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Short communication

Lumped kinetics for supercritical water oxidation of oily sludge

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ABSTRACT

Oxidation of oily sludge in supercritical water was studied in batch reactor under the conditions of reaction temperature from 390 to 450 °C, pressure up to 25 MPa, and time from 1 to 10 min. The oily sludge oxidation undergoes a parallel-consecutive reaction pathways, in which it first decomposes to intermediates of aliphatic ketones, aldehydes and carboxylic acids with conjugated double bonds and via low molecular mass organic acids to the final product carbon dioxide. A 4-lump kinetic model was proposed to describe supercritical water oxidation of oily sludge. The experimental data obtained were used to estimate the six kinetic constants and the corresponding activation energies in the model. The model testing results revealed that the model predictions were in good agreement with the experimental results. The model helps us get good insight into the performance of the batch reactor that would be useful for optimization of supercritical water oxidation of oily sludge.

Keywords: Oily sludge; Supercritical water; Oxidation; Lumped kinetics; Reaction pathway

1. Introduction

Supercritical water oxidation (SCWO), occurring in water above water critical point (Tc = 374 °C and Pc = 22.1 MPa) is a promising and efficient process to treat hazardous organic compounds. When exceeding water critical point, the values of density, dielectric constant, and ionic product of water drop down, so supercritical water acts as a non-polar solvent of high diffusivity and excellent transport properties. In the presence of an oxidant such as O_2, the dense, high temperature environment characteristic of the SCWO process results in rapid and complete oxidation of organic species to CO_2, H_2O, and N_2. SCWO is an emission-free and discharge-free alternative to incineration (Mahmood and Elliott, 2006).

Oily sludge usually contains plenty of waste oil. This waste oil is a mixture of compounds, mainly hydrocarbons. Advance analyses on waste oil show that it is composed of 40–52 wt% alkanes, 28–31 wt% aromatics, 7–22.4 wt% resins, and 8–10 wt% asphaltenes (Marks et al., 1992). Oxidative degradation of such compounds involves a myriad of successive and simultaneous reactions. This makes it unrealistic to envisage comprehensive kinetic studies based on exhaustive mechanistic considerations. At the other extreme, overall power-law kinetic rate approaches are often too simple to adequately describe the SCWO of complex mixtures. The lumped kinetics approach, which has been widely used in solid-catalyzed wet oxidation (Belkacemi et al., 2000), often offers a suitable trade-off between tedious mechanistic/kinetic formalisms and oversimplified power-law representations. No attempt in studying the lumped kinetics in SCWO of oily sludge has been found in the literature. This article presents, for the first time, a rigorous lumped kinetics framework for SCWO of oily sludge. Our hope upon initiating this investigation, was to provide support for designing SCWO reactors for commercial scale.

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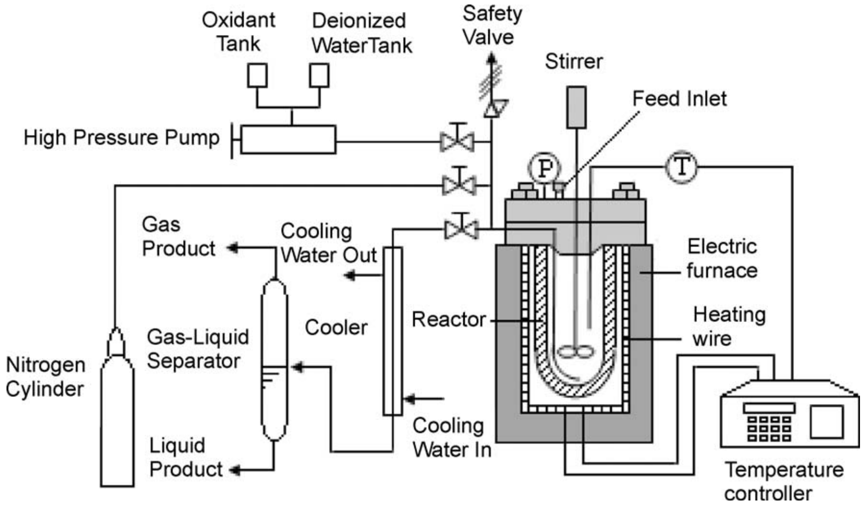

Fig. 1 – Schematic diagram of the experimental setup.

