Apparatus for investigation of heat transfer to H₂O/CO₂ mixtures in both near-critical and supercritical regions

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Abstract. Supercritical H₂O/CO₂ mixtures are the working fluid in a novel power generation system with coal gasified in supercritical water, so their heat transfer behaviors are important to design heat transfer devices. However, heat transfer to supercritical mixtures has received few attention. Here, we designed and established an apparatus to measure the forced convection coefficients and constant pressure heat capacities of H₂O/CO₂ mixtures in both near-critical and supercritical regions. The highest mixture temperature is designed to be 873 K with the highest pressure of 25 MPa and with the CO₂ mass fraction up to 25%. Results show that our apparatus is stable in both near-critical and supercritical regions, which is challenging for high-temperature and high-pressure experiments. Furthermore, our apparatus has lower uncertainties than those in previous studies.

1. Introduction

Our collaborators and we have been investigating a novel power generation system with coal gasified in supercritical water [1]. The coal is gasified in supercritical water in the gasification reactor with the organic matter converted to H₂ and CO₂, while with N, S, P, Hg and other elements deposited as inorganic salt ash or slag attributed to the unique properties of supercritical water. Therefore, pollution production including NOₓ, SOₓ and PM2.5 are intrinsically eliminated in this system compared to conventional coal-fired power plants. The working fluid in this system is supercritical H₂O/CO₂ mixtures (~ 600°C, 25 MPa), so the forced convection coefficients and constant pressure heat capacities are important thermophysical properties to design heat exchangers or other heat transfer processes. However, heat transfer to supercritical mixtures has received few attention [2-4]. Therefore, in this paper, an apparatus has been set up to measure these properties of H₂O/CO₂ mixtures in both near-critical and supercritical regions. To reach steady state for measurements are challenging in apparatus design, especially in the near-critical region.

2. Apparatus Design

2.1 Process configuration

As shown in Figure 1, de-ionized water is pressurized to 25 MPa by an OBL plunger metering pump and then heated to target temperature by Preheaters 1 and 2. High-purity carbon dioxide from gas cylinders is liquefied in the storage tank, pressurized to 25 MPa by an OBL plunger metering pump, and
then heated to the same temperature as water by Preheater 3. H₂O and CO₂ are mixed at a buffer vessel and then heated or cooled to a prescribed temperature at the test section inlet by Preheater 4. After passing the test section, the mixture flows through a condenser and a pressure regulating valve. Then, the H₂O/CO₂ mixture at low temperature and pressure is separated and flow out of the apparatus. The apparatus was designed to be an open system instead of a closed loop to achieve constant component mass fraction. The H₂O/CO₂ mixture has two phases with different component mass fractions in liquid and vapor phases if the mixture is cooled to subcritical temperature before circulated. Considering security and stability, the regenerative heat exchanger that pre-heats the water using the high temperature mixture coming from the test section is not used in the apparatus.

![Figure 1. Schematic of apparatus.](image)

To reach steady state for measurements are challenging in apparatus design, especially in the near-critical regions, because the thermophysical properties of H₂O vary significantly in this region. Therefore, H₂O and CO₂ feeding systems, and automatic control system are specifically designed. H₂O and liquefied CO₂ flow through the metering plunger pump, pulse damper, mass flow meter and back-pressure valve in the feeding system before preheaters. The pulse damper is used to eliminate flow oscillation generated from the pump. The metering pump can be automatically adjusted with a feedback controller according to the output data of the mass flow meter. Therefore, the flow rate throughout the apparatus is expected to be stable. The pressure in the test section is controlled by the regulating valve at the outlet of the condenser. This valve can be automatically adjusted with a feedback controller according to the output data of the pressure transducer at the test section inlet. Therefore, the pressure throughout the test section is expected to be stable. Preheater and test tubes are electrically heated by direct current power with low voltages and high currents. Temperatures at preheater outlets and test section inlet are controlled by the power supply which can be automatically adjusted with feedback controllers according to the output data of thermocouples at each location. Therefore, the temperatures throughout the apparatus are expected to be stable.

2.2 Data reduction

Figure 2 shows the schematic diagram of the vertical test section, which is a Φ6.35×1.65 mm smooth tube. The heated length of the test section is 2 m. An unheated, 250 mm long tube is installed at the inlet of the test section to assure fully developed flow in the test section. The thermocouple arrangement in test section is also shown in Figure 2. Totally 30 K-type thermocouples are used to measure the tube outer wall temperatures, \( T_{ow} \) in 10 locations with three thermocouples spot welded on the top, bottom and side surfaces for each location. The bulk fluid temperatures were measured at the test section inlet and outlet with thermocouples inserted inside the fluid through special customized union tee fittings. The local fluid enthalpies can be linearly interpolated from the known inlet and outlet bulk enthalpies.
[5] with the local fluid temperatures, $T_{b,x}$, referenced from NIST REFPROP and the results reported by our collaborators [6]. The electrical power was defined as a product of the effective value of the voltage and current. The fluid pressure at the outlet of the test section was measured by the EJA 530E pressure transducer. As summarized in Table 1, the temperatures of the supercritical H$_2$O/CO$_2$ mixtures range from 300 to 500 °C, the test section inlet pressure is 25 MPa and the CO$_2$ mass fractions range from 0 to 0.25 in our designed experiments.

