INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–8

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Characteristics of rice husk tar pyrolysis by external flue gas

Ming Zhai[*], *Xinyu Wang*, *Yu Zhang*, *Peng Dong*, *Guoli Qi*

School of Energy Science and Engineering, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China

ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form
9 July 2015
Accepted 11 July 2015
Available online xxx

Keywords:
Biomass pyrolysis
Rice husk oil
Rice husk tar
Tar distillate
External flue gas
Tar cracking

ABSTRACT

Biomass tar is a major problem in both pyrolysis and gasification of biomass. Considering the process and conditions of tar formation, an external flue gas pyrolysis system for rice husk tar pyrolysis was designed. The characteristics of rice husk tar pyrolysis by external flue gas were investigated. The GC–MS analysis was applied to analyze the composition of rice husk tar and its distillate. TGA was carried out to investigate the properties of rice husk tar and its distillate. Results show that when the temperature is below 500 °C, the liquid product of rice husk pyrolysis is rice husk oil; when the temperature reaches about 700 °C, PAHs increase significantly and the liquid product is tar; when the temperature reaches 800 °C, a large amount of charcoal liquid is produced. There are many similarities between rice husk tar and its distillate. After distillation, the content of the primary compounds like naphthalene, anthracene, phenol and its derivative increases, while the content of fluorene and phenanthrene decreases. Temperature plays an active role in the pyrolysis of rice husk oil and tar, and the proportion of compounds in the pyrolysis product. The weight loss of rice husk tar distillate can be divided into three regions, and it reaches a maximum at about 160 °C. The experimental data provide a reference to the optimization of the operating conditions for rice husk pyrolysis and tar cracking.

Introduction

Biomass pyrolysis is an extremely complex process. The essence of pyrolysis phenomenon is a series of complex chemical reactions including organic macromolecules cracking successively and forming volatile matter and solid product at specific temperatures. The pyrolysis of biomass can be regarded as a linear superposition of the pyrolysis of cellulose, hemicelluloses and lignin [1]. Cellulose and hemicelluloses mainly produce volatile substance [2]. Lignin can be cracked into char, tar, wood vinegar and gaseous product. The product yield depends on several factors, such as chemical composition, heating rate, the final temperature of the reaction and the structure of the reactor [3].

Biomass tar is a complex mixture of all organic contaminants that are produced by the process of pyrolysis and gasification [4]. Tar can potentially condense as liquid or solid at operation condition of vaporizer, gas transmission pipeline and gas generator. There are different definitions on the tar, but it is usually believed that the tar is mainly composed of large molecular aromatic hydrocarbon material. The most appropriate one is defined by Milne et al.: The organics, produced under thermal or partial oxidation regimes of any

* *Corresponding author*. Tel.: +86 18646218082.
E-mail address: zhaiming@hit.edu.cn (M. Zhai).

http://dx.doi.org/10.1016/j.ijhydene.2015.07.045
0360-3199/

organic material, are called tar [5]. Under the thermal regime of biomass, the amount of tar produced is mainly determined by temperature. For common biomass, the amount of tar produced reaches a maximum at around 500 °C while it declines as temperature increase or decrease. There are thousands of compounds in biomass tar, and more than 100 have been analyzed, but it is still hard to analyze all of them. The composition of tar produced varies with types of biomass. Besides, limited by analytical instruments and analytical methods, there are different results, but it can be confirmed that the primary compounds are no less than 20, most of which are derivatives of benzene and PAHs [6].

Biomass tar is a major problem in both pyrolysis and gasification of biomass. It is a high viscous liquid condensed that blocks and contaminates the pipelines. Hence, tar is strongly undesirable. Tar composition and amount depend on several factors, such as the fuel properties, the operating conditions (temperature, pressure, residence time), the type of gasifier, the gasification agents, the use of catalysts, and the method of tar sampling and analysis. Tar removal technologies include treatment inside the reactor and gas cleaning after the reactor [7]. Several methods are well known, such as physical treatment, thermal cracking, plasma cracking, and catalytic reforming [8,9]. These include modification of operating conditions such as temperature [10–11], pressure [12], gasification agents [13], residence time [14], design of the gasifier [15], secondary oxidization [16] and addition of catalysts [11, 17]. Post-gasification tar reduction usually employs washing, but this process contaminates water heavily. The preferred option for tar reduction is through process control in the gasifier and the use of additives and catalysts to modify operation conditions [18]. Three groups of catalysts are reported: natural catalysts, alkali-based catalysts and metal-based catalysts [19]. In general, produced gas with low tar content can be obtained at high-temperature. Primary tars are formed during the early stages of biomass pyrolysis inside the particles at temperatures between 200 and 300 °C [20]. As temperature increases the total tar content gradually decreases [21] due to tar cracking and steam reforming [22]. Therefore, high-temperature thermal cracking is considered as the most promising one for tar reduction in large-scale applications due to its fast reaction rate, and high reliability [23–25]. However, it may have a negative impact on the heating value of the produced gas as a result of increasing the temperature by means of more combustion [26].

