A numerical study of natural convection properties of supercritical water (H₂O) using Redlich–Kwong equation of state

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Abstract. In this article, the Crank-Nicolson implicit finite difference method is utilized to obtain the numerical solutions of highly nonlinear coupled partial differential equations (PDEs) for the flow of supercritical fluid (SCF) over a vertical flat plate. Based on the equation of state (EOS) approach, suitable equations are derived to calculate the thermal expansion coefficient (β) values. Redlich–Kwong equation of state (RK-EOS), Peng-Robinson equation of state (PR-EOS), Van der Waals equation of state (VW-EOS) and Virial equation of state (Virial-EOS) are used in this study to evaluate β values. The calculated values of β based on RK-EOS is closer to the experimental values, which shows the greater accuracy of the RK-EOS over PR-EOS, VW-EOS and Virial-EOS models. Numerical simulations are performed for H₂O in three regions namely subcritical, supercritical and near critical regions. The unsteady velocity, temperature, average heat and momentum transport coefficients for different values of reduced pressure and reduced temperature are discussed based on the numerical results and are shown graphically across the boundary layer.

Keywords. Supercritical water; Crank-Nicolson scheme; RK-EOS; PR-EOS; virial-EOS; VW-EOS; correlation.

1. Introduction

Growing environmental concerns and increasing health consciousness among consumers for healthy and clean food make green technologies in food processing imperative in the near future. For this reason, alternate green technologies are gaining lot of attention to obtained products for a sustainable processing, energy saving and thereby avoiding ecological damage. Supercritical fluids being environmental friendly and green solvents not only used extensively to achieve the above said objectives but also found to have special thermodynamic properties. For instance, supercritical fluids found to have liquid like solvents property as well as gas-like diffusivity. Also, these special properties of SCF are tunable and which give an instant advantage in handling and use for specific application.

The academic significance and wide range of engineering applications have made heat transfer to supercritical fluids an essential research topic over several decades. It is one of the general and complicated examples of single-phase natural convection flow problem. The development of systems such as, supercritical fluid extraction (SFE), supercritical water biomass valorization (SCBV), supercritical water oxidation (SCWO), supercritical pressure

water-cooled reactor (SCWR), supercritical water fluidized bed reactor (SCWFBR), power engineering, etc. operating at supercritical pressures and temperatures necessitates the thorough understanding of heat transfer problem under this regime. Understanding is also essential towards the optimal design of such systems. In modern chemical and other industries there are many systems in which supercritical fluids are used as propellants or coolants. It is a well-known fact that, the supercritical boilers are used in the steam turbine cycles for several years. The single-phase supercritical water flow in the boiler tubes eliminates the need of a steam drum to separate steam from the liquid water. For example, the supercritical heat transfer process was studied by Yoshiaki Oka *et al* [1] and some of the findings are utilized for the design of the supercritical water-cooled systems and the fast breeder reactors.

Another important application of heat transfer to supercritical water (H₂O) is in the waste management industry. The idea is to eliminate the poisonous materials and toxic aqueous waste by a method called supercritical water oxidation (SCWO). It is well-known that, at normal pressure and temperature, H₂O is an excellent solvent for most of the polar inorganic compounds whereas for the majority of organic compounds which are non-polar water is not a suitable solvent. On the other hand, the supercritical water is the best solvent for most of the organic materials but not for

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Figure 1. (a) Idealized phase diagram with region of study under consideration. (b) Physical configuration and coordinate system of the present problem.

inorganic salts. This idea leads to the development of supercritical water oxidation systems. More details about the experimental study of supercritical water and its applications in different supercritical fluid systems in various industries can be found in the available literature [2–10].

Due to the large number of engineering and pharmaceutical applications, supercritical fluids are studied widely in the last few decades both theoretically as well as experimentally. Thus, the thermodynamic behavior of supercritical fluid flow past different geometries is a significant research problem in the field of fluid dynamics. It is clear from the literature that, supercritical fluids are used in many branches of science and industries, for instance, chemical engineering, drug delivery, chromatography, power engineering, extraction and purification of chemical compounds, preparation of nanoparticles for medical benefit, aerospace engineering, etc. The detailed properties of various supercritical fluids including supercritical water and their advantages are found in some of the available literature [11–21]. In view of such interesting properties of supercritical water discussed above, the authors have chosen this fluid for the present study.

