Fuel Processing Technology 119 (2014) 263–271

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Co-pyrolysis of biomass with waste tyres: Upgrading of liquid bio-fuel

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ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form 29 August 2013
Accepted 23 November 2013
Available online 8 December 2013

Keywords:
Pyrolysis
Biomass
Waste tyre
Bio-oil
Upgrading

ABSTRACT

Co-pyrolysis of forestry wastes and waste tyres is carried out using different facilities: a fixed bed reactor and a continuous auger reactor. Remarkably, only one phase is found in the liquid fraction, which is not achieved by mixture of the pure liquids. In addition, positive effects between waste tyre and biomass are evidenced, being more notable even synergetic in the auger reactor. It is found that whilst acidity, density and oxygen content decrease, pH and calorific value increase with respect to the merely biomass pyrolysis liquid, leading to upgraded bio-oil. Upgrading process is linked to the presence of radical interactions between waste tyres and biomass pyrolysis products. In addition, it is observed that the addition of waste tyres to the feedstock blend is significantly decreasing the amount of aldehydes and phenolic compounds, which is beneficial for improving the stability of the new bio-oils.

1. Introduction

The use of renewable sources and waste valorisation is increasing because of several factors, which include global warming, negative environmental impact due to the use of fossil fuels and the increase of energy demand and availability of waste materials. Therefore, it is necessary to study how to improve current processes to obtain an energy benefit with a minimum of environmental impact. Pyrolysis valorisation process shows some advantages (environmental and technical) with respect to other valorisation processes. The most important one is the production of a liquid fuel that can be easily stored and transported. In addition to this liquid fraction, solid and gas fractions are produced, which can also be used as fuels (solid and gas fractions) or be valorised for the production of activated carbon (solid fraction). Thus, the study of pyrolysis processes to find the best operational conditions is of great interest.

There are several reviews focused on biomass pyrolysis for liquid fuel production [1–4]. Generally speaking, it can be stated that the characteristics of the liquid fraction, such as appearance, miscibility, density, viscosity, distillation, and ageing for liquids, markedly depend on the feedstock, the type of reactor, the process conditions and the efficiency of the condensation system [2]. Nonetheless, the pyrolysis liquid product, also called bio-oil, has chemical and physical properties well documented in the literature [5], see Table 1. As fuel, bio-oil has several environmental advantages over fossil fuels since it is renewable, locally produced and has lower environmental impact (close to CO_2/GHG neutral, no SOx emissions, 50% lower NOx emissions) [3]. However, it presents some disadvantages for its application as fuel such as high water content, high viscosity, poor ignition characteristics and corrosiveness [1], as well as high oxygen content, high solids content and chemical instability [4]. Pyrolysis liquids are unstable due to their high amount of reactive oxygen-containing compounds [6]. The instability is seen as a viscosity increase during storage, which, connected with the formation of water, finally leads to the separation of a lignin-rich bottom sludge [7]. Due to their structural water, bio-oil has been shown to be immiscible with diesel oil or other hydrocarbon fuels [8,9]. Hence, an increasing number of methods for bio-oil upgrading are being investigated and developed for improving the quality of bio-oil. The processes to get improved bio-oils mainly include hydroprocessing and catalytic cracking, although other processes such as esterification and reactive distillation have also been evaluated [4].

On the other hand, scrap tyres are a non-destructible and non-biodegradable waste through time making their post-treatment and/or their recycling difficult [10]. After their life cycle, tyres become wastes and only a few can be re-used. As the disposal of scrap tyres in landfills is prohibited in Europe, it is necessary to find an alternative route to take advantage of their high potential as an energy and raw material source. There are many different manufacturers and countless different formulations available all over the world; the composition of the tyres being influenced by both the tyre grade and manufacture processes. Consequently, tyre pyrolysis, as a process to recover tyre energy, offers products that may also vary in terms of yield, chemical composition and characteristics. These properties depend not only on the source and grade of the tyres, but also, on the reactor configuration, efficiency in heat transfer and experimental conditions [10]. Even so, tyre pyrolysis liquids (a mixture of paraffins, olefins and aromatic compounds) have

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http://dx.doi.org/10.1016/j.fuproc.2013.11.015

Table 1
Typical properties of wood pyrolysis bio-oil, tyre pyrolysis liquid and diesel fuel.

Property	Bio-oil	Tyre-oil	Commercial diesel no. 2
Moisture (wt.%)	15–30	0–4	0–0.02
pH	2–3	4–7	5–6
TAN (mg KOH/g)	90–110	5–10	0–0.5
Density at 15 (kg/m^3)	1100–1200	900–950	820–845
Viscosity at 40 ºC (cSt)	15–30	3–6	2–4.5
Elemental composition (wt.%)			
C	54–58	80–90	84–87
H	5–7	8–12	11–15
O	35–50	0–2	0.0
N	0–0.2	0.4–1.0	0.01–0.3
S	0–0.1	0.8–1.5	0–0.01
Ash (wt.%)	0–0.2	0–0.2	0.0
HHV (MJ/kg)	16–19	40–44	42–46

been found to have almost coincidental results regarding the marginal moisture and oxygen content. In addition, it is worth highlighting that some physico-chemical properties of the tyre pyrolysis liquids are fairly comparable to those found in commercial automotive diesel fuels, as shown in Table 1. These facts, together with their miscibility with diesel fuel [11] have encouraged their use as a replacement for conventional liquid fuels in compression ignition engines as shown in [12–14]. However, further studies are necessary to utilise tyre derived oils as a liquid fuel or feedstock, since higher sulphur content and wider distillation range than commercial fuels can be problematic.