Conventional biomass pyrolysis and gasification reactors like fix-bed reactors and fluidize beds use the flue gas and heat produced by partial combustion of the biomass itself for pyrolysis and gasification. Since the heating value of biomass is low, the temperature of the flue gas produced is fairly low. Therefore, the tar content in the product gas is considerably high. To reduce the tar content, we proposed a scheme that uses an external burner to produce high-temperature anaerobic flue gas and heat by combustion of part of the produced gas for pyrolysis and gasification. The pyrolysis and gasification were separated in the reactor, and the heat self-sustain was achieved by using 15.4%–20.5% of the total produced gas for combustion [27]. Although the produced gas was diluted by the flue gas, more tar content converted to non-condensable hydrocarbons, and the heating value of the gas may not be affected much. To verify the scheme experimentally, it is necessary to conduct an in-depth study on the characteristics of biomass tar pyrolysis and the physicochemical properties of the tar.

Considering the process and conditions of tar formation, an external flue gas pyrolysis system for rice husk tar pyrolysis was designed. The characteristics of rice husk tar pyrolysis by external high-temperature anaerobic flue gas and heat such as yield of pyrolysis products, composition of the liquid product, and properties of rice husk tar were investigated. Propane was used as the fuel in combustion for producing external flue gas because it was easy to control the composition and the temperature of the flue gas, but it could be replaced by produced gas from pyrolysis and gasification. The aim of this study is to provide the experimental data of the yield of the rice husk pyrolysis products, composition of the tar and the properties of the tar for the reference to the optimization of the operating conditions.

Material and methods

Rice husk is selected as the material for pyrolysis. The Proximate and ultimate analysis of rice husk is shown in Table 1. The external flue gas is illustrated in Fig. 1 which mainly consists of an external burner, a fix-bed reactor for pyrolysis, and a condenser. Considering high-temperature flame was generated in the burner, stainless steel mesh was wired on the inner wall, and refractory concrete and construction aggregate were applied inside. Thermal insulation material was covered outside the burner. Propane and supplied in the burner was tangential. An observation window was set on the end face of the burner for observing the ignition and burning condition. The fix-bed reactor was for rice husk pyrolysis. Stainless steel featured by refractory concrete was installed on its inner wall.

Rice husk was fed to the grid plate initially, and valve 17 was open and valve 16 was closed. Propane and air sufficiently combusted in the burner. The flue gas analyzer was used to measure the oxygen content of the flue gas and adjust the proportion of propane and air to ensure there was no extra oxygen in the flue gas. When the temperature at the exit of the burner was stable, valve 16 was opened and valve 17 was closed so that the high-temperature flue gas produced from the burner entered the fix-bed reactor for the pyrolysis of rice husk. Then, the mixture of volatile matter and high-temperature flue gas entered into the condenser. The condensed tar flew into the deposition tank, and the non-condensable gas was discharged. The tar condensed in the condensing tube of the condenser was dissolved by acetone solution and collected and calculated to determine the total mass of the tar condensed. The operating condition is shown in Table 2. The GC–MS analysis was applied to analyze the composition of rice husk tar and its distillate. TGA was carried out to investigate the properties of rice husk tar and its distillate.

Results and discussion

Yield of pyrolysis products

Fig. 2 shows the yield of the pyrolysis products. The gas yield varies little as the temperature increases below 500 °C. When

Please cite this article in press as: Zhai M, et al., Characteristics of rice husk tar pyrolysis by external flue gas, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.07.045