Any fluid which exists above its thermodynamics critical point can be termed as supercritical fluid (SCF). The

detailed explanation about the definition and properties of SCF can be found in the available literature [22–24]. The variations in thermodynamic properties of SCF, however, are so dramatic across the pseudo-critical temperature, that the fluid at temperatures higher and lower the pseudo-critical point is called as vapor-like or liquid-like, respectively. The pseudo-critical temperature is slightly greater than the critical temperature and increases with pressure. All these definitions are well understood with the help of a typical P-T diagram of supercritical water which is shown in figure 1(a). The much better introduction to the advantages, properties, and applications of supercritical fluids was given by McHugh and Krukonis [25].

In the field of fluid dynamics and engineering, the problems related to free convection heat transfer attracted the attention of many scientists because of their huge advantages. For an instance, solar collectors, cooling of electronic devices, space heating and geothermal structures, etc. uses the concept of convective heat transfer. However, the analytical results for this type of non-linear problems are not yet available in the literature. One such significant problem of free convection from a non-isothermal vertical plate was analyzed by Sparrow and Gregg [26]. The similar problem with transient effects along the vertical plate was studied by Takhar *et al* [27]. Thus, many of the authors used different conventional techniques [28, 29] to improve the natural convection heat transfer process. The steady-state natural convective flow over a vertical plate with variable heat flux in SCF region was investigated by Teymourash *et al* [30]. Also, they shown that, the applicability of Boussinesq's approximation in SCF region and based on RK-EOS, they derived the suitable equation for β . The same problem was continued by Khonakdar and Raveshi [31] by considering the mixed convection case. Their investigation presents that, RK-EOS model was the suitable model to study the thermodynamic behavior of fluids in supercritical region when compared to other EOS models. Thus, the process of low heat transfer to water, ethylene glycol, engine oil, etc., becomes an obstacle for natural convection heat transfer. Therefore, to overcome this difficulty the concept of SCF was introduced in a great deal. Hence, the investigation related to these types of problems using supercritical fluid concept is very important in the present days because of their increased industrial and bio-engineering applications as discussed above.

However, having above difficulty in consideration, authors have made an attempt to investigate the thermodynamic behavior of water in supercritical region. Thus, the objective of present study is achieved by considering supercritical water for numerical simulations. In the present study, incompressible flow with Boussinesq's approximation is assumed to derive the flow equations in SCF region. Numerical results are produced by using Crank-Nicolson implicit method. Influence of flow parameters on behavior of water in supercritical region is investigated and discussed in terms of flow profiles and compared with the existing results.

According to authors' knowledge, this particular problem is not yet reported in the literature mainly due to the complexity of such unsteady state supercritical flow in terms of obtaining governing equation and performing numerical simulation. Also, we have extensively presented non-dimensional graphs in the present study in three regions namely subcritical, supercritical and near critical regions whereas most of the available literature [30, 31] deals with steady-state and give less importance to the non-dimensional graphs. It is to be noted that most of the practical applications under supercritical condition behave as unsteady state problem so it is vital to understand heat transfer to such systems.

2. Equation of state approach

From the available literature [30, 31] it is observed that, the assumption of constant values for thermal expansion coefficient in SCF region gives rise to incorrect results. Thus, in order to overcome this difficulty, authors have taken the aid of EOS approach namely RK-EOS and VW-EOS. This problem is well illustrated in figure 1(a) by considering supercritical region under study. So, it is concluded that, the evaluation of β through a suitable equation of state (EOS) is required. Using RK-EOS [32], the best suitable equation is obtained to determine β . The generalized definition of RK-EOS which is considered in this study for gases is $P = \frac{R^*T'}{V^* - b} - \frac{a}{\sqrt{T'}(V^*(V^* + b))}$. Also, the common definition of thermal expansion coefficient is $\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T'} \right)_P$. Where all the symbols are detailed in nomenclature section. Further, the RK-EOS can be re-written in terms of compressibility factor (Z) as:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (1)$$

where $Z = \frac{PV^*}{R^*T'}$, $A = \frac{aP}{\sqrt{T'}(R^*T')^2}$, $B = \frac{bP}{R^*T'}$ are obtained from [33]. The constants $A = 0.42748 \left(\frac{P}{P_c} \right) \left(\frac{T_c}{T'} \right)^{2.5}$ and $B = 0.08662 \left(\frac{P}{P_c} \right) \left(\frac{T_c}{T'} \right)$ are obtained from RK-EOS, where $T_c = 647.30$ K and $P_c = 22.090$ MPa are critical temperature and pressure of water. At the end the equation of β based on RK-EOS [32] is shown below.

$$\beta = \frac{1}{T'} \left[1 - \left(\frac{3.5AB + 2ZB^2 + BZ - 2.5AZ}{3Z^3 - 2Z^2 + Z(A - B) - B^2Z} \right) \right] \quad (2)$$

