the reaction rate constants. It is observed that the concentration profiles are decreasing as the chemical reaction parameter increases. Same trend for all three cases of \( k_\infty=1, N_R=0.7 \) and \( N_R=1 \) were obtained.
Fig. 3. Concentration profile trends as a function of $\eta$ for different values of chemical reaction parameter with radiation ($N_R=0.7$ and $N_R=1$) and without radiation ($k_0=1$).

Fig. 4 shows the results for a velocity profile for different cases with and without radiation. The overlapping of velocity profile curves is due to uncoupled flow and energy equation as discussed by Bataller [5]. It is evident that thermal radiation influences the temperature distribution of the boundary layer but not the velocity profile and concentration distribution. Validation of predicted results was performed through comparisons with Ferdows [7] for both temperature and concentration profiles. Only the concentration graph is presented in this paper and Fig. 5 presents a comparison of the concentration profile ($\phi$) for different orders of reaction $n=0,1,2$ of Ferdows [7] and the present numerical method.

![Velocity profile as a function of $\eta$ for cases with radiation ($N_R=0.7$ and $N_R=1$) and without radiation ($k_0=1$)](image)

**TABLE 1. PREDICTED VALUES FOR CASES WITH AND WITHOUT RADIATION**

<table>
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<tr>
<th>$\eta$</th>
<th>$k_0=1$</th>
<th>$N_R=0.7$</th>
<th>$N_R=1$</th>
<th>$k_0=1$</th>
<th>$N_R=0.7$</th>
<th>$N_R=1$</th>
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<td>0.0034</td>
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<td>6</td>
<td>0.0025</td>
<td>0.0425</td>
<td>0.0304</td>
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</table>

**TABLE 2. PREDICTED VALUES FOR DIFFERENT CHEMICAL REACTION PARAMETER VALUES FOR RADIATION $N_R=0.7$**

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$C_r=3.29$</th>
<th>$C_r=2.44$</th>
<th>$C_r=1.75$</th>
<th>$C_r=1.22$</th>
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<td>0.0000</td>
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</table>
Table 1 summarizes the calculated values of the rate of heat transfer $\theta'(0)$ and the rate of mass transfer $\phi'(0)$ for $k_0=1$ and cases with radiation, $N_R=0.7$ and 1. Similarly, the calculated value of the mass transfer for four values of chemical reaction parameter for a case with radiation $N_R$ of 0.7 is summarized in Table 2.

IV. CONCLUSION

In this paper, laminar boundary layer flow over a plate in the presence of a chemical reaction and thermal radiation was considered. With the use of a similarity transformation, the partial differential equations were transformed to ordinary differential equations and then solved with a fourth order Runge-Kutta shooting method. Numerical solutions were obtained for temperature and concentration profiles, velocity and temperature gradients across the boundary. Two cases for radiation $N_R=0.7$ and 1 and a case without radiation $k_0=1$ was evaluated, and the numerical results showed the effectiveness of the uncoupled flow equation with the thermal equation to predict the temperature and concentration values. It was shown that thermal radiation has an appreciable role in the boundary layer of the flow. The thermal boundary layer thickness is increased with the impact of thermal radiation and was noted that temperature gradient is maximum a point away from the wall and the concentration profile is decreasing as the chemical reaction parameter increases.

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