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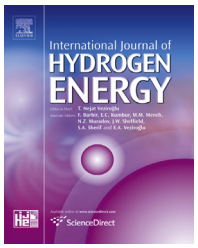

Catalytic decomposition of biomass tar compound by calcined coal gangue: A kinetic study

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ABSTRACT

The kinetics of thermal decomposition of biomass tar was studied using phenol as a model compound under isothermal conditions by a two stage micro fluidized bed reactor. Calcined coal gangue and γ-Al_2O_3 were employed as catalyst, particularly gangue representing one type of catalyst for tar decomposition that prepared by the thermal conversion of inferior coal. The Friedman method and integral method were employed for the determination of kinetic parameters for forming H_2 and CO by phenol decomposition. The results demonstrated that the activation energy for generating H_2 was lower compared with CO, indicating that the reactions for forming H_2 was easier in phenol decomposition. Higher activation energies for H_2 and CO generating were obtained using gangue as catalyst, implying that the catalytic performance gangue was slightly lower toward phenol decomposition process due to the high content of SiO_2 in gangue.

Introduction

With regard to global issues of sustainable energy and environmental protection, biomass thermal conversion is considered to be a promising technology in reaching targets for renewable energy and greenhouse gases emissions reduction [1]. However, a serious problem in the utilization of biomass gas from thermal conversion, such as pyrolysis or gasification, is the trouble with tar contained in the gas [2–4]. Tars are formed during the thermal decomposition of biomass in series of complex reactions. Tar can be defined as a complex mixture of condensable fraction of the organic products, which are largely aromatic hydrocarbons, including single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbon (PAH) hydrocarbons [5,6]. Tars may condense on cooler surfaces downstream, leading to blockage and fouling problem in some equipments. In addition, operational problems may be caused as a result of the possible formation of aerosols and soot formation [7,8]. Thus, researching on tar elimination from the product gas is becoming increasingly attractive.

Tar reduction by using a hot gas cleaning catalyst has been widely considered as a potential method to convert tar into clean gases at lower temperature [9,10]. Among all the catalysts, char from the pyrolysis of coal or biomass has become of interest because char production and tar reduction can be

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simultaneously implemented inside the reactor by controlling the parameters and configuration [11,12]. Coal gangue is the unexpected product of coal mining with average production of 10% during the raw coal production in China [13]. Coal gangue has low carbon content and high oxides content (both metallic oxides and nonmetallic oxides) [14,15], implying that the ash of gangue has catalytic performance toward biomass tar. Thus, this material can be chosen as a catalyst for the tar decomposition.

The catalytic decomposition characteristics of biomass tar have been studied using char and char-supported catalysts from biomass or coal. Phenol, benzene and naphthalene are usually chosen as model compounds. The conversion of naphthalene and phenol was carried out by El-Rub et al. [16] to compare the catalytic performance of biomass chars with other catalysts, founding that biomass chars gave the good phenol and naphthalene conversion. Zhang et al. [17] studied the *in situ* tar reforming of coal tar using brown coal char, showing that the major components of tar cracked over the hot char bed. Coal chars were employed as well by Wang et al. [18] to catalyze the tar reforming reactions during the pyrolysis and gasification of brown coal, the results showing that chars derived from brown coal showed excellent catalytic activity for tar reforming and the formation of large aromatics in tar was enhanced. The catalytic property of coal and biomass char depends upon the metallic oxides in the ash. Thus, there are reasons to believe that the coal gangue has the catalytic performance toward tar due to its high metallic oxides content.

A significant fraction of biomass tars originates from pyrolysis and gasification products mainly composed of phenolic compounds [19,20]. Phenol and phenolic compounds are identified as typical representatives by Morf et al. [21] for the secondary tar component class. Phenol appeared in all tar classes as precursor or intermediate and belonged to the problematic producer gas impurities for the practical application of biomass gasification. The simplest phenolic model compound with a phenyl and a hydroxyl, which is phenol, has been chosen as a surrogate for primary tar, as a first step toward developing an advanced elementary kinetic model [22]. A thorough understanding of pyrolysis kinetics of phenol is a key component in the efficient design of its decomposition processes. However, there have been very few works on detailed kinetic mechanism for phenol decomposition against well-controlled thermal conditions with analysis of products.

Thermogravimetric analysis (TGA) has been generally used to analyze kinetics of gas–solid reactions based on monitoring the mass variation of a spot sample under a specified heating program. For isothermal conditions, the fluidized bed reactor can be used to obtain kinetic parameters based on measuring the releasing of major gas components in the thermal degradation of the tested sample [23–25]. As suggested by Yu et al. [26,27], compared with TGA, the micro fluidized bed reactor has the advantage in the minimized diffusion inhibition, online feed of reactant sample, quick heating for isothermal conditions, and the test at arbitrary temperatures and in various gaseous atmospheres. Toward liquid materials like biomass tar in this work, the micro fluidized bed reactor was therefore employed to calculate the kinetics and analyze the reaction mechanism based on the measured time-series of product gas composition.

Since a large amount of coal gangue is produced during coal mining activities and its potential toward biomass tar decomposition. The decomposition characteristics of biomass tar using gangue as catalyst has both theoretical research meaning and practical applicative values. The aim of this work is to deeply understand the phenol conversion process using calcined coal gangue as catalyst and γ-Al_2O_3 were employed as control. The kinetics of phenol catalytic decomposition was investigated experimentally at intermediate temperatures (750–850 °C) to predict the formation of light gases (H_2 and CO) under isothermal conditions using a two-stage fluidized bed reactor.

Experimental methods

Sampling

The ultimate and proximate analyses of coal gangue are shown in Table 1. In order to avoid the influence of volatiles and fixed carbon of gangue on the gas generation of phone decomposition, the gangue was calcined for about 30 min at 850 °C under air atmosphere until it turned into creamy-white before the test. The chemical composition of the gangue after calcination was analyzed as well and listed in Table 1. It can be seen that the ash of gangue after calcination mainly consists of SiO_2 which is inert toward tar decomposition. The most abundant of the metallic oxides is Al_2O_3, which accounts for 31.5% of the ash. Thus, γ-Al_2O_3 was chosen as a catalyst in comparison to study the catalytic characteristics of gangue for phenol decomposition. The particle size of calcined gangue and γ-Al_2O_3 was in the range of 100–150 μm.

Table 1 – Chemical composition of coal gangue.

Sample	Gangue
Proximate analysis (wt.%, db)	
Moisture	1.27
Volatile	10.21
Fixed Carbon	33.74
Ash	54.78
Ultimate analysis (wt.%, daf)	
Carbon	74.38
Hydrogen	4.73
Oxygen (diff)	18.92
Nitrogen	1.58
Sulfur	0.39
Elemental ash analysis (wt %)	
SiO_2	57.2
Al_2O_3	31.5
Fe_2O_3	3.13
CaO	0.64
K_2O	0.46
Na_2O	0.85
MgO	0.93
P_2O_5	0.03
SO_3	0.01

Notes: db: dry basis; daf: dry ash free basis; diff: calculated by difference.