Similarly, the final expressions for thermal expansion coefficient based on PR-EOS [34], VW-EOS [35] and Virial-EOS [36] are given in the following equations.

$$\beta = \frac{1}{T'} + \left(\frac{(Z^2 + A - 2(Z + 3B) - 2B + 3B^2) \left(\frac{\partial B}{\partial T'} \right)_P + (Z + B) \left(\frac{\partial A}{\partial T'} \right)_P}{(3Z^3 + (2B - 2)Z^2 - BZ - 3ZB^2 + AZ)} \right) \quad (3)$$

$$\beta = \frac{1}{T'} \left[1 - \left(\frac{Z^2B - 2ZA + 3AB}{3Z^3 - 2Z^2(B + 1) + AZ} \right) \right] \quad (4)$$

$$\beta = \frac{1}{T'} \left[1 + \left(\frac{0.8944\phi T_r^{*-7.2} - 1.0972T_r^{*-4.6} - 0.083T_r^{*-3.0}}{\frac{1}{P_r^*} - 0.083T_r^{*-1.0} - 0.472T_r^{*-2.6} + 0.139\phi - 0.172\phi T_r^{*-5.2}} \right) \right] \quad (5)$$

Where, ϕ is acentric factor, $T_r^* \left(= \frac{T'}{T_c} \right)$ and $P_r^* \left(= \frac{P}{P_c} \right)$ are reduced temperature and reduced pressure, respectively.

3. Description of the flow model

In the present problem, we consider the transient, two-dimensional, laminar buoyancy driven supercritical water flow past a vertical flat plate with x -axis along the axial coordinate of the plate and y -axis is taken normal to the plate, which is shown in figure 1(b). At the beginning ($t' = 0$) it is assumed that, fluid and the plate are of same temperature (T'_∞). When the flow starts ($t' > 0$) it is assumed that, $T'_w (> T'_\infty)$ and it is same for all time $t' > 0$. Due to this temperature difference in the boundary layer region, there occurs a density variation and this change in density interact with the gravity (g), causes the natural convection flow. Since, flow scale of the velocity is very small, hence viscous dissipation is neglected from the heat equation. The Boussinesq's approximation is reliable in supercritical region which is shown in [30, 31, 37]. With the above assumptions, the governing fluid flow equations are expressed as follows:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (6)$$

$$\rho \left(\frac{\partial u}{\partial t'} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = \rho g \beta (T' - T'_\infty) + \mu \frac{\partial^2 u}{\partial y^2} \quad (7)$$

$$\frac{\partial T'}{\partial t'} + u \frac{\partial T'}{\partial x} + v \frac{\partial T'}{\partial y} = \alpha \frac{\partial^2 T'}{\partial y^2} \quad (8)$$

The necessary conditions for the above Eqs. (6)-(8) are as follows

$$\left. \begin{array}{ll} t' \leq 0 : & T' = T'_\infty, u = 0, v = 0 \quad \forall x \text{ and } y \\ t' > 0 : & T' = T'_w, u = 0, v = 0 \quad \text{at } y = 0 \\ & T' = T'_\infty, u = 0, v = 0 \quad \text{at } x = 0 \\ & T' \rightarrow T'_\infty, u \rightarrow 0, v \rightarrow 0 \quad \text{as } y \rightarrow \infty \end{array} \right\} \quad (9)$$

To non-dimensionalized the above governing equations with boundary conditions, the following non-dimensional quantities are used

Table 1. Critical values of water tabulated based on experimental data [39].

Selected compound	P_c (MPa)	T_c (K)	V_c^* (cm ³ /mol)	M (kg/mol)	D_c (kg/m ³)	Z_c (-)
Water	22.090	647.30	55.95	0.01801528	322.0	0.229

Figure 2. Grid independent test for velocity and temperature profiles in supercritical fluid region.

