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Pressurized pyrolysis of dried distillers grains with solubles and canola seed press cake in a fixed-bed reactor

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HIGHLIGHTS

- Biomass waste was pyrolyzed in a fixed bed reactor at different pressures.
- Pressure had a significant effect to the product yield and compositions.
- Bio-oils had significant fatty acids and their amount was increased by pressure.
- The elemental composition of products was affected by the operation pressure.
- Surface area of chars was lower during pyrolysis under higher pressure.

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ABSTRACT

Pressurized pyrolysis of biomasses was carried in a fixed bed reactor to obtain gases, bio-oils and chars at elevated temperatures. The products were characterized by GC–MS, FTIR, viscometer, SEM, BET and EDXRFS methods. Experiments were performed at 1, 5 and 10 bar pressure and 400, 500 and 600 °C temperatures. The experimental results show that in all the experimental condition the yield of bio-oil from DDGS as higher than that of canola. Yield of non-condensable gases and chars increased, while that of liquid products decreased by pressure. Increