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Effect of the Counter-Ion Form of Acidic Polymer on Its Degradation in Subcritical Water

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Summary

Water that maintains its liquid state at the temperature range of 100°C to 374°C (critical temperature) under pressurized conditions is called subcritical water. Subcritical water has two distinct features: one is a lower relative dielectric constant at higher temperature, and another is a high ion product. The latter feature indicates that subcritical water itself acts as an acid or base catalyst due to high concentrations of hydrogen and hydroxyl ions. Based on this property, subcritical water is expected to be usable for recovering constituent components of polymers in food and agricultural wastes or extracting functional substances from natural resources. Acidic polysaccharides, such as pectin and alginic acid, are found in food and agricultural wastes as well as neutral polymers such as starch and cellulose. The acidic polysaccharides are consisted of some kinds of uronic acids, the counter-ions of which are hydrogen, sodium, potassium ions and so on. In order to efficiently recover the constituent uronic acids from the wastes by their subcritical water treatment, kinetic aspects are required on both hydrolysis of the polysaccharides and degradation of the constituent uronic acids. The kind and counter-ion type of uronic acids would affect their degradation kinetics. In this context, degradation kinetics of galacturonic and glucuronic acids in hydrogen and sodium forms in subcritical water was examined using a tubular reactor.

Regardless of the counter-ion form, glucuronic acid and sodium glucuronate was more easily degraded than galacturonic acid and sodium galacturonate. For both the uronic acids, the sodium form was more fragile than the hydrogen form. The degradation process of galacturonic acid obeyed the first-order kinetics at any temperature. The Weibull probabilistic equation was applied to describe the degradation process of sodium galacturonate. These substrates were almost completely decomposed at prolonged reaction times. However, the degradation of sodium glucuronate leveled off at a fraction of remaining substrate (about 0.07), and was described by a modified Weibull-type equation. During the degradation of glucuronic acid, glucuronolactone was reversibly produced. From the observation, a reaction scheme for the degradation of glucuronic acid in subcritical water was proposed. The changes in the concentration of glucuronic acid and glucuronolactone were analyzed based on the kinetic equations derived from the scheme. The calculated results are found to be in satisfactory agreement with the experimental ones.