Journal of Analytical and Applied Pyrolysis 110 (2014) 382–389

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Hydrothermal liquefaction of lignite, wheat straw and plastic waste in sub-critical water for oil: Product distribution

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ARTICLE INFO

Article history:
Received 19 June 2014
Accepted 14 October 2014
Available online 23 October 2014

Keywords:
Lignite
Wheat straw
Plastic waste
Hydrothermal liquefaction
Sub-critical water

ABSTRACT

Product distribution and character of the products during hydrothermal liquefaction of Jingou lignite, wheat straw and plastic waste in sub-critical water are investigated in an autoclave. The effects of blending ratio of lignite, wheat straw and plastic waste, temperature, initial nitrogen pressure and additives on product distributions are also studied. The results indicate that blending ratio of lignite, wheat straw and plastic waste, liquefaction temperature, initial pressure and additives all could influence the product distributions during hydrothermal liquefaction. When the blending ratio of Jingou lignite, wheat straw and plastic waste is 5:4:1, there exists synergism effect for oil yield, and the oil yield and the gas yield are all the highest at this ratio. The total conversion increases when the temperature increases from 260 °C to 300 °C and then decreases. For the oil yield, when the temperature increases from 260 °C to 280 °C, oil yield decreases, while when the temperature increases from 280 °C to 320 °C, the oil yield increases. Moreover, adding tourmaline during hydrothermal liquefaction of lignite, wheat straw and plastic waste could get higher oil yield, higher total conversion and higher quality oil than that when adding the traditional catalyst.

1. Introduction

Coal liquefaction can make clean coal into oil, and it also can reduce pollution. However, up to now, the cost of coal liquefaction is still very high. Biomass, such as wheat straw, is a kind of cheap, abundant and renewable energy source [1–5]. Furthermore, plastic wastes are also abundant. However, there are many difficulties for people to use them efficiently and cleanly and most of the biomass and plastic wastes are abandoned. The main processing mode today for plastic wastes is incineration or landfill deposition [6,7]. As we have known, the major elements of plastic wastes and biomass are carbon and hydrogen, and they have higher H/C ratio than coal. Then they can be used as rich hydrogen additive during coal liquefaction [8–11]. Moreover, the traditional solvent used in liquefaction is tetranap, which is one of the organic solvent. Using tetranap not only makes the cost high, but also harms the human beings. As we have known, water is cheap and clean, and it can form a single phase with liquefied products in subcritical state; moreover, it also can separate naturally from hydrophobic products as a different phase at normal temperatures and pressures [12–18]. Furthermore, hydrogen supply during sub-critical water extraction is effective for obtaining compounds with low oxygen content, but hydrogen is expensive. Fortunately, biomass and plastic waste can be cheap sources of hydrogen when they are added in sub-critical water. Previous studies showed that there exists synergistic effect in the co-liquefaction of coal and rice straw [19]; and literatures also showed that co-liquefaction of plastic wastes with aromatic-rich materials such as coal could yield synergistic effects and increase the production of oil [20]. Besides that, studies also showed that the addition of biomass to plastic waste high density polyethylene (HDPE) liquefaction could make the reaction conditions milder, and enhance the conversion of HDPE at lower temperature, implying the synergistic effect of biomass and HDPE [21]. Thus, co-liquefaction of coal, biomass and plastic waste in sub-critical water is proposed. In this paper, the products distribution during co-liquefaction of lignite, wheat straw and plastic waste was investigated, and the characters of the products were also studied. This study will help us to understand further the process and mechanism of co-liquefaction of coal, biomass and plastic waste.

2. Materials and methods

2.1. Samples

Jingou lignite (JG), wheat straw (WS) and plastic waste polyethylene terephthalate (PET) we used are all from Linfen in Shanxi

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http://dx.doi.org/10.1016/j.jaap.2014.10.004
0165-2370/

Table 1
Proximate and ultimate analysis of the coal, wheat straw and plastic waste.

Sample	Proximate analysis (wt.%)					Ultimate analysis (wt.%, ad)				
	M_{ad}	A_{ad}	V_{ad}	V_{daf}	FC_{ad}	C	H	N	O[a]	S
Jingou lignite	11.70	25.75	22.45	32.43	7.67	49.66	3.06	0.83	43.58	2.87
Wheat straw	7.94	5.33	77.26	89.08	9.47	40.48	5.60	0.85	52.93	0.14
Plastic waste	0.14	0.04	90.8	90.96	9.02	61.88	4.29	0.03	33.76	0.04

[a] By difference.

Province of China. The samples were all first air-dried and then crushed, grounded and sieved from 0.15 mm to 0.25 mm. Table 1 is the results of proximate and ultimate analysis of the coal, wheat straw and plastic waste.

