Heat transfer to the turbulent flow of supercritical water where glucose oxidation is taking place

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Summary

Heat transfer to and from water under supercritical pressure is of practical importance when supercritical water technology is developed to commercialization. It is usual for a supercritical water process that heat requirement for achieving supercritical state is large and total energy efficiency for a plant is impractically low without heat recovery, or that recovery of heat from water under supercritical state leads to improvement of the system economy. Heat transfer characteristics of turbulent flow of water have been studied in 1960s and 70s, but it was only for the pure water system, and effects of neither solutes nor reactions taking place, which are essential for actual supercritical plants of recent interest, have been studied.

In this study, effects of chemical reaction on heat transfer characteristics were studied experimentally. As a model reaction, glucose oxidation was employed. Aqueous solutions of glucose and oxygen were mixed at the inlet of the tubular test section, and then heat transfer coefficient to the flow where glucose oxidation was taking place was measured by applying direct current to the section while measuring the surface temperature of the outer wall. Direct current application allowed the flow being heated at a constant heat flux. Inner surface wall temperature could be determined by solving Fourier's equation through the tube wall. Bulk temperature of the fluid could be obtained from enthalpy increase of the fluid, which in turn was determined from the applied heat and heat released by the oxidation reaction. Heat transfer coefficient was calculated using this heat flux, inner surface wall temperature, and bulk temperature using Newton's law of cooling.

As a result, effect of reaction was prominent in subcritical temperature range, causing large increase in heat transfer coefficient compared to pure water. This result is of importance in designing supercritical water gasification or oxidation plant in terms of heat recovery.

Introduction

Heat transfer to supercritical water has been studied in purpose of applying the obtained knowledge to high-pressure high-temperature boiler used at a large power plant that could be run at a high efficiency. Several researchers developed correlations for heat transfer to supercritical fluid (Petukhov, 1963; Krasnshchekov, 1966.; Yamagata, 1972). In these studies, pure water was employed since in power plants ultra-pure water was employed as heat transfer medium to avoid possible corrosion and formation of scaling. However, due to the recent interest in use of supercritical water as reaction medium as in supercritical water gasification and supercritical water oxidation, requirement for the heat transfer characteristics to the supercritical water solution of chemical compounds, to the supercritical water suspending solid particles, and/or supercritical water in which chemical reactions are taking place, have arisen. Unfortunately, the knowledge of these heat transfer characteristics is not well obtained. In previous study, the authors conducted measurement of heat transfer coefficient for turbulent flow of supercritical water mixture with methanol and acetone in tubular reactor (Matsumura, 2005). The heat transfer coefficient for supercritical water mixture was well expressed with the modified Yamagata's equation with critical parameters used for those of mixtures. In this study, the authors conducted the measurement of heat transfer coefficient to supercritical water in which chemical reactions were taking place.

Experimental Method

Experimental set-up is shown in Fig. 1. A tubular reactor made of stainless steel (id.: 4.35 mm, od.: 6.35 mm, length: 1 m) was employed as a reactor. Oxidation of glucose in supercritical water was employed, and aqueous solution of glucose and aqueous solution of hydrogen peroxide were delivered to the reactor using two high-pressure pumps. Hydrogen peroxide solution was preheated using a molten-salt bath to a desired temperature with a residence time sufficient to decompose all hydrogen peroxide to oxygen and water. The glucose solution was mixed with the hydrogen peroxide solution just at the entrance of the reactor so that rapid heating up to the reaction temperature was achieved, and rapid start of reaction takes place. In the reactor, oxidation of glucose in supercritical water took place with heat of reaction, and degradation of glucose resulted. After passing through the reactor, the effluent was cooled down, depressurised, and collected for analysis. TOC analysis and HPLC analysis for unconverted glucose concentration was made.

To measure the heat transfer coefficient of the flow of supercritical water in which glucose oxidation is taking place, direct electric current was applied to the reactor wall, while reactor itself being electrically insulated. Generation of Joule's heat inside the reactor wall resulted in heat transfer to the fluid at a constant heat flux. To determine the value of heat transfer coefficient, difference between inner wall temperature and fluid bulk temperature is needed since the heat flux is available from the voltage and current applied to the reactor wall and the inner surface area of the reactor. In this study, the inner wall temperature was determined by measuring the outer wall local temperature of the reactor, and applying Fourier's Law for the heat conduction across the reactor wall. For this purpose the local temperatures of the outer surface of the reactor was measured at 7 points along the flow using K-type thermocouples. The temperature of the bulk flow was determined from the local enthalpy of the flow. The temperature of the flow at the inlet of the reactor was measured



Fig. 1. Experimental set-up.