$$\left. \begin{aligned} X &= Gr^{\frac{-11}{12}} \frac{x}{l}, Y = \frac{y}{l}, U = Gr^{\frac{-11}{12}} \frac{ul}{\vartheta} \\ V &= \frac{vl}{\vartheta}, t = \frac{\vartheta t'}{l^2}, \theta = \frac{T' - T'_\infty}{T'_w - T'_\infty} \\ Gr &= \frac{g\beta l^3 (T'_w - T'_\infty)}{\vartheta^2}, Pr = \frac{\vartheta}{\alpha} \end{aligned} \right\} \quad (10)$$

in Eqs. (6)–(8), the resultant dimensionless equations are expressed as follows:

$$\frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} = 0 \quad (11)$$

$$\frac{\partial U}{\partial t} + U \frac{\partial U}{\partial X} + V \frac{\partial U}{\partial Y} = Gr^{1/12} \theta + \frac{\partial^2 U}{\partial Y^2} \quad (12)$$

$$\frac{\partial \theta}{\partial t} + U \frac{\partial \theta}{\partial X} + V \frac{\partial \theta}{\partial Y} = \frac{1}{Pr} \left(\frac{\partial^2 \theta}{\partial Y^2} \right) \quad (13)$$

Following non-dimensional boundary conditions are used to solve the Eqs. (11)–(13).

$$\left. \begin{aligned} t \leq 0: & \quad \theta = 0, U = 0, V = 0 \quad \forall X \text{ and } Y \\ t > 0: & \quad \theta = 1, U = 0, V = 0 \quad \text{at } Y = 0 \\ & \quad \theta = 0, U = 0, V = 0 \quad \text{at } X = 0 \\ & \quad \theta \rightarrow 0, U \rightarrow 0, V \rightarrow 0 \quad \text{as } Y \rightarrow \infty \end{aligned} \right\} \quad (14)$$

The physical model which is considered in this study has number of advantages in supercritical fluid extraction

industries, nuclear reactors, solar collectors, green technology, cryogenic containers, electronic equipment, etc. Also, in refrigeration systems, vertical plates are used for suspending the glass beakers, and many other cases.

4. Implicit finite difference method (FDM)

The above non-dimensional equations are coupled, highly non-linear and transient nature. Hence, to solve these Eqs. (11)–(13) with Eq. (14), the following finite difference equations are written in accordance with Eqs. (11)–(13).

$$\begin{aligned} & \frac{U_{l,m}^{n+1} - U_{l-1,m}^{n+1} + U_{l,m}^n - U_{l-1,m}^n}{2\Delta X} \\ & + \frac{V_{l,m}^{n+1} - V_{l,m-1}^{n+1} + V_{l,m}^n - V_{l,m-1}^n}{2\Delta Y} \\ & = 0 \end{aligned} \quad (15)$$

$$\begin{aligned} & \frac{U_{l,m}^{n+1} - U_{l,m}^n}{\Delta t} + U_{l,m}^n \left(\frac{U_{l,m}^{n+1} - U_{l-1,m}^{n+1} + U_{l,m}^n - U_{l-1,m}^n}{2\Delta X} \right) \\ & + V_{l,m}^n \left(\frac{U_{l,m+1}^{n+1} - U_{l,m-1}^{n+1} + U_{l,m+1}^n - U_{l,m-1}^n}{4\Delta Y} \right) \\ & = Gr^{1/12} \left(\frac{\theta_{l,m}^{n+1} + \theta_{l,m}^n}{2} \right) \\ & + \left(\frac{U_{l,m-1}^{n+1} - 2U_{l,m}^{n+1} + U_{l,m+1}^{n+1} + U_{l,m-1}^n - 2U_{l,m}^n + U_{l,m+1}^n}{2(\Delta Y)^2} \right) \end{aligned} \quad (16)$$

$$\begin{aligned} & \frac{\theta_{l,m}^{n+1} - \theta_{l,m}^n}{\Delta t} + U_{l,m}^n \left(\frac{\theta_{l,m}^{n+1} - \theta_{l-1,m}^{n+1} + \theta_{l,m}^n - \theta_{l-1,m}^n}{2\Delta X} \right) \\ & + V_{l,m}^n \left(\frac{\theta_{l,m+1}^{n+1} - \theta_{l,m-1}^{n+1} + \theta_{l,m+1}^n - \theta_{l,m-1}^n}{4\Delta Y} \right) \\ & = \left(\frac{\theta_{l,m-1}^{n+1} - 2\theta_{l,m}^{n+1} + \theta_{l,m+1}^{n+1} + \theta_{l,m-1}^n - 2\theta_{l,m}^n + \theta_{l,m+1}^n}{2Pr(\Delta Y)^2} \right) \end{aligned} \quad (17)$$

The solutions of the Eqs. (15)–(17) are obtained in the rectangular region with $X_{max} = 1, X_{min} = 0, Y_{max} = 20$ and $Y_{min} = 0$, where Y_{max} be corresponds to $Y = \infty$ which is away from the temperature and velocity boundary layers. The 100×500 grid system with size 0.01 (along with the x -axis), 0.04 (along with the y -axis) and 0.01 (time step size Δt) is used for grid independent test (refer figure 2) and for producing consistent results with respect to

Table 2. The β values in supercritical region using NIST data [39] for different T' and P .

