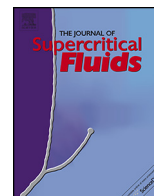




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Primary reactions of lignite-water slurry gasification under the supercritical conditions

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ABSTRACT

The experimental research of lignite-water suspension gasification under the supercritical conditions of water was carried out. The conversion of lignite was studied under the pressure 24 MPa in two temperature range: 290–360 and 390–500 °C without and with additives. Calculation of the activation energies of the reactions of gases formations had shown that NiO–MoO₃–Al₂O₃ had acted as a catalyst, sodium and calcium hydroxides had behaved as reactants. The general scheme of the mechanism on formation of the gas products containing H₂, CH₄ and CO₂ was examined. It was shown that at the subcritical temperature the gas products were formed mainly from hydrogen of coal and oxygen of mineralized water. Carbon of lignite behaves like an acid, and water is as a base at the subcritical temperature; they switch their roles at the supercritical temperature. 80% of hydrogen and oxygen of gas products were of water origin at the supercritical temperature. C, O and H conversions at initial rates of reactions with gases distribution have been synchronously analyzed for primary reactions clearing. It had found that the gasification of lignite-water suspension under the supercritical pressure had at least four types of interactions: thermal decomposition of coal, carbon oxidation by oxygen of water as well as hydrolysis and hydrocracking of coal. Oxidation of carbon was dominant for the process at the subcritical temperature on water. Hydrolysis of C–C bonds of coal was the main at the supercritical parameters of water.

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1. Introduction

Gasification of the aqueous suspensions of carbon materials (coal and/or biomass) under the supercritical conditions [1–3] is at the great interest because of the prospect of the production of valuable raw material for the chemical and petrochemical industry – synthesis gas. Last one can be converted to methanol or C₂–C₄ alcohols, ethers as well as gasoline and diesel fuel [4,5] or used to production of hydrogen [6–8].

Traditional processes of gasification are carried out at the temperature of about 800–1000 °C [9]. Lower temperature limit is followed to achieve a sufficient rate of gasification of biomass. And the top temperature is for the most types of coal [9–11].

One way to reduce the operating temperature of chemical process is the addition of catalysts [12–14]. Thus, supercritical steam gasification (600–700 °C, 23–30.0 MPa) of carbon materials (such as coal and biomass) to hydrogen can be catalyzed with the compounds of iron (Fe₂O₃, Fe₃O₄) [15–18], and Ni [19–22], Rh, Ru, Pt,

Pd as metals or deposited on the carrier [13,23,24], cerium oxides [25,26] and molybdenum oxide [24]. Compounds of alkali and alkaline earth metals (Na, K, Cs, Ca, Mg) [19,21,27–29] and carbon [30,31] could also be the catalysts.

The second way for temperature reduction is to use the supercritical water as reactive medium. Gasification of carbon compounds to methane at a temperature around critical (350–400 °C, 30.0–56.0 MPa) is usually carried out in the presence of potassium or calcium carbonates [30,32]. Gasification in hot compressed water (215–265 °C, 29.0–56.0 MPa) is investigated on the example of model biomass compounds like glucose, sorbitol, methanol and glycol in the presence of heterogeneous catalysts (Pt, Ni, Ru, Rh, Pd, Ir) [30,33,34]. Coal gasification is investigated just above 400 °C [35,36]. Lignite gasification below 380 °C is studied insufficiently.

Today the mechanism of traditional coal steam gasification is well developed with general scheme given in [37,38]. It includes an initial stage of fast pyrolysis of coal, the interaction of formed tar and carbonaceous compounds with water vapor and carbon dioxide, steam reforming of methane and volatile hydrocarbons as well as water gas shift reaction. The processes occur at temperatures above 600 °C under the atmospheric or slightly elevated pressure. It was shown that the steam gasification of carbon

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occurs by radical mechanism. Syngas, *n*-alkanes and aromatic compounds are dominated among its products. Kinetic model of steam gasification of coal is developed by Blackwood [37], Mühlen [38] and improved by Hart with Calo [39] and Mitchell [40,41].

But the proposed mechanisms for steam gasification couldn't be applied for the supercritical gasification. Firstly, it is because of their substantial differences of technological parameters. Thus, temperature of the supercritical conversion is twice lower than for steam gasification (300–500 against 800–1200 °C); the pressure is higher in order (24 and 2 MPa respectively); the reaction medium is at the sharply divergent conditions, although represented by the same agent (supercritical fluid against superheated steam). Synthesis gas CO + H₂ is the main product of steam gasification. Gaseous product of the supercritical gasification of brown coal suspension has no carbon monoxide within detection limits up to a temperature of 500 °C.

The second, the mechanism of steam gasification does not take into account the interaction of the supercritical water with the mineral part of lignite. The main organic matter of Alexandria lignite is kolinit. It also contains teletenit, leptynit and inertinit. The lignite humidity in raw state ranges from 35 to 65%, it dries up under storage to 15–25%. The mineral substance is a third part of the organic mass. The major minerals are quartz, kaolinite, montmorillonite, gypsum, and pyrite. The minor minerals are feldspar, garnet, biotite, calcite, zeolites, tourmaline, muscovite, magnetite, rutile, opal, and limonite [42].

The third, the mechanism should take into account the properties of water and aqueous suspension at the supercritical conditions. The replacement of gas or liquid reaction medium to the supercritical fluid has led to changes medium's properties. In the process of gasification of aqueous suspensions in the state of supercritical fluid is transferred to one of the reagents gasification – water. In particular, under the pressure of 25 MPa density of hot compressed water slowly reduced to 840–730 kg/m³ when it had heated to 200–300 °C [43,44]; dielectric permittivity ϵ is decreased from 40 to nearly 20 with the increase of ionic product to three orders (from 10⁻¹⁴ to 10⁻¹¹) [45,46]. Further heating from 300 °C to the critical temperature decreases the density of water more than doubled, with a further reduction to the dielectric constant ϵ to 10. The subcritical water reveals an increased solubility of organic compounds.

Under the conditions of supercritical temperature and pressure the density of water is less than 300 kg/m³, the dielectric constant is reduced to 6 [45,47]. So the supercritical water is a poor solvent for ionic compounds such as inorganic salts [48] but completely miscible with many organic compounds and gases [46,49,50]. Above the critical temperature the water ionic product decreases rapidly to 10⁻¹², but will increase with increasing pressure. It allows to predict that the subcritical water is a source of ions H₃O⁺ and OH⁻ that initiate ion reactions. At the supercritical state the water molecules react by radical mechanism through the formation of radicals H• and •OH [7,51].

So, to date the mechanism of the gasification of lignite-water suspension under the supercritical conditions of water isn't cleared completely. In this regard, the purpose of the study was to determine the general scheme of the mechanism for lignite-water slurry gasification under the supercritical conditions of water. We have made it from the assessment of primary transformations of three main elements into gaseous products: carbon, hydrogen and oxygen. It's clear that carbon is from lignite. But hydrogen and oxygen could release from both lignite and water. So the experimental results of lignite and water conversion have made possible the evaluation of the contribution of some elementary reactions in the general scheme of the gasification process.

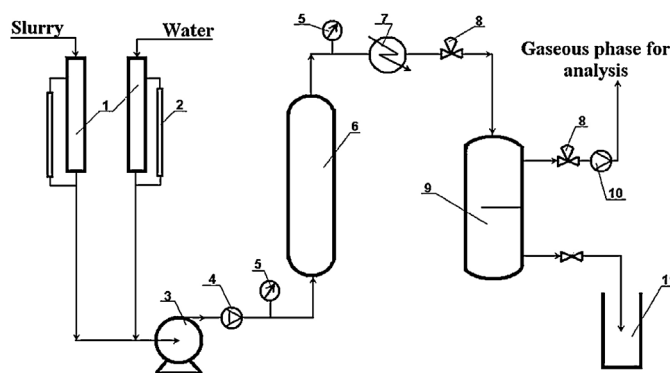


Fig 1. The laboratory set of lignite-water suspension gasification: 1–feedstock reservoirs; 2–level meter; 3–high pressure pump; 4–back valve; 5–manometers; 6–reactor; 7–condenser; 8–pressure regulator; 9–separator; 10–gas meter; 11–reservoir for liquid and solids.

2. Material and methods

2.1. Materials

Alexandria lignite (Ukraine) has quality rating of: $W = 2.7$, $A^d = 24.8$, $C^{daf} = 62.66$, $H^{daf} = 6.0$, $S^{daf} = 4.96$, $N^{daf} = 0.98$, $O = 25.4\%$. Lignite-water slurry was prepared by mixing of lignite (fraction of 50 μm) and deionized water in mass ratio 3/7.

Gasification at the supercritical conditions was carried out at the laboratory unit (Fig. 1) with semiflow reactor (pos. 6, useful capacity of 100 cm³). Firstly, the lignite-water slurry was filled up into the reactor. Then additional portion of water was pumped into the reactor (6) to provide the supercritical pressure by water (≥ 22.1 MPa). The working pressure was kept up forced at level of 24 ± 0.1 MPa. After this, reactor was heated to the desired temperature under the water pumping with constant discharge 27 g/h.

All the experiments were performed under the pressure of 24 MPa in two ranges of temperature: 290–360 and 390–450 °C. When the system had reached to operating temperature, the water suspension of lignite had been converting under the supercritical pressure ($P = 24$ MPa) for six hours. The products from the reactor (6) were directed to the separator (9), where the gas, liquid and solid phases were separated. The gas phase was containing hydrogen, carbon dioxide and/or monoxide, and methane. Liquid phase had unconverted lignite-water slurry. Solid phase was charcoal. No recirculation of gaseous product or water-lignite suspension was used.

The accumulated gas phase was passed to chromatographic analysis every hour. The content of H₂, CO, CO₂, and CH₄ in the gas phase was determined using a chromatograph “Chrom-5” (Czech Republic) with the detector of thermal conductivity. Gases were divided into chromatographic column from stainless steel with length of 1.5 m and an internal diameter of 3 mm. The column was filled with 10% NiSO₄ deposited on SKT coal. Carrier-gas was the purified argon with discharge 24 cm³/min. The column and evaporator temperatures were 60 and 120 °C respectively. The detector current was 0.04 A. The gas sample was introduced into the chromatographic column with dispenser of 0.245 cm³. The analysis of gas content was carried out using the method of absolute calibration at the heights of chromatographic peaks.

2.2. Reactive additives

Firstly the lignite conversion was studied without any additives, only with own mineral substance as control run. Later lignite conversion was studied with three additives: commercial sodium and calcium hydroxide as alkaline ones and commercial nickel-

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