2. Experimental

2.1. Apparatus and procedure

The experiments were conducted in a laboratory-scale, batch reactor with a volume capacity of 650 ml designed to a maximum temperature and pressure of 450 °C and 40 MPa. Fig. 1 shows a schematic diagram of the laboratory-scale, batch reactor system used in this work. All wetted parts, from the pumps to the condenser, were made of stainless steel (1Cr18Ni9Ti). The stirrer was used to keep from the formation of char resulting from thermal cracking of oily sludge at the walls of the reactor. The electric furnace was used as heater. The heating wires of electric furnace were placed below and around the reactor. The reaction temperature was monitored directly using thermocouple (inserted inside the reactor) and controlled within 1 °C by a temperature controller. Before the experiment, the reactor was loaded with oily sludge and deionized water to bring the total volume of liquid to 95–130 ml. Then, nitrogen gas was used to purge the reactor for 10 min. After purging, the reactor was heated about 65 min. Upon reaching the reaction condition of reaction temperatures from 390 to 450 °C and pressures from 25 MPa, reaction temperature remained stable within 1 °C, then the specified amount of H_2O_2 was pressured and fed into the reactor using a syringe pump within 2 s at room temperature. Hydrogen peroxide was used as a source of oxygen. The initial concentration of H_2O_2 is 18148 mg l^{-1} and O_2 excess is 427%. The reaction was conducted for a given reaction time from 1 to 10 min. After the reaction, the sample valve of reactor was opened and the effluent was cooled rapidly in a shell and tube heat exchanger and then depressurized to ambient condition. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder. Gaseous samples were collected with sample tubes.

2.2. Materials and analytical methods

Hydrogen peroxide (analysis purity, 35 wt% aqueous solution) was used as a source of oxygen. The oily sludge was obtained from a crude oil storage tank in the 4th oil production plant of Daqing oil fields. The oily sludge sample contains 58.5 wt% oil, 23.2 wt% water, and 18.3 wt% inorganic particle. The oil contains 37.3 wt% alkanes, 25.4 wt% aromatic hydrocarbons, 36.3 wt% resins, and 1.1 wt% asphaltines.

Analysis of total organic carbon (TOC) in oily sludge and in water was performed respectively using a TOC analyzer (SSM-5000A, Shimadzu) and a TOC analyzer (TOC-VCPH, Shimadzu). Determination of UV_{254} was performed by a spectrophotometry (UV-2550, Shimadzu). A pH meter (PHS-25, Shanghai Precision Scientific Instrument Co., Ltd.) was used to determine pH. A gas chromatograph (SP3420, Beijing Beifenruili Analytic Instrument Co., Ltd.) equipped with a flame ionization detector (FID) was used to analyze the acetic acid content. The column used was 3 m long with 3 mm diameter packed with 80–100 mesh GDX-103 + 2% H_3PO_4. Samples of 1 μl were injected into a hydrogen carrier flow (30 ml/min). The acetic acid was added as external standard for calculation of concentrations. Gas samples were analyzed using a gas chromatograph (GC-14C, Shimadzu) with a thermal conductivity detector (TCD). The carbon molecular sieve column (TDX-01) was used to separate the carbon monoxide and carbon dioxide from gaseous samples. Argon was used as the carrier gas. The system was calibrated with a standard gas mixture containing H_2, O_2, N_2, CO, CO_2 and CH_4.

3. Results and discussion

Table 1 displays the experimental conditions and results obtained from oxidation experiments. As it is shown in Table 1, that CO_2 and CO account for higher percentage of total mass balance. CO_2 and CO can be the only gaseous products detected without regard for trace amounts of H_2 and CH_4. The yield of CO is one order of magnitude higher than that of acetic acid. It had been proved that main refractory intermediate is not acetic acid but carbon monoxide in supercritical water oxidation of oily sludge (Cui et al., 2009). The sum of yields of CO_2, CO and acetic acid is not equal to 100%. The yield of acetic acid is lowest among liquid products. It is found that carbon content in acetic acid is significantly lower than TOC in liquid product. This shows that acetic acid is not only liquid product.

In Figs. 2 and 3, UV_{254} and pH of liquid products are shown as a function of reaction time at different temperatures. Fig. 2 indicates that stronger absorption at 254 nm appears to liquid products. UV_{254} decreases with reaction time. It was found by Onwudili and Williams (2006, 2007a) that PAHs such as pyrene, phenanthrene, naphthalene, fluorene and biphenylene can