P (MPa)	P_r^*	T' (K)	T_r^*	β (1/K)
42	1.90	680	1.05	0.00870524
47	2.12	685	1.058	0.00706514
52	2.35	690	1.06	0.00625072
57	2.58	700	1.08	0.00580162
62	2.80	710	1.09	0.00527782

time. The FDM procedure begins by solving the Eq. (13) for temperature field. Then, the solution of Eqs. (12) and (11) gives the required velocity field, respectively. At the $(n+1)^{\text{th}}$ iteration, the Eqs. (16) and (17) reduce to the following tridiagonal form:

$$a_{l,m}\xi_{l,m-1}^{n+1} + b_{l,m}\xi_{l,m}^{n+1} + c_{l,m}\xi_{l,m+1}^{n+1} = d_{l,m}$$

where ξ represents the unsteady variables θ and U . More details about the FDM procedure can be found in the available literature [38]. The convergence criterion was chosen as 10^{-5} in the present study.

5. Results and discussion

5.1 Accuracy of Redlich–Kwong equation

All the necessary thermodynamic critical values related to water at critical point are summarized in table 1. Also, tables 2, 3, 4, 5 and 6 contain the β values calculated based on NIST data [39], RK-EOS [32], PR-EOS [34], VW-EOS [35] and Virial-EOS [36] using critical values which are

Table 3. The β values in supercritical region using RK-EOS [32] for different T' and P .

P (MPa)	P_r^*	T' (K)	T_r^*	A	B	Z	β (1/K)
42	1.90	680	1.05	0.718557	0.156772	0.370624	0.00519329
47	2.12	685	1.058	0.789506	0.174155	0.398064	0.00438779
52	2.35	690	1.06	0.857758	0.191286	0.425734	0.00383819
57	2.58	700	1.08	0.907014	0.206683	0.457919	0.00351868
62	2.80	710	1.09	0.952204	0.221647	0.489058	0.00324976

Table 4. The β values in supercritical region using PR-EOS [34] for different T' and P .

P (MPa)	P_r^*	T' (K)	T_r^*	A	B	Z	β (1/K)
42	1.90	680	1.05	0.718557	0.156772	0.370624	0.01086299
47	2.12	685	1.058	0.789506	0.174155	0.398064	0.00976906
52	2.35	690	1.06	0.857758	0.191286	0.425734	0.00891179
57	2.58	700	1.08	0.907014	0.206683	0.457919	0.00805048
62	2.80	710	1.09	0.952204	0.221647	0.489058	0.00728957

Table 5. The β values in supercritical region using VW-EOS [35] for different T' and P .

P (MPa)	P_r^*	T' (K)	T_r^*	A	B	Z	β (1/K)
42	1.90	680	1.05	0.726827	0.226235	0.426129	0.00276652
47	2.12	685	1.058	0.801523	0.251320	0.460637	0.00235725
52	2.35	690	1.06	0.873986	0.276041	0.495023	0.00207474
57	2.58	700	1.08	0.930846	0.298261	0.530229	0.00190547
62	2.80	710	1.09	0.984179	0.319855	0.564338	0.00176662

Table 6. The β values in supercritical region using Virial-EOS [36] for different T' and P .

P (MPa)	P_r^*	T' (K)	T_r^*	A	B	Z	β (1/K)
42	1.90	680	1.05	0.718557	0.156772	0.370624	0.01234717
47	2.12	685	1.058	0.789506	0.174155	0.398064	0.03194622
52	2.35	690	1.06	0.857758	0.191286	0.425734	0.19807718
57	2.58	700	1.08	0.907014	0.206683	0.457919	0.03880659
62	2.80	710	1.09	0.952204	0.221647	0.489058	0.02331828

Table 7. The β values in supercritical region using RK-EOS [32] for different P_r^* with fixed $T_r^* = 1.004$.

