Lv Pengmei, Ph.D., “Study on the characteristics of hydrogen production from biomass catalytic pyrolysis and gasification”, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, August, 2003.

Abstract

Under the background of being confronted with serious energy crisis and environment pollution, the world is dedicated in the research and development of hydrogen energy and has got some achievements. The prospective future of hydrogen rich gas from biomass gasification makes it a major concern of researchers all over the world. The technology of biomass air gasification produces a gas with low hydrogen content and quite a lot of tar, which impedes its further application. Steam introduction and catalysts application are two effective methods to increase hydrogen content and decrease tar yield. In this study, an original investigation on the properties of biomass fast catalytic pyrolysis and its kinetics model has been performed and important conclusions are achieved. Then one small-scale fluidized bed is developed to perform biomass catalytic gasification and fluid-cracking catalysts and catalysts used in fixed bed reactor are employed together in the process. This innovative method simplifies the experimental facility and gets good results for cracking tar and producing hydrogen-rich gas.

Biomass catalytic pyrolysis is the main reaction that occurs in the process of biomass catalytic gasification. To have a study on its characteristics is helpful to optimize the technique of biomass catalytic gasification in the fluidized bed. By means of thermogravimetry, the properties of biomass catalytic pyrolysis are investigated. The results reveal that a temperature range of 600-700 °C is suitable for fuel gas production from biomass pyrolysis. A higher temperature is favourable for higher gasification efficiency and a longer gas residence time benefits more gaseous products. The pyrolysis rate of cellulose is the fastest among the samples tested in this study, from which it can be inferred that it is suitable for the process of gasification aimed at getting gaseous products. Calcined dolomite takes effect on tar cracking when temperature is over 600 °C and then 2 weight loss peaks are observed on the thermogravimetry curve of biomass pyrolysis. Nickel-based catalyst has effect on tar cracking even at a rather low temperature and its function can’t be observed on the curve of weight loss curve. The catalytic pyrolysis of 2 kinds of wood sawdust, one kind of lignose and cellulose can be modeled by one first-order reaction. The activation energy of cellulose pyrolysis is the highest, being 142-156 kJ/mol, and the one of lignose is the lowest, being about 25 kJ/mol.

Then an apparatus for fast pyrolysis of biomass is designed and set up to simulate the fast heating rate in the fluidized bed. The features of biomass fast catalytic purolysis in the apparatus are studies, while the kinetics model of biomass catalytic pyrolysis is put forward. The results show that both calcined dolomite and nickel-based catalyst can elecate the hydrogen content greatly. The nickel-based catalysts has a stronger effect and the hydrogen content is nearly doubled. The content of CH_4 can be reduced a lot through the use of nickel-based catalysts. Calcined dolomite can also decrease the content of CH_4 to a smaller extent. The model is a combination of three-stage model and second-reaction model and it assumes that biomass first decomposes to gaseous products, tars and chars via three competitive reactions and the tars go through a second cracking reaction to produce gases and chars. The proposed model fits well with the calculated

date go from pyrolysis tests of wood and sawdust, lignose and cellulose. The calculated reaction order of n ranges betweem 0.66 and 1.57; the value of n calculated from biomass pyrolysis with nickel-based catalyst is larger than the one calculated from the use of calcined dolomite. When dolomite is used with temperature being lower than 800 °C, the activation energy of tar cracking is higher than biomass pyrolysis. Therefore it is concluded that calcined dolomite needs to be used at a temperature higher than 800 °C.

And then the characteristics of hydrogen rich gas production from biomass air-steam gasification in the fluidized bed are studied. The concept of Hydrogen Yield Potential is put forward to have a deeper analysis on hydrogen production from biomass. From the experimental results, it can be seen that higher reactor temperature, proper equivalence ratio (ER) and steam to biomass ratio (S/B), being 0.23 and 2.02 respectively in the current study, is more favorable for hydrogen production. The smaller biomass particle size will also contribute to more hydrogen yield. The highest hydrogen yield, 71g H^2/kg biomass (wet basis), is achieved at a reactor temperature of 900 °C, ER of 0.22, S/B of 2.70.

At last, with use of dolomite in the fluidized-bed gasifier and a use of nickel-based catalysts in the fixed bed reactor downstream the gasifier, the properties of hydrogen yield from biomass are investigated. At the exit of the catalytic reactor, the content of H_2 and CO_2 is increased and the content of CH_4, CO and CO_2 is decreased. In the gaseous products, the average content of H_2 exceeds over 50 vol %; CO_2 content is lowered to below 1 vol % and nearly half of CH_4 is converted after the catalytic reactor. Over the ranges of experimental conditions examined, the highest gas yield gets to 130.28 g H_2/kg biomass, wet basis. The tar cracked by nickel-based catalysts is over 50 wt %. The lifetime test of 350 minutes for nickel-based catalyst shows that a higher temperature will extend its lifetime. The hydrogen conversion and tar cracking in the catalytic reactor can be described by one first-order reaction model.

The above study provides a quite systematic understanding on the properties of hydrogen-rich gas production from biomass catalytic pyrolysis and gasification. It supplies some fundamentally idea on the theory and experiments of hydrogen production from biomass.