![Figure 2. Schematic of test section.](image)

Table 1. Experimental parameters

| Fluid temperature (°C) | Pressure (MPa) | CO$_2$ mass fraction (%) | Mass velocity (kg m$^{-2}$ s$^{-1}$) | Inner diameter (mm) | Heat flux (kW m$^{-2}$) | Flow direction |
|------------------------|----------------|-------------------------|-------------------------------------|---------------------|------------------------|----------------|
| 350-450                | 24             | 0-0.25                  | 800-1600                            | 3.05                | 20-200                 | Vertical upward and downward |
|                        |                |                         |                                     |                     |                        | Horizontal        |

The heat absorbed by fluid in the test section is calculated by

$$Q = U \times I \times \eta$$

(1)

where $U$ is the voltage and $I$ is the current applied on the test tube measured by transducers, and $\eta$ is electrical heating efficiency which is calibrated by the bulk fluid enthalpy gains between test section inlet and outlet in supercritical water experiments. The heat flux on the inner wall is

$$q = \frac{Q}{\pi dL}$$

(2)

where $d$ and $L$ are the inner diameter and length of the test tube. Then, the local heat transfer coefficient is expressed as

$$HTC = \frac{q}{T_{iw} - T_{b,x}}$$

(3)

where the tube inner wall temperatures $T_{iw}$ is determined from the one-dimensional heat conduction equation with internal heat source for fully-circumferential uniform heating condition [7]. All the data were monitored and collected by a computer equipped with a data acquisition board connected with all the sensors used in the experiments. The relative estimated uncertainties in the experiment were summarized in Table 2.

Table 2. Relative estimated uncertainties.

| Parameter               | Uncertainties |
|-------------------------|---------------|
| Pressure (MPa)          | 0.1%          |
| Pressure difference (kPa)| 0.1%         |
| Mass flux (kg m$^{-2}$ s$^{-1}$) | 2.3%       |
| Mass fraction (%)       | 2.9%          |
| Electrical power (kW)   | 1.4%          |
| Fluid temperature (°C)  | 0.6°C         |
3. Results and Discussion

3.1 Stability test

Figure 3 shows the appearance of our established apparatus. Figure 4(a) shows the variations of the test section pressure and inlet temperature with time in the supercritical region for the condition that the CO$_2$ mass fraction is 9.9%, the mass velocity is 1270 kg m$^{-2}$ s$^{-1}$ and the heat flux is 60 kW m$^{-2}$. Results show that the pressure oscillation is below ±0.03 MPa and the temperature oscillation is below ±0.2°C for 24 MPa and supercritical temperatures. Figure 4(b) shows the variations of the test section pressure and inlet temperature with time in the near-critical region for the condition that the CO$_2$ mass fraction is 10.2%, the mass flux is 1596 kg m$^{-2}$ s$^{-1}$ and the heat flux is 60 kW m$^{-2}$. Results show that the pressure oscillation is below ±0.03 MPa and the temperature oscillation is below ±0.3°C for 24 MPa and near-critical temperatures.

| Heat flux (kW m$^{-2}$) | 2.2% |
|-------------------------|------|
| Heat transfer coefficient (kW m$^{-2}$ K) | 18.1% |

Figure 3. Photographs of (a) pumps and mass flow meters, (b) preheaters and test section, (c) condenser, (d) electric controlling and power supplies and (e) automatic control interface.
Figure 4. Stability test (a) in the supercritical region for the condition that the CO\textsubscript{2} mass fraction is 9.9\%, the mass flux is 1122 kg m\textsuperscript{-2}s\textsuperscript{-1} and the heat flux is 60 kW m\textsuperscript{-2}; (b) in the near-critical region for the condition that the CO\textsubscript{2} mass fraction is 10.2\%, the mass flux is 1596 kg m\textsuperscript{-2}s\textsuperscript{-1} and the heat flux is 60 kW m\textsuperscript{-2}.

3.2 Accuracy validation
The measured forced convection heat transfer coefficients were compared with those calculated using the Mokry correlation [8]. Figure 5 shows that the measured and correlated results agree well demonstrating that the experimental data in our experiments was reliable.

4. Conclusion
In summary, we established an apparatus to investigate the heat transfer behavior of H\textsubscript{2}O/CO\textsubscript{2} mixtures in both near-critical and supercritical regions. The apparatus is stable and the measurement uncertainties of forced convection heat transfer coefficients were analyzed and are expected to be below 20\%.

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