Phenolic Wastewater Treatment *via* Catalytic Gasification

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Abstract

Phenolic wastewater comes mainly from coking, gas, and petrochemical plants, and other industrial sectors, as well as petroleum cracking ethylene, synthetic phenol, poly Thalidomide fibers, organic pesticides, and the phenolic resin production process. Phenolic compounds are monitoring our priority persistent organic compounds, having already been included in the column of carcinogenic single ring aromatics. In this paper, catalytic supercritical water gasification was applied to treat the phenolic wastewater. The influence of alkali on the gasification of phenolic wastewater with NaOH as catalyst at 580ºC, 27MPa was investigated. The results showed that the NaOH addition increased H_2 fraction and gas yield. The reaction mechanism was analyzed.

Introduction

Phenolic wastewater originated from many sources covering chemical, oil shale retorting, and coking plants, in addition to oil refineries. Phenolic wastewater poses a major hazard, and contains a wide range of industrial pollutants such as phenols, cyanides, unsaturated hydrocarbons, and polycyclic and heterocyclic compounds, which can induce carcinogenesis, teratogenesis, and mutagenesis [1-6]. Furthermore, phenolic wastewater is on the priority list of 12 pollutants to be controlled by the U.S. Environmental Protection Agency [7, 8]. At present, domestic and foreign common methods for treating phenolic wastewater include mainly physical, chemical, and biochemical methods. But the treatment effects are not very satisfactory and are high in operating cost [9-17].

Supercritical water gasification (SCWG) is a promising technology since it can produce hydrogen by complete gasification of organic matters in water without a drying procedure, which is an energy-intensive process and requires pretreatment of aqueous feedstock in conventional gasification processes. Furthermore, supercritical water has an extraordinary ability to suppress char formation during the decomposition of organic compounds [18-21]. Char is known to be a refractory byproduct formed in a significant amount during steam gasification of biomass at atmosphere [22], or hydrothermal treatments of glucose and cellulose [23] in hot liquid water at temperatures up to 350ºC (sub-critical water conditions) unless appropriate catalysts are used. These impressive abilities of supercritical water to treat organic materials are based on its unique thermo physical properties [24]. Under SCWG conditions, water is not only a solvent, but also an active reactant contributing to gasification chemistry [25].

In this study, the influence of NaOH in SCWG of phenolic wastewater was studied. Firstly, the gasification performance of phenolic wastewater with and without NaOH in supercritical water was compared. Then the influence of the accumulative alkali in the reactor on the subsequent gasification of phenolic wastewater without alkali was studied with a longer residence time.

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Experiments

Apparatus and Method

The experiments were conducted in a laboratory-scale batch reactor with a volume of 650 mL designed to a maximum temperature and pressure of 600ºC and 40 MPa. The flow diagram of the experimental setup is shown in Fig. 1. 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 result from thermal cracking of phenolic wastewater at the walls of the reactor. The electric furnace was used as heater. The heating wires of the electric furnace were placed below and around the reactor. The reaction temperature was monitored directly using thermocouple (inserted inside the reactor) and controlled within 1ºC by a temperature controller (Beijing Huaimi Instrumentation Co., N-9000 Digital Controller). Before the experiment, the reactor was loaded with phenolic wastewater and deionized water to bring the total volume of liquid to 100-140 mL. Then, nitrogen gas was used to purge the reactor for 20 min. After purging, the reactor was heated for about 60 min. Upon reaching the reaction condition of reaction temperature 580ºC and pressure 27 MPa, reaction temperature remained stable within 1ºC, then the specified amount of NaOH was fed into the reactor at room temperature. The reaction was conducted for a given reaction time from 15 to 65 min. After the reaction, the sample valve of the reactor was opened and the effluent was cooled rapidly in a shell and tube heat exchanger and then depressurized to ambient conditions. 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.

Chemical Analysis

The gas yield was measured by a wet type flow meter. The composition of the gas product was analyzed by gas chromatography (Perkinelmer Clarus 680) with a thermal conductivity detector (TCD). The high-purity helium is used as carrier gas (purity > 99.999%). A carbon molecular sieve column (TDX-01) purchased from Shanghai Datian Analytic Instrument Co., Ltd. in China is used, operating at 75ºC for 3 min, heating at 55ºC/min ramp to 145ºC, and holding for 15 min. The determination of the sodium content in the aqueous sample was conducted in inductively coupled plasma-atomic emission spectrometry.