P (MPa)	P_r^*	T' (K)	T_r^*	C_p (J/mol*K)	μ (10^{-6} Pa*s)	k (W/m*K)	ρ (kg/m ³)	β (1/K)
42	1.90	650	1.004	118.03	71.655	0.47478	611.58	0.00389922
47	2.12	650	1.004	110.70	74.002	0.48777	628.21	0.00337783
52	2.35	650	1.004	105.45	76.065	0.49944	642.36	0.00300580
57	2.58	650	1.004	101.45	77.922	0.51014	654.74	0.00272414
62	2.80	650	1.004	98.267	79.624	0.52008	665.79	0.00250187

Figure 3. (a) Comparison of β curves plotted based on RK-EOS, other EOS models and experimental values for water at 30 MPa; (b) Expanded graph between the temperature 680 K to 850 K. **Figure 4.** (a) Comparison of β curves plotted based on RK-EOS, other EOS models and experimental values for water at 35 MPa. (b) Expanded graph between the temperature 720 K to 880 K.

listed in table 1. With the aid of tables 2, 3, 4, 5 and 6 it is observed that, the β values calculated based on RK-EOS are nearer to experimental values when compared to PR-EOS, VW-EOS and Virial-EOS. Also, the graphical accuracy of Redlich–Kwong equation is presented in figures 3 and 4. Further, the related information of the figures 3 and 4

and the comparison between thermal expansion coefficient of water with carbon dioxide (refer figure 5) is given in the “Appendix” section.

The local Nusselt number values for vertical plate with constant surface temperature are plotted as a function of the Rayleigh number for supercritical water and it is shown in

Figure 5. The β curves at different pressures for (a) water and (b) carbon dioxide.

Figure 6. Nu_X as a function of Ra_X for water at $T_r^* = 1.01$ and $P_r^* = 1.35$.

figure 6. An empirical correlation was given in [41] applies to a wide range of Rayleigh numbers and near critical region i.e.,

$$Nu_X = 0.68 + \frac{0.67Ra_X^{1/4}}{\left[1 + \left(\frac{0.492}{Pr}\right)^{9/16}\right]^{4/9}} \quad (18)$$

Figure 6 clearly demonstrates that, Redlich–Kwong equation is the suitable EOS approach to investigate the thermodynamic behavior of water in supercritical region.

Figure 7. Comparison of velocity and temperature values with results of [27].

This is also reflected in the RK-EOS curve in figure 6 which is being closer to the experimental correlation curve.

5.2 Flow variables

To justify the present numerical technique, the computer-generated flow profiles U and θ are compared with those of existing results [27] for $Pr = 0.7$ and $Gr = 1.0$. From figure 7 it is noticed that, the present results are in good agreement with results of [27]. Computer generated

Figure 8. Transient velocity profile close to the hot wall for different (a) P_r^* and (b) T_r^* .

Figure 9. Transient velocity profile away from the hot wall for different (a) P_r^* and (b) T_r^* .

numerical data for water in supercritical region with respect to flow parameters such as reduced pressure (P_r^*) and reduced temperature (T_r^*) is presented in terms of graphs in the succeeding sections. Also, for the different set of P_r^* and T_r^* , β values are obtained and tabulated in tables 7 and 8.

(i) Transient velocity: From figures 8(a) and (b) it is observed that, the magnitude of the velocity overshoots decreases for magnifying P_r^* or T_r^* values, and time required to attain steady-state enhances. Similarly, figures 9(a) and (b) indicate that, as P_r^* or T_r^* increases the magnitude of the overshoots of the velocities and time to reach the steady-state increases. Also, from figures 8 and 9, it is noticed that, velocity decreases with respect to time in SCF region for all P_r^* or T_r^* values.

(ii) Steady-state velocity: Figures 10(a) and (b) show that, the steady-state velocity decreases while steady-state time increases for amplifying P_r^* or T_r^* values. Also, for all values of P_r^* or T_r^* in supercritical region, i.e., $1 < Y < 1.8$ the velocity is suppressed and opposite behavior is noticed for $Y > 1.8$. From these figures, it is noted that, the velocity profile begins with the zero value, attains the highest value and further decreases to zero along Y axis.

(iii) Transient temperature: In the figures 11(a) and (b), initially temperature profiles increase with time, attain the temporal peak, again decrease, further slightly increase, and at the end reach the asymptotic steady-state. Also, the magnitude of the temperature overshoots decreases and time to reach the steady-state amplifies for

Table 8. The β values in supercritical region using RK-EOS [32] for different T_r^* with fixed $P_r^* = 1.04$.