Relative to biomass and waste tyre co-pyrolysis, Cao et al. [15] concluded that co-pyrolysis of sawdust and waste tyre using a fixed bed reactor can inhibit the unsuitable formation of PAHs produced by pyrolysis of tyre alone. The authors also showed a synergetic effect between both feedstocks, which was reflected in an improvement of the pyrolytic liquid quality in terms of density, viscosity and elemental composition when compared to the liquid obtained from only biomass pyrolysis. Thus, it would be very interesting to study the co-pyrolysis of both feedstocks in a continuous facility such as an auger reactor, since it is well-known that the type of reactor and process conditions could lead to different properties of the liquid fuel. In fact, co-pyrolysis of wood biomass and polymers such as polyethylene and polypropylene showed that the composition and the nature of both, biomass and synthetic polymers, as well as pyrolysis conditions have a great influence on the yield, the chemical structure and the physical properties of products [16].

This study aims to evaluate the co-pyrolysis of forestry waste woodchips containing bark and waste tyre scraps (using blends up to 20% of waste tyre) as a way of upgrading the physico-chemical properties of the bio-oil obtained from solely biomass. Co-pyrolysis of biomass with a feedstock of different composition could offer a simple route for upgrading the bio-oil in one step avoiding or minimising the need for additional catalytic stages. In the first place, a thermogravimetric study was carried out to determine the temperature interval where simultaneous devolatilisation of both feedstocks takes place. Secondly, the co-pyrolysis process was evaluated both in a fixed bed reactor and in a continuous auger reactor, in which pyrolysis of scrap tyres [17,18] and forestry wastes [19] have been run successfully before. Finally, chemical and physical properties of the different pyrolysis fractions obtained were determined for both reactors.

2. Experimental

2.1. Feedstock

Pine woodchips (15 mm of nominal size) and waste-tyre scraps (5 mm of nominal size) were used for the experiments. The biomass consisted of Aleppo pine (*Pinus halepensis*) containing bark from forestry wastes and it was dried prior to the experiments (moisture content of 4.0 wt.%). The waste-tyre scraps were composed of rubber without the steel thread and the textile netting (moisture content of 0.9 wt.%). The ultimate analysis of both materials was carried out in a Carlo Erba EA1108 instrument, the moisture content was determined according to ISO-589-1981; the ash content was measured according to ISO-1171-1976 and the volatile matter was determined according to ISO-5263-1974. The heating value was measured experimentally with a calorimetric bomb IKA C-2000 and determined according to UNE164001EX for the biomass and according to ISO-1929-76 for the waste-tyres. Table 2 shows the feedstock characterisation.

2.2. Thermogravimetric analysis

Three experiments from room temperature to 700 ºC at 10 ºC/min were performed for each feedstock and for a mixture of 80 wt.% biomass and 20 wt.% waste tyre (80/20). This 80/20 mixture is the maximum blend of waste tyre present in the feedstock since the aim of this paper is to upgrade the properties of the liquid fraction obtained from solely biomass. The solid weight loss and temperature were recorded in a thermobalance SETARAM Setsys. The sample weight used in all experiments was 20 mg and the carrier gas was nitrogen at 150 l_N/min.

2.3. Fixed bed reactor

Pyrolysis was carried out in a Kanthal fixed bed reactor (74 cm length and 1.6 cm internal diameter) in order to study feedstock devolatilisation in a small scale, see Fig. 1. Samples of 20 g were pyrolysed using nitrogen as carrier gas (0.8 l_N/min) previously preheated. The reactor was heated externally with an electrical heater at 80 ºC/min to the final pyrolysis temperature of 500 ºC. The reaction time was set to 15 min. An ice-cooled trap was used to collect the liquids. Liquid and solid yields were obtained by weight, while the gas yield was calculated by the gas composition sampled in a gas bag. Each run was performed three times and the value reported for each yield is the average value with its absolute error. Different feedstock mixtures on mass basis were studied in the fixed bed reactor: 100% of biomass (100/0); 90% of biomass and 10% of waste tyres (90/10); 80% of biomass and 20% of waste tyres (80/20) and 100% waste tyres (0/100).

2.4. Auger reactor

In order to test the scalability of the process, an auger reactor pilot plant described in detail in previous publications [17–19] was used. The experimental setup presents an excellent reproducibility and stability and is able to process up to 15 kg/h of waste tyres. Thus, a thermal inlet power of around 150 kW_{th} is achieved when merely waste tyres are used as feedstock. This type of reactor not only promotes the continuity of the process, but also controls key variables of the pyrolysis process such as the mass flow rate and the residence time of the feedstock inside the reactor.

Table 2
Proximate and ultimate analyses and calorific value of forestry waste and waste tyres.

Proximate analysis on dry basis (wt.%)	Forestry waste	Waste tyres
Ash	1.1	3.8
Volatiles	81.8	64.2
Fixed carbon	17.1	32.0
Ultimate analysis on dry basis (wt.%)		
Carbon	49.6	87.9
Hydrogen	6.4	7.4
Nitrogen	0.2	0.3
Sulphur	0.0	1.1
Oxygen[a]	43.8	0.0
HHV as received (MJ/kg)	19.5	38.6
LHV as received (MJ/kg)	18.0	37.0

[a] By difference.