Results and Discussion

SCWG of Phenolic Wastewater without NaOh Addition

Phenolic wastewater was gasified without catalyst addition at 580ºC and 27 MPa in the batch reactor for a long reaction time. For comparison, the concentration of the
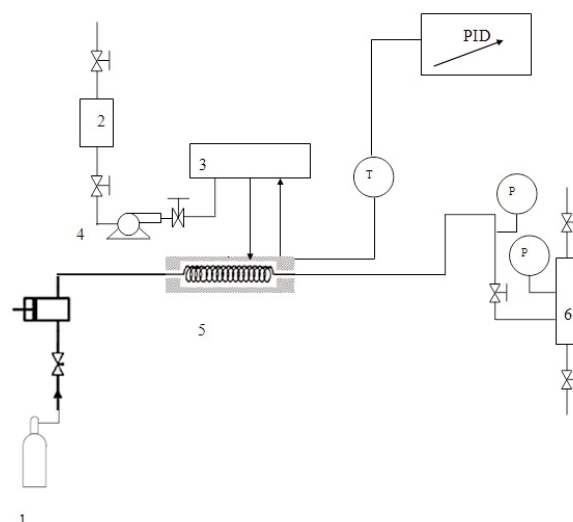

Fig. 1. Schematic diagram of the experimental setup.
1 – Nitrogen tank, 2 – Oxidant tank, 3 – Heater, 4 – High-pressure pump, 5 – Reactor, 6 – Gas-liquid separator

phenolic wastewater is kept at 6000 mg/L for all the experiments in this study. H_2, CH_4, CO, and CO_2 were main compositions of the gas product. The results changed with the reaction time changing (Fig. 2). It can be seen that CO fraction increased with the reaction time and the H_2 fraction decreased. This may be because the reactant concentration in the reactor increased with more phenolic wastewater fed into the reactor in a longer reaction time. The previous literatures indicated that high concentration of biomass is hard to decompose and gasify [24]. More CO, lower gasification rate, and less H_2 were generated in the process of SCWG of biomass with higher concentration, and they are consistent with the variation trend of gasification results at an earlier stage. Moreover, during the process of SCWG, reaction environment in the reactor are changed by phenolic wastewater decomposition. The generated intermediates from decomposition of phenolic wastewater may have negative effects on WGS reaction, which led to higher CO fraction and lower H_2 fraction. After 20 min of reaction, the gas product reached a stable state and remained constant. The gas product under the stable state contained about 27% CO, 34% CO_2, 9% CH_4, and 30% H_2, and the gas yield was 16 mol/kg.

SCWG of Phenolic Wastewater with 25 mg/L NaOH

When catalyst (25 mg/L NaOH) was added to the reactor for SCWG of phenolic wastewater at 27 MPa and 580ºC, the composition and yield of gas product was shown in Fig. 3. The variation was different from non-catalytic gasification. After reaction of 35 min, the composition of gas was stable. The composition of gas product is mainly about 4% CO, 42.5% CO_2, 48% H_2, and 5.5% CH_4 under the stable state. Less CO and more H_2 were generated comparing with the gas product obtained from non-catalytic gasification as described above. This difference was report-
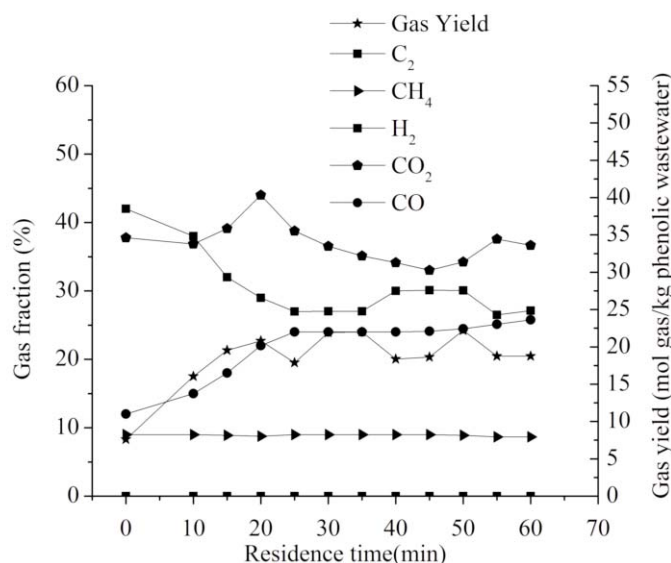
Fig. 2. The composition and total yield of the gas product from SCWG of phenolic wastewater (580ºC, 27 MPa, 6000 mg/L).

ed in several literatures that are attributed to the acceleration of WGS reaction by alkali. In addition, the gas yield increased owning to the presence of NaOH. The total gas yield reached about 21 mol/kg when reaction time was 45 min, which was higher than noncatalytic gasification of phenolic wastewater (about 16 mol/kg).

For SCWG of phenolic wastewater without NaOH addition, another difference was that the gasification results with adding 25 mg/L NaOH took a longer time to reach the stable state. The composition of gas took about 35 min to reach the stable state with adding 25 mg/L NaOH as the catalyst. For the gas yield, longer time was taken (about 45 min). Both of them were longer than SCWG of phenolic wastewater without catalyst addition (20 min, Fig. 2).

