Chemical Engineering Journal 285 (2016) 157–163

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Hydrothermal conversion of scrap tire to liquid fuel

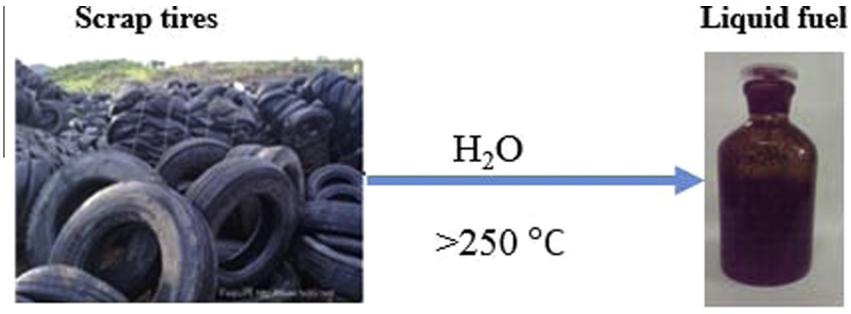
Lei Zhang, Bo Zhou, Peigao Duan *, Feng Wang, Yuping Xu

Department of Applied Chemistry, Henan Polytechnic University, No. 2001, Century Avenue, Jiaozuo, Henan 454003, PR China

HIGHLIGHTS

- Scrap tires can be hydrothermally converted to high quality liquid fuel.
- T (°C) was the most influential factor affecting the quality of the liquid products.
- The liquid products mainly consists of unsaturated hydrocarbon and aromatics.
- 60 wt.% of the chemical energy in the ST was retained in the liquid products.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 June 2015
Received in revised form 28 September 2015
Accepted 1 October 2015
Available online 9 October 2015

Keywords:
Hydrothermal liquefaction
Scrap tire
Sub- and supercritical water
Liquid fuel

ABSTRACT

The hydrothermal liquefaction of scrap tires (ST) using a stainless-steel batch reactor is examined in this study. The effects of reaction temperature (from 200 to 430 °C), corresponding pressure (from 0 to 28 MPa), time (from 20 to 120 min), H_2O/ST mass ratio (from 0/3 to 12/3), and atmosphere (air, CO_2, CO, H_2, and N_2) on the yields of product fractions (liquid products, gas, and char) and the properties of the liquid products were examined. Of the variables examined, temperature was the most influential factor affecting the yield and quality of the liquid products. Under optimal conditions, the highest liquid product yield of 52.73 wt.% was achieved. Thermal decomposition of the ST begins at approximately 120 °C and finishes at approximately 500 °C. The addition of water made the complete conversion of ST milder than that its direct pyrolysis (without water). During hydrothermal liquefaction, water was partly incorporated into the liquid products. The liquid products, which are highly viscous at room temperature and flow with difficulty, had higher heating values of approximately 44.20–45.09 MJ/kg. The liquid products mainly consisted of unsaturated hydrocarbons and aromatics, and approximately 60 wt.% of the chemical energy in the ST was retained in the liquid products in these conditions. The gaseous products were mainly CO_2, H_2, and CH_4. This study suggests that ST can be hydrothermally converted into a high quality liquid fuel.

1. Introduction

Approximately 1.4 billion scrap tires (STs) are discarded annually worldwide due to increasing number of vehicles on the road [1], corresponding to an estimated 17 million tons of STs each year. This figure is estimated to increase by 2% every year. The accumulation of large quantities of STs has become a major environmental issue. Burning the tires is usually prohibited because of air pollution concerns, and burying them can lead to landfill contamination [2]. One possible solution to the problem of tire disposal is to convert STs into fuels and other useful hydrocarbon products through thermal and thermo-chemical processes such as combustion [3], pyrolysis [4,5], gasification [6] and liquefaction [7].

Of those thermo-chemical processes, pyrolysis is considered to be an environmentally friendly process that involves the thermal

* Corresponding author. Tel.: +86 (0391) 3986820; fax: +86 (0391) 3987811.
E-mail address: pgduan@hpu.edu.cn (P. Duan).

http://dx.doi.org/10.1016/j.cej.2015.10.001
1385-8947/

decomposition of STs into low molecular weight products under an inert atmosphere [8–11]. Tire pyrolysis produces three principal products: liquid products, gas, and char. The liquid products and gas, comprising roughly half of the pyrolysis products by weight, have an energy content similar to conventional fuels [12]. The pyrolysis of STs is usually performed at very high temperatures (above 400 °C), thus increasing the operating cost of pyrolysis plants [2]. Alternatively, efforts have been made to use subcritical or supercritical water to degrade STs in comparatively milder conditions [13–18]. Supercritical water (SCW) has proven useful for decomposing a variety of materials [19] because it acts as a strong nucleophile, leading to a direct attack on the polymer backbone. One disadvantage of using water as a solvent compared to other organic solvents is its high critical pressure; however, the easy separation of water from the resulting oil and the negligible cost of the water are great advantages. SCW exhibits characteristics of a non-polar organic solvent; water is miscible with rubber that consists of non-polar styrene-butadiene rubber (SBR) or natural rubber (NR). Compared with subcritical water, STs are decomposed much more completely in supercritical water, and the production of tar is often prohibited [18]. Previous studies [13–18] suggested that the destruction efficiency and the distribution of liquid products were strongly dependent upon operating conditions such as reaction temperature, reaction time, reaction pressure, oxidant concentration, and initial gas phase composition. However, these previous studies only used Fourier transform infrared spectroscopy (FT-IR) and gas chromatography–mass spectrometry (GC–MS) to characterize the liquid products. The elemental compositions of the liquid products are not available. Considering the ongoing research centered on liquid fuel production from STs and the rapid developments in the field of hydrothermal liquefaction (HTL), further information is needed.

