THE KINETICS OF NON-CATALYZED SUPERCRITICAL WATER REFORMING OF ETHANOL

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ABSTRACT

Agriculturally produced ethanol, a renewable resource, may be reformed non-catalytically into hydrogen by a novel process utilizing supercritical water, which acts synergistically both as a solvent and as a reactant. By utilizing supercritical water as a reaction medium, many pitfalls of catalytic reformation may be avoided, including catalyst poisoning due to feedstock impurities, catalyst fouling by carbon deposition, and catalyst deactivation. Supercritical water is water above its critical point, 374°C and 22.1 MPa, and exhibits both liquid and gas-like properties and acts a non-polar solvent. Since supercritical water is denser than steam, supercritical water reactors have the potential of being smaller than their catalytic counterparts.

The kinetics of supercritical water reformation of ethanol were experimentally studied using a 1 liter Inconel® 625 Grade 1 alloy tubular reactor. For the experimental study, the temperature was varied between 901 K and 983 K, the water feed rate was varied between 6.4 g/min and 19.7 g/min, the ethanol feed rate was varied between 0.17 g/min and 2.2 g/min, and the pressure was fixed at 24.2 MPa. All ethanol fed was converted into gaseous products: hydrogen, carbon dioxide, methane, ethane, and carbon monoxide, in order of mole fraction from highest to lowest.

Hydrogen was produced by two competing reactions: the direct reformation of ethanol into hydrogen and carbon oxides and the pyrolytic decomposition of ethanol into hydrogen, methane, and carbon oxides. In addition, there is a third, undesirable, reaction

that remarkably occurs in a water-rich environment: the dehydration of ethanol to form ethene and the subsequent hydrogenation of ethene to form ethane. In addition, a low abundance of carbon monoxide in relation to carbon dioxide is indicative that the forward water-gas shift reaction is taking place. Arrhenius activation energies for the direct reformation reaction and the pyrolytic decomposition reaction were also regressed.