P (MPa)	P_r^*	T' (K)	T_r^*	C_p (J/mol*K)	μ (10^{-6} Pa*s)	k (W/m*K)	ρ (Kg/m ³)	β (1/K)
23	1.04	680	1.05	140.53	27.400	0.12475	124.83	0.00779849
23	1.04	685	1.058	127.60	27.435	0.11945	119.63	0.00695381
23	1.04	690	1.06	117.54	27.506	0.11523	115.20	0.00630350
23	1.04	700	1.08	102.81	27.723	0.10897	107.92	0.00535973
23	1.04	710	1.09	92.503	28.003	0.10465	102.11	0.00470110

Figure 10. Steady-state velocity profile against Y at $X = 1.0$ for different (a) P_r^* and (b) T_r^* . **Figure 11.** Transient temperature profile close to the hot wall for different (a) P_r^* and (b) T_r^* .

increasing P_r^* and T_r^* values in the SCF region. Also, in the proximity of hot wall of the plate the transient temperature is magnified for increasing P_r^* or T_r^* values.

(iv) Steady-state temperature: In figures 12(a) and (b), the temperature curves begin with $\theta = 1$ and decreases along Y direction, and at the end attains ambient fluid

Figure 12. Steady-state temperature profile against Y at $X = 1.0$ for different (a) P_r^* and (b) T_r^* .

Figure 13. Average wall shear stress ($\bar{C}_f$) for different (a) P_r^* and (b) T_r^* .

temperature ($\theta = 0$). Also, for magnifying P_r^* or T_r^* values, the steady-state time enhanced. For lower values of P_r^* or T_r^* , the temperature curves appear to be close to the hot wall of the plate and move away from the hot wall for higher values of P_r^* or T_r^* .

5.3 Friction and heat transport coefficients

Due to the large number of pharmaceutical and engineering uses the dimensionless average skin-friction and heat transport coefficients are computed by the following equations.

$$\bar{C}_f = \int_0^1 \left(\frac{\partial U}{\partial Y} \right)_{Y=0} dX \quad (19)$$

$$\bar{Nu} = - \int_0^1 \left(\frac{\partial \theta}{\partial Y} \right)_{Y=0} dX \quad (20)$$

From figures 13(a) and (b) it is seen that, $\bar{C}_f$ is suppressed for magnifying values of P_r^* or T_r^* , and time to reach the steady-state increases. This is because in the proximity of hot wall velocity is decreased for amplifying values of P_r^* or T_r^* and this fact is presented clearly through

Figure 14. Average Nusselt number ($\bar{Nu}$) for different (a) P_r^* and (b) T_r^* .

Figure 15. Nu_X as a function of Ra_X for water at (a) fixed T_r^* and various values of P_r^* ; (b) fixed P_r^* and various values of T_r^* .

the figures 8 and 10. Similarly, from figures 14(a) and (b) it is viewed that, in the beginning time the $\bar{Nu}$ curves coincide with one another and these curves split after some time interval. This is because convective heat transfer process is suppressed under the influence of conduction process in the beginning time. Also, for increasing values of P_r^* or T_r^* , $\bar{Nu}$ decreases. This is for the reason that, in supercritical fluid region, temperature field is enhanced with increase in P_r^* or T_r^* , which results in the negatively magnifying values in Nusselt number (refer Eq. (20) and figure 12). Similarly, the effect of P_r^* or T_r^* on local Nusselt number (Nu_X) as a function Rayleigh number (Ra_X) is illustrated through figures 15(a) and (b). From these figures it is clear that, T_r^* has considerable effect on Nu_X profile when compared to the

P_r^* . This observation shows that the slight change in temperature field produces the considerable variations in Nu_X profile in supercritical fluid region.

5.4 Physical quantities of interest and flow profiles in three regions

For the first time an attempt has been made to study the average skin friction coefficient and Nusselt number in three regions, namely, subcritical region, near critical region and supercritical region. Figure 16(a) illustrates that, the transient velocity field is enhanced when temperature and pressure vary from subcritical region to the

Figure 16. Flow curves in three regions: (a) unsteady curves; (b) steady-state curves; (c) average wall shear stress and Nusselt number curves.

supercritical region, on the other-hand opposite behavior is seen for time-dependent thermal curves. Also, the time to reach the temporal maxima is suppressed when the temperature and pressure vary from under-critical region to SCF region.

It is seen from figure 16(b) that, the steady-state velocity curves amplified when flow changes from under-critical region to supercritical region, but the behavior of thermal curves is observed to be opposite. Also, the steady-state time decreases when temperature and pressure changes from subcritical to SCF region.

Figure 16(c) illustrates that, in supercritical region, for all pressure and temperature values, Nusselt number curves are merged with one another initially. This observation demonstrates that, conduction process only occurs at the beginning in three regions. Further, C_f and Nu

enhanced when flow varies from under-critical region to SCF region.