As described above, at the earlier stage the increasing concentration and the generated intermediates played a negative role in gasification, which increased the CO fraction and decreased total gas yield, the H_2 fraction. However,

variation tendency of the catalytic gasification results with 25 mg/L NaOH was opposite to non-catalytic gasification of phenolic wastewater. At the earlier stage, CO fraction was continuously decreasing, while H_2 fraction and gas yield were continuously increasing. The opposite variation tendency depended on the precipitation of alkalis in the reactor. As described above, because the inorganic matters kept low solubility in supercritical water and they can precipitate in the reactor. The precipitation of the alkali can lead to the accumulation of the alkali in the reactor within a longer reaction time. It is known that from Le Chatelier's principle, when concentration of alkali increased, the reaction equilibrium is shifted to the positive direction. That is conducive to WGS reaction. In addition, concentration of alkali increased and it led the percentage of activated molecular in unit volume increased. It is known that from collision theory, increasing the percentage of activated molecular in unit volume will lead to higher effective collision
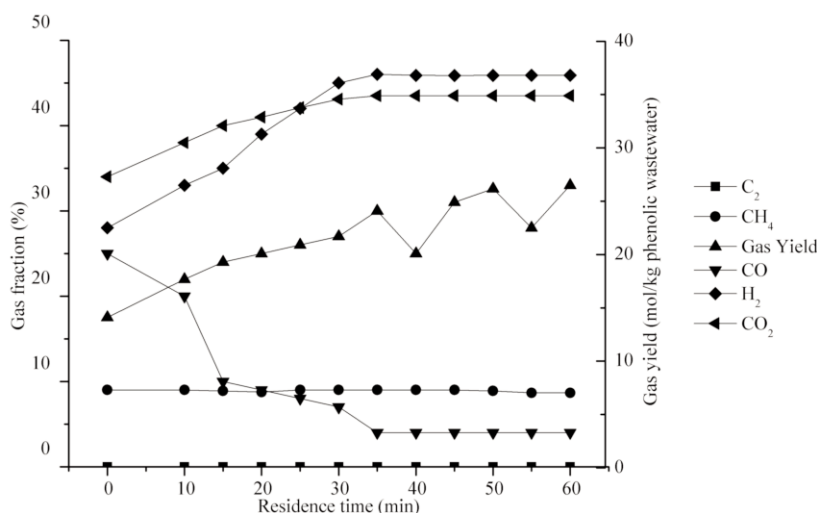

Fig. 3. The composition and total yield of the gas product from SCWG of phenolic wastewater with 25 mg/L NaOH as the catalyst (580ºC, 27 MPa, 6000 mg/L).

and more reaction probability of particles. As a result, a different variation tendency was obtained from that without catalyst, where the H_2 fraction and gas yield increased and the CO fraction decreased with the reaction time in the earlier stage. This may also be the reason for the longer unstable time in NaOH-catalyzed SCWG of phenolic wastewater than non-catalytic gasification.
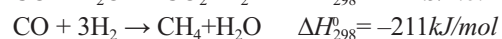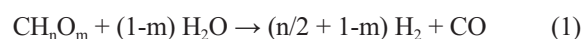
SCWG of Phenolic Wastewater with 75 mg/L NaOH

We also conducted phenolic wastewater treatment via SCWG with 75 mg/L NaOH as the catalyst at 27 MPa and 580ºC. The results also varied with the reaction time at the earlier stage because of NaOH (Fig. 4). The composition of gas and yield from this experiment took less time to reach the stable state compared with SCWG of phenolic wastewater with 25 mg/L NaOH. The composition of gas took about 20 min to reach the stable state (Fig. 4), and it is almost half that with 25 mg/L NaOH. As described above, concentration of alkali in the reactor and their catalytic effect can improve owning to the precipitation and accumulation of Na salts. This caused H_2 fraction increase and CO fraction decrease. While enough alkali for SCWG of phenolic wastewater is accumulated in the reactor after a certain time, the results reached a stable state. The composition of gas from SCWG of phenolic wastewater with 75 mg/L NaOH took less time to reach stable state. The reason may be that the concentration of Na^+ salts provided with 75 mg/L NaOH in this experiment was more than that with 25 mg/L NaOH. Reaction speed for SCWG of phenolic wastewater with 75 mg/L NaOH is faster than that with 25 mg/L NaOH. Therefore, it reached the saturated state more quickly than that with 25 mg/L NaOH.