2.2. Experimental setup and procedure

The co-liquefaction experiments were carried out in a 250 ml autoclave. Each time 10.00 g JG lignite, wheat straw, plastic waste, or mixtures of the three samples were put into the reactor together with 80 ml deionized water. Before the liquefaction experiment, the reactor was filled with nitrogen to the desired initial pressure (2.0–5.0 MPa) and sealed; then the reactor was heated to the desired temperature at 10 °C/min by a furnace and then stayed for required time. After reaction the reactor was cooled to room temperature and depressurized to atmospheric pressure. The residue was taken out, dried and further analyzed.

2.3. Fractionation of liquefaction products

The gas products were analyzed by Algien 7890 A gas chromatograph. The solid and liquid products were extracted by hexane, benzene and tetrahydrofuran (THF), here the reagents (bought from Guangfu Fine Chemical Research Institute of Tianjin, China) are all analytically pure agents. After extraction, the products were separated into oils (hexane soluble), asphaltene (hexane insoluble but benzene soluble), preasphaltene (benzene insoluble but tetrahydrofuran soluble), and residues (tetrahydrofuran insoluble) as shown in Fig. 1 [8].

2.4. Calculation of liquefaction products yield

The yields of liquefaction products were calculated as:

$$\text{Oil yield (O, \%)} = \frac{w_O}{w_{JG} + w_{WS} + w_{PET}} \times 100\%;$$

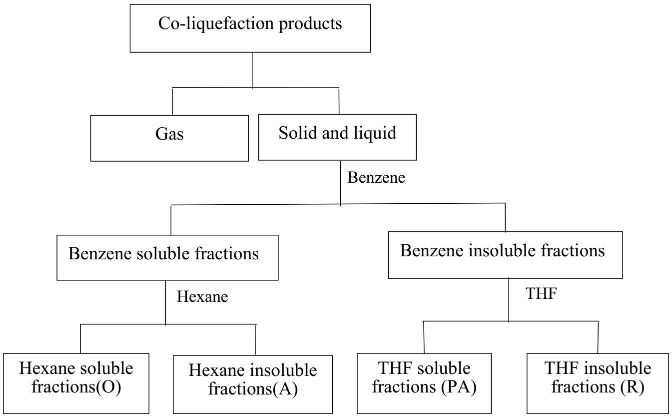

Fig. 1. Fractionation procedure of liquefied product.

$$\text{Asphaltene yield (A, \%)} = \frac{w_A}{w_{JG} + w_{WS} + w_{PET}} \times 100\%$$

$$\text{Preasphaltene yield (PA, \%)} = \frac{w_{PA}}{w_{JG} + w_{WS} + w_{PET}} \times 100\%$$

$$\text{Residue yield (R, \%)} = \frac{w_R}{w_{JG} + w_{WS} + w_{PET}} \times 100\%$$

$$\text{Gas yield (G, \%)} = 100\% - (\text{O} + \text{A} + \text{PA} + \text{R})\%$$

$$\text{Total conversion (TC,\%)} = 100\% - R\%$$

where w_{JG} is the mass of Jingou lignite, (g); w_{WS} is the mass of wheat straw, (g); w_{PET} is the mass of the plastic waste, (g); w_O is the mass of the oil, (g); w_A is the mass of the asphaltene, (g); w_{PA} is the mass of the preasphaltene, (g); w_R is the mass of the residue, (g).

Moreover, in order to examine the synergistic effect during co-liquefaction of Jingou coal, wheat straw and plastic waste, the weighted mean values of the co-liquefaction conversion and liquefied products yield are calculated based on the individual liquefaction result of Jingou lignite, wheat straw and plastic waste. The calculated value is obtained as follows: assuming that there is no interaction between Jingou lignite, wheat straw and waste plastic during co-liquefaction, thus the liquefied products yield from co-liquefaction should be equal to the weighted mean value of the individual liquefaction of Jingou lignite, wheat straw and plastic waste, and this value is defined as calculated value (Cal.) [22].

2.5. TG analysis

Thermo gravimetric (TG) analysis was carried out on a SETARAM TGA92 analyzer. Each time 13.00 mg sample was placed into an alumina crucible and heated from 25 °C to 300 °C at 10 °C/min under nitrogen with the flow rate of 60 ml/min, and then heated to 900 °C at 15 °C/min and finally stayed at 900 °C for 30 min. Moreover, differential thermal gravity (DTG) analysis also was done.

3. Results and discussion

3.1. TG–DTG analysis of lignite, wheat straw and waste plastic and their mixtures

Fig. 2 shows the TG/DTG curves of Jingou lignite, wheat straw and plastic waste and their mixtures. From Fig. 2(a) it can be observed that at 200 °C the wheat straw begins to decompose and at 317 °C the weight loss rate is the highest, and about 70% of wheat straw loses when the temperature is 500 °C. The plastic waste (PET) begins to decompose at 400 °C, and the maximum weight loss rate appears at 435 °C; and about 84% of the weight looses when the temperature increases to 500 °C. The weight of lignite first decreases at 100 °C, and then about 45% of the weight looses when the temperature increases from 350 °C to 800 °C, and at 495 °C the weight loss rate is the highest. From Fig. 2(a) one