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with a K-type thermocouple, which allowed calculation of the enthalpy of the inlet flow. By adding the amount of heat from the Joule's heat and heat of reaction, enthalpy of flow at a specific point in the reactor was determined. By knowing the enthalpy, temperature at the location was then obtained. To convert enthalpy to temperature, or temperature to enthalpy, it was assumed that the flow was water, since the concentration of glucose employed was as low as 0.05 mol L⁻¹ at room temperature. The heat of reaction up to specific residence time in the reactor was determined by measuring the temperature increase at the exit of the rector, by changing residence time inside the reactor. Experimental conditions are shown in Table 1.

Results and discussions

Heat of reaction for the reaction taking place in the reactor was found to be almost constant for residence time ranging from 0.5 to 4 s, and around 50 kJ kg⁻¹-water. This indicated release of the heat of reaction was almost completed at the entrance region of the reactor. However, TOC of the reactor effluent decreased with residence time, and indicated that gasification of the feedstock continued without apparent heat of reaction. The glucose was almost completely decomposed at the exit of the reactor.



Fig. 2. Effect of oxygen on local heat transfer coefficient.

Before measuring the heat transfer coefficient of the supercritical flow in which glucose oxidation was taking place, the effect of oxygen in the flow was determined. It was possible that oxygen added to the flow for oxidation itself could affect the heat transfer to the fluid by changing the phase and thermodynamic characteristics of the flow. The obtained heat transfer coefficients are shown in Fig. 2 with the heat transfer coefficients for the case where only supercritical water was present. As can be shown, the effect of oxygen is small.

Then, the effect of product gas was measured by mixing the glucose and oxygen far before the entrance of the reactor so that gasification product was fed to the reactor. It was again possible that the oxidation products changed the phase behaviour and thermodynamic characteristics of the flow, which in turn affected the heat transfer characteristics. The result is shown in Fig. 3, again with the heat transfer coefficients for the case where only supercritical water was present. In this case slight increase in the heat transfer coefficient is observed in the subcritical temperature range by the reaction products. This may be due to the presence of gas bubbles that disturbed the flow and enhanced the heat transfer. This explains why the effect of the addition of the reaction product is negligible in the supercritical temperature region where homogeneous phase is expected.

The effect of the glucose oxidation is shown in Fig. 4. In this case, increase in the heat transfer coefficient by the reaction taking place in supercritical water is prominent in the subcritical temperature range. Again the effect is negligible in the supercritical temperature range. This fact suggests that this increase in the heat transfer coefficient is again due to the phase behaviour. However, the increase is by far large compared to the case when only reaction product was added. Thus, it should be considered to be due to the formation or increase in the volume of gas phase caused by the oxidation reaction. It should be stressed that it is NOT the existence of the gas phase in the flow, but the production/increase in volume of the gas phase that disturbs the flow and enhance the heat transfer.



Fig. 3. Effect of oxidation product on local heat transfer coefficient.



Fig. 4. Effect of glucose oxidation on local heat transfer coefficient.

This finding is of importance when heat exchanger is designed for heat recovery in supercritical water gasification or oxidation. It is known that at the temperature range close to the critical temperature, temperature increase is slow due to the increase in specific heat. This results in longer heat exchanger or larger area for the heat transfer. Since precious metal utilization is needed due to the corrosive condition around critical point, this large area for the heat transfer results in high cost of the process. The finding in this study suggest that if we could cause the formation of gas phase in this temperature region, like adding oxygen to the flow in this region, or by placing gasification catalyst in this region, there should be large improvement in heat transfer characteristics, and thus can reduce the heat transfer area, which in turn reduce the plant cost.

Conclusion

The effect of reaction on heat transfer to the flow of supercritical water was prominent in subcritical temperature range, causing large increase in heat transfer coefficient compared to pure water, and negligible in supercritical temperature range. This fact indicates that this increase is due to the phase behaviour of the flow, and disturbance of the flow by production of bubble, or increase in the volume of gas phase by the reaction should be the reason. This result is of importance in designing supercritical water gasification or oxidation plant in terms of heat recovery.

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