Hence, the objective of the present work was to determine the influence of several different variables such as temperature (200–430 °C), reaction time (20–120 min), H_2O/ST mass ratio (0/3–12/3) and reaction environment (air, CO_2, CO, H_2, and N_2) on product fraction yield from the HTL of ST, and to determine the properties of the liquid products. Then, the physical and chemical properties of liquid products were analyzed in detail using GC–MS and elemental analysis, respectively.

2. Experimental section

2.1. Materials

A car ST was obtained from a local recycling station and was mechanically ground into small particles (0.3–0.5 mm) using a file. The ST powder was composed of rubber without the steel and textile netting components of the tire. The ash content was determined by the ignition of a known weight of the ST at 600 °C until all of the carbon had been removed. The ash residue represented the inorganic constituents of the ST. The fixed carbon content was determined by subtracting the summation of the volatile matter and the ash content found in the total sample mass. A reactor was loaded with ST and subjected to the same dichloromethane treatment used to remove liquid products post reaction to determine the dichloromethane soluble materials. The C, H, N, O, and S of the ST were determined using an elemental analyzer (Flash2000 CHNS/O, Thermo Fisher Scientific, USA) by the direct combustion method. The inorganic compositions of the microalgae and ST were measured by X-ray fluorescence (XRF) using a Bruker S8 TIGER XRF spectrometer. The results of the proximate and ultimate analyses of the ST powder are included in Table 1. All other chemical reagents used for the experiments were of analytical grade, and distilled water was used as the solvent.

Table 1
(a) Characteristics of scrap tire.

Proximate analysis (wt.%, dry basis)				Ultimate analysis (wt.%, dry basis)				
VM	CS	FC	A	C	H	N	S	O
72	12	19	9	78.70	7.47	1.40	1.90	1.63

VM: volatile matter; CS: CH_2Cl_2 soluble material; FC: fixed carbon; A: ash; M: moisture.

(b) Inorganic composition (×10 wt.%, dry basis) of scrap tire

Al	Si	P	Cl	K	Ca
0.15	2.01	0.08	0.42	1.08	6.22
Ti	Fe	Cu	Co	Zn	Br
0.38	4.42	0.50	0.31	65.45	0.72

A custom-made high-pressure and corrosion-resistant batch reactor was used to conduct the HTL experiments, which allowed for the recovery of both the liquid- and gas-phase products in a single run. The total internal volume of the reactor is 36.4 mL. Prior to its use in experiments, the reactor was loaded with water and seasoned at 400 °C for 4 h to remove any residual organic material from the reactors and to expose fresh metal walls to supercritical water. All of the reactors used in the present study were heated using a molten-salts bath that consisted of potassium nitrate and sodium nitrate at a mass ratio of 5:4.

2.2. Procedure

As in a typical HTL experiment, 3 g of ST powder and a certain amount of water were loaded into the reactor before it was sealed. The loaded reactor was then placed into the molten-salts bath that was pre-heated to the desired temperature. The temperature inside the reactor reached the desired temperature after a few minutes, depending on the reaction temperature, at which point the reaction time was set to zero. The saturation pressure inside the reactor is temperature-dependent; increasing the temperature increases the saturation pressure. The temperature was controlled by an Omega temperature controller connected to a thermocouple residing in a thermowell in the reactor. After the pre-set reaction time had passed, the reactor was removed from the molten-salts bath and submerged into a cold water bath for approximately 15 min. The cold reactor was dried with a hair dryer. The total gas production was quantified from the weight difference of the reactor before and after the gas was vented. Details about the subsequent isolation of liquid products and char were similar to previously reported [20]. The yield of each product fraction was calculated as its mass divided by the mass (dry basis) of STs loaded into the reactor.

Duplicate independent runs were conducted under identical conditions to determine the uncertainties of the experimental results. The results reported herein represent the mean values for the two independent trials. Uncertainties are reported as the experimentally determined standard deviations.

2.3. Products analysis

A GC-7900 (Shanghai Techcomp Scientific Instrument Co., Ltd.) gas chromatograph equipped with a thermal conductivity detector (TCD) was used to analyze the gas products. A 15 ft × 1/8 in i.d. stainless steel column packed with 60 × 80 mesh Carboxen 1000 (Supleco) separated each component in the mixture. Argon with a column pressure of 0.18 MPa served as the carrier gas for the analysis. Two consecutive analyses of the gas mixture were taken for each reactor. The temperature of the column was held at 70 °C for 120 min. The mole fraction of each gaseous component was determined via calibration curves generated from analysis of