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Kinetic study on catalytic gasification of a modified sludge fuel

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Abstract

A new type of mixture fuel, sludge–oil–coal agglomerate (SOCA), was catalytically gasified with steam in a thermobalance reactor under atmospheric pressure. All the four catalysts studied (K_2CO_3, CaO, NiO and Fe_2O_3) were found capable of enhancing the steam gasification rate and significantly increasing the conversion of carbon. The ranking of catalytic activity was found to be $K_2CO_3 \gg CaO > NiO > Fe_2O_3$. A modified volumetric-reaction model in the literature was used to describe the conversion behavior of the steam gasification studied by evaluating the kinetic parameters. Expressions of the apparent gasification rates for SOCA were presented for the design of catalytic gasification processes.

Keywords: Sludge; Coal; Oil; Steam gasification; Catalyst; Thermobalance; Kinetics

1. Introduction

The catalytic gasification of coal has been studied extensively to develop efficient and economic processes for converting coal to clean fuel gas (Haga, Nogi, Amaya, & Nishiyama, 1991; Mckee, Spiro, Kosky, & Lamby, 1985). The gasification reaction of carbon with steam is:

$$C + H_2O = CO + H_2 \qquad \Delta H = 118.9\,\text{kJ/mol}$$

Alkali, alkaline earth and transition metals present in the mineral matter of raw coal, or added artificially by physical mixing or impregnation, are effective catalysts for the above reaction (Kwon, Kim, Kim, & Park, 1989). The group-VIII metals (iron and nickel) are active only in the elemental state, require higher temperature than alkali metals and are easily poisoned by sulfur. The methods of catalyst preparation and addition have significant effects on the catalytic activity in coal gasification. Alder, Hüttinger, and Minges (1984) claimed that for transition metals wetting of the catalyst can enhance gas adsorption by the catalyst. Therefore impregnation is popularly applied as the method for catalyst addition.

Sludge, with a carbon content of around 50% (Werther & Saenger, 2000) and produced in large quantities in many countries, is a new resource for gasification processes. Wet sewage sludge from waste water treatment plant with a water content of above 80% needs to be de-watered and dried to a water content of less than 60% before its use as a fuel. Furthermore a bad smell is inevitable during the above processing. Instead, wet sewage sludge can be used directly as a component for making a fuel mixture, e.g., sludge–oil–coal agglomerate (SOCA) (Kang, Lee, Ryu, & Lee, 2007), thus eliminating both de-watering and drying and avoiding the bad smell during processing. In addition,

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Nomenclature

A	pre-exponential factor (1/h)
E	activation energy (kJ/mol)
k	average reaction rate defined by Eq. (6) (1/h)
P_{H_2O}	partial pressure of steam (atm)
R	gas constant (8.314 J/mol K J/mol K)
t	reaction time (min)
T	reaction temperature (K)
W	sample mass at certain time (g)
W_{ash}	mass of ash (g)
W_o	initial mass of char on dry base (g)
X	carbon conversion

Greek letters

α, β	constants in Eq. (2)

the unnecessary inorganic components in sludge can be separated through the gasification of SOCA and waste oil can be converted to fuel.

The rate of catalytic gasification of coal or wood was found (Song & Kim, 1993) to be determined by their carbonaceous structure and the method of sample preparation, their anions and pretreatment procedures, and also by the quantity and chemical form of metallic elements, either inherent or added as catalysts. Since the properties of SOCA are expected to be different from those of its constituents (coal, sludge, and oil) the catalytic steam gasification behavior of the modified sludge calls for careful investigation. Based on literature survey, four catalysts were selected, K_2CO_3, CaO, NiO and Fe_2O_3 in this study. The aims of this study are (1) to evaluate the catalytic activities of the four catalysts in the steam gasification of SOCA and (2) to provide kinetic information of steam gasification of SOCA for the design of gasification processes.

2. Experimental

2.1. Ultimate analysis and proximate analysis

The activated sludge process involves sewage treatment in which air or oxygen is forced into the sewage liquor to develop a biological floc which reduces the organic contents of the sewage. Activated sludge, the active biological material produced in activated sludge plants, is a brown floc, largely composed of saprophytic bacteria but also with an important protozoan flora mainly composed of amoebae, Spirotrichs, Peritrichs including Vorticellids and a range of other filter feeding species. Both aerobic and anaerobic bacteria exist in the activated sludge, but the preponderance of species is facultative, capable of living in either the presence or absence of dissolved oxygen.

The mass fractions of the components in SOCA are: sludge 14–22%, oil 13–17%, and coal 65–70%. The ultimate and proximate analyses of SOCA are presented in Table 1, indicating that the content of carbon in this fuel is as high as 70%, the content of hydrogen is around 6% while that of oxygen varies.

Table 1
Ultimate and proximate analyses of activated SOCA

Ultimate analysis (wt.%)		Proximate analysis (wt.%)	
Carbon	79.7	Moisture	8.74
Hydrogen	6.38	Volatile	44.57
Nitrogen	1.19	Fixed carbon	40.02
Sulfur	0.46	Ash	6.67
Oxygen	5.6	HHV (kcal/kg)	7530

Proximate analysis shows that the moisture content is quite low, below 10%, the volatile matter is fairly high and fixed carbon is around 40%. The higher heating value is higher than the average value of 6000 kcal/kg for coal.

2.2. Sample preparation (SOCA + catalyst)—impregnation method

The new fuel, SOCA was ground and screened to 0.7 mm, weighed and soaked for 2 or more days in a solution or slurry (because some catalysts are insoluble in water) of a catalysts whose loading was 7 wt.% (mass of impregnated salt per unit mass of SOCA), and then excess solution was removed by vacuum filtering, and the sample was heated to 150 °C under vacuum for 24 h.

2.3. Experimental equipment

The thermobalance, shown schematically in Fig. 1, consists of a reactor, 0.055 m i.d. × 1.0 m high, made of stainless-steel tube and equipped with a 3 kW external electrical heater. Steam was generated from an electric steam generator which consists of a 1/8 in. copper tube, 1.0 m in length, on which was coiled a flexible electrical heater. The flow rate of steam was controlled by a micro-pump. The temperature of the thermobalance was controlled by a K-type thermocouple located 5 mm below a stainless-steel wire-mesh sample basket suspended from an electronic balance (Mettler Toledo), and the mass signal of the balance was recorded by a personal computer to monitor the change of mass during experiment. More detailed explanation can be found in our previous study (Sun et al., 2007).

All experiments were carried out after first flushing the thermobalance with N_2 gas. When the reactor was heated to the desired reaction temperature under nitrogen flow, the sample was placed in the sample basket through the hatch and the sample basket was lowered to the center of the reactor using a motor-driven winch. There was a rapid initial mass loss within several minutes due to the evolution of moisture and volatile matter from the sample. Then the mass of the sample became constant and a mixture of steam and N_2 was introduced into the reactor for gasifying the sample during which, the variation of the sample mass was recorded continually every 3 s. When the sample mass became nearly constant again, which signifies completion of gasification, the gas flow was switched to air to burn out the residual carbon. The content of ash could then be determined.