It is also worth noting that similar gasification results were gained from phenolic wastewater with different concentrations of NaOH at the stable state. After a reaction time of 20 min, the composition of gas product from phenolic wastewater with 75 mg/L NaOH reached stable state (Fig. 4). The composition of gas is mainly about 48% H_2, 43% CO_2, 2% CO, and 4.5% CH_4. This was very similar to the gas product from phenolic wastewater with 25 mg/L NaOH in the stable state under the same reaction condition. The gas yield from SCWG of phenolic wastewater with 75 mg/L NaOH is about 21 mol/kg, which is also close to that with 25 mg/L NaOH as the catalyst (about 20.9 mol/kg). These results may be related to the accumulation of alkali in the reactor.

Reaction Pathway

According to previous works, the main reactions in the gasification of organic compounds in SCW include steam reforming (Reaction (1)), water gas shift reaction (Reaction (2)) and methanation reaction (Reactions (3) and (4)) [26].

$$CH_nO_m + (1-m)\, H_2O \rightarrow (n/2 + 1-m)\, H_2 + CO \qquad (1)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{298}^0 = -41 kJ/mol \qquad (2)$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H_{298}^0 = -211 kJ/mol \qquad (3)$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H_{298}^0 = -223 kJ/mol \qquad (4)$$

It is seen that the reforming reaction in the synthesis gas has two parallel reactions: CH_4 is generated and H_2 is consumed for 1:3 ratio during the methanation reaction (3), which is extremely detrimental for H_2 conversion; the water gas shift reaction (4) is needed. Of course these two reactions cannot be very complete, so the final product will be a resulting gas steam reforming (2) of the product (referred to as synthesis gas). Obviously, to increase the conversion rate of H_2 it is necessary to promote the water gas shift reaction (4), inhibiting the methanation reaction (3).
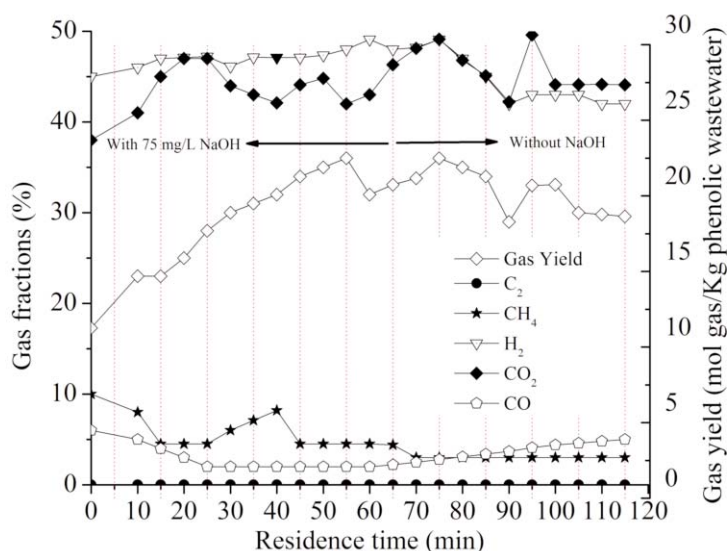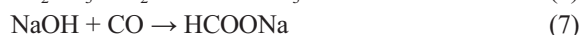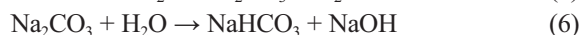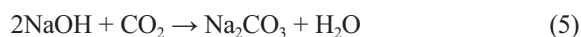

Fig. 4. The composition and total yield of the gas product from SCWG of phenolic wastewater with 75 mg/L NaOH and without NaOH (580°C, 27 MPa, 6000 mg/L).

In supercritical water, NaOH interact with phenolic wastewater and generated water-soluble products and oils, the former can be gasified to generate H_2, CO, CO_2, and CH_4, which promotes water-gas shift reaction in the positive direction, so as to promote H_2.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (5)$$
$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH \quad (6)$$
$$NaOH + CO \rightarrow HCOONa \quad (7)$$
$$HCOONa + H_2O \rightarrow NaHCO_3 + H_2 \quad (8)$$
$$2NaHCO_3 \rightarrow CO_2 + Na_2CO_3 + H_2O \quad (9)$$
$$H_2O + CO \rightarrow H_2 + CO_2 \quad (10)$$

Conclusions

In this paper, catalytic supercritical water gasification was applied to treat phenolic wastewater. The influence of alkali on the gasification of phenolic wastewater with NaOH as catalyst at 580ºC, 27MPa was investigated. The results showed that the NaOH addition increased H_2 fraction and gas yield. The gas product was mainly composed of H_2, CO, CH_4, and CO_2 in SCWG of phenolic wastewater at 27 MPa and 580ºC. The presence of NaOH increased H_2 fraction and decreased CO fraction in the gas product via promoting WGS reaction, and it also increased the gas yield. The precipitated alkali in the reactor still showed high catalytic effect on the subsequent gasification of phenolic wastewater without further addition of the alkali. The catalytic activity was slightly reduced, owning to the transformation of NaOH to Na_2CO_3 and $NaHCO_3$.

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