6. Conclusions

In the present investigation, based on the equation of state approach, a suitable equation for β is derived. Further, with the aid of RK-EOS a numerical model is developed in order to analyze the thermodynamic properties and behavior of water in supercritical region. Based on the proposed numerical model, present problem is tackled in great detail. From the contemporary study it is noticed that, to solve the natural convection problems in supercritical region, RK-EOS is the suitable model. Also, to predict the free convection properties of supercritical fluids, RK-EOS is the

appropriate model, because β values calculated using RK-EOS are nearer to experimental values. Thus, from the above numerical discussion following point are listed.

- Magnitude of the transient velocity overshoots of supercritical water increases for increasing values of P_r^* or T_r^* .
- The steady-state velocity decreases as P_r^* or T_r^* amplifies. On the other-hand, opposite behaviour is noticed for temperature profile.
- The transient temperature profile increases in the neighborhood of the hot wall of the plate for the increasing values of P_r^* or T_r^* .
- The average momentum ($\bar{C}_f$) and heat transport ($\bar{Nu}$) coefficients decrease for increasing values of P_r^* or T_r^* .
- The unsteady and steady-state velocity enhanced when temperature and pressure change from subcritical to SCF region. While temperature field is suppressed.
- The average skin-friction coefficient ($\bar{C}_f$) and Nusselt number ($\bar{Nu}$) amplified when flow varies from under-critical region to SCF region.

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Appendix

The variations noticed in β curves for different pressures based on NIST data [39], RK-EOS [32], PR-EOS [34], VW-EOS [35] and Virial-EOS [36] is illustrated in figures 3 and 4. Further, in case of liquids at low pressure, β values increase with magnifying temperature field. On the other hand, reverse behavior is observed for low pressure gases. Additionally, it is noticed that, isotherms at high pressure exhibits the liquid-like behavior for small temperature values. Whereas, isotherms at higher temperature values show the gas-like behavior. Further, these isotherms attain the maximum value at transcritical temperature which may not be equal to critical temperature. It is clear from figures 3 and 4 that, all isotherms attain the ideal gas

[40] behavior at higher temperatures. Also, it is clear that, once the non-supercritical fluids are adjacent to the thermodynamic critical point, β diverges and assumption of constant β produces the incorrect results in supercritical fluid region. Thus, from figures 3 and 4 it is observed that, the obtained values based on RK-EOS are closer to the NIST data values when compared to PR-EOS, VW-EOS and Virial-EOS. Further, the numerical model based on RK-EOS approach can easily predict the natural convection heat transfer characteristics of water accurately in supercritical region.

Also, figures 5(a) and (b) depict the isothermal curves of β at five different pressures for water and carbon dioxide, respectively. Supercritical carbon dioxide has large number of engineering and industrial applications in day-to-day life ranging from coolants, refrigerant to separation and purification of chemical compounds. Because of these reasons heat transfer problems are extensively studied using carbon dioxide as a model fluid. If supercritical water is to be used in industrial and day-to-day application replacing well established fluid like carbon dioxide it is necessary to have a fluid whose characteristics are well known to that of already established fluid like carbon dioxide. For this particular reason we have compared both the properties of well-known supercritical carbon dioxide and water in the present study. From these figures it is noticed that, at higher pressures, the β curves will be smoother and its variations decrease against temperatures for both fluids H_2O and CO_2 . It is also noticed that, at the definite reduced temperature ($T_r^* = 1.0$) and reduced pressure ($P_r^* = 1.0$), the β of carbon dioxide has higher values when compared with that of water.

List of symbols

$\bar{C}_f$	dimensionless average momentum transport coefficient
g	acceleration due to gravity
Gr	Grashof number
$\bar{Nu}$	average heat transport rate
k	thermal conductivity of the fluid
C_p	specific heat capacity at constant pressure
Pr	Prandtl number
Nu_X	local Nusselt number
Ra_X	local Rayleigh number
l	height of the plate
t'	dimensional time
t	dimensionless time
T'	dimensional temperature
P	dimensional pressure
V^*	molar volume
R^*	gas constant
Z	compressibility factor
u, v	velocity components in (x, y) coordinate system

U, V	dimensionless velocity components in (X, Y) coordinate system
x	axial coordinate
y	normal coordinate
X	dimensionless axial coordinate
Y	dimensionless normal coordinate

Greek symbols

α	thermal diffusivity
β	thermal expansion coefficient
θ	dimensionless temperature
ρ	fluid density
μ	fluid viscosity
ν	kinematic viscosity of fluid

Subscripts

w	wall conditions
∞	ambient fluid conditions
r	reduced characteristics
c	critical condition
l, m	grid levels in (X, Y) coordinate system

Superscripts

n	time level
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