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# Hydrogen production by partial oxidation gasification of a phenol, naphthalene, and acetic acid mixture in supercritical water

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## ABSTRACT

A mixture of phenol, acetic acid, and naphthalene was partially oxidized in supercritical water in order to produce hydrogen. The effects of temperature, oxidation ratio (OR), reaction time, and reactant concentrations on gaseous distributions, gasification efficiencies, and reactants removal efficiencies were investigated. Furthermore, the effects of oxygen on the main intermediate products were analyzed, and possible degradation pathways were proposed. Results indicated that higher temperatures significantly promoted the H<sub>2</sub> yield. In addition, small amounts of oxygen (OR < 0.2) accelerated the production of H<sub>2</sub> and CH<sub>4</sub>. The maximum H<sub>2</sub> gasification efficiency (240.25%) and H<sub>2</sub> yield (70.16 mmol g<sup>-1</sup>) were obtained at 560 °C, 25 MPa, reaction time of 20 s and OR of 0.2. Longer reaction time enhanced the gasification efficiencies in 10 s, while the effect was little when reaction times longer than 10 s. The concentrations of the reactants did not significantly influence the gasification efficiencies.

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## Introduction

The conversion of waste biomass and high concentrated organic wastewater to hydrogen could simultaneously recover resources and reduce pollution. Supercritical water (SCW) has been used in many studies as a solvent for the gasification of organic wastes to hydrogen [1,2]. Under supercritical conditions (T > 374 °C and P > 22.1 MPa), SCW behaves very differently than water at ambient temperatures. Under these conditions, SCW exhibits 'organic like'

characteristics, such as a low dielectric constant, and is miscible with gases and many organic substances. Due to these characteristics, SCW could be used to overcome mass transfer limitations across phase boundaries [3].

Many studies have shown that phenol, acetic acid, and naphthalene are the main intermediates during the supercritical water gasification (SCWG) of lignin, cellulose, and other organic wastes [4,5]. The conversions of these intermediates are the key rate controlling steps, which determine the final gaseous product distributions. Thus the

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studies on gasification of phenol and other refractory compounds in SCW were gained increasing attention. Gokkaa et al. investigated the effects of temperature, pressure and catalyst on reaction rate for phenol SCWG and the composition of the gas and liquid products. Results showed that the dominant liquid compound was glycolic acid [6]. Williams et al. suggested phenoxyacetic acid could undergo a hydrogenation to produce phenol and acetic acid in SCWG reaction [5]. However, this is a fundamental issue: indeed, since biomass is an agglomerate of several compounds, it is useful to understand the gasification characteristics of the mixture of the model compounds. A first example of work showing the interactions among different biomass constituents was provided by Goodwin and Rorrer: the authors gasified xylose and phenol in micro-structured device [7]. Another example is represented by the work by Weiss–Hortala. The mixture of glucose and phenol at a mass fraction of 1wt% at 450–550 °C, in the presence of  $K_2CO_3$  catalyst was gasified in supercritical water. They observed that, compared to the single compounds, the SCWG of their mixture gave a gas yield lower than their sum. In other words, phenol was observed to play an inhibitory effect on glucose gasification, which was attributed to the activity of phenol as a free radical scavenger [8]. Castello and Fiori studied the mixture of glucose and phenol in supercritical water gasification process at 400 °C and 25 MPa, which revealed that phenol likely inhibits de-carboxylation reactions and it advantages the pathways involving dehydration reactions [2]. Also the ternary mixtures of cellulose, xylan and lignin were gasified [9]. In addition, Yoshida and Oshima's work showed that, for phenol and other aromatic compounds, the cleavages of aromatic ring hardly occur at temperature around 400 °C, at which some undesirable polymerization of fragments took place during gasification. On the other hand, they found that the partial oxidation is effective to depolymerization [10]. Other researchers also proved that the partial oxidation is an effective way to depolymerization, which also reduces energy-consumption [11]. However, to date there is a lack of studies found in the literatures on partial oxidative gasification of ternary mixtures in SCW, which is important for a better understanding of the open-rings process during partial oxidative gasification.

In the present work, the partial oxidative gasification of the ternary mixtures of phenol, acetic acid, and naphthalene was carried out in a continuous tubular reactor. The effects of temperature, oxygen ratio (OR), reaction time and reactant concentrations on the gaseous product distributions, gasification efficiencies of hydrogen and carbon, and removal efficiencies of the total organic carbon (TOC) and reactants were evaluated. In addition, the possible effects of oxygen on the degradation pathways of the reactants were also investigated.

## Experiment

### Materials

Phenol, acetic acid, and naphthalene (analytical grade) were purchased from China National Medicines Co., Ltd. Hydrogen peroxide ( $H_2O_2$  30 wt% purity, China National Medicines Co., Ltd.) was used as an oxidant. Except for the following part of

“2.4 Effects of reactants concentrations on gas yields and reactants removal efficiencies”, the mass concentration of the phenol, naphthalene and acetic acid was 1 wt%, respectively.

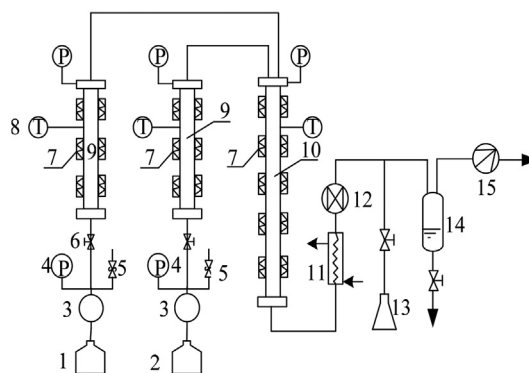
### Apparatus and procedures

The experiments were performed using a continuous flow SCWG reactor. As shown in Fig. 1, the reactor was made of Hastelloy C276, which was designed for temperature of 650 °C and pressure of 40 MPa. The pre-heater and reactor tube are heated by electrical heating wires (5.5 kW) packed with insulation course outside the wall. The temperature was controlled by four K-type thermocouples and one temperature controller. The solution from the feed and  $H_2O_2$  reservoir were pumped by two high-pressure metering pump to the pre-heater and reactor, respectively, and the flow rate was controlled by transducer. Then the solution was mixed into the reactor.

After reaction, the products were cooled down in a heat exchanger and depressurized by a back-pressure regulator (Badger Meter Inc.) to normal temperature and pressure. The liquid product was collected in conical beaker. The gas–liquid mixture was separated in a gas–liquid separator and the volumetric flow rate of gaseous product was measured by a wet type gas meter. And the gaseous product was collected in gas bag. Before each run, the residues from previous experiments were rinsed by deionized water to minimize their possible effects on the following experiments. The gas bag was vacuumed before each collection to avoid the influence of mixing air as far as possible.

### Analysis

The gas composition was determined using a gas chromatograph (Shanghai, GC-112) equipped with a thermal conductivity detector (TCD) and a 3 m × 3 mm TDX-01 packed column; helium was served as the carrier gas and the flow rate and the pressure were 18.5 ml min<sup>-1</sup> and 0.42 MPa, respectively; the column temperature was maintained at 50 °C and



**Fig. 1** – Schematic diagram of the apparatus. (1) feed tank, (2) hydrogen peroxide tank, (3) high-pressure pump, (4) pressure gauge, (5) safety valve, (6) pin valve, (7) heat wire, (8) thermocouple, (9) pre-heater, (10) reactor, (11) cooler, (12) back pressure valve, (13) liquid product collector; (14) gas–liquid separator; (15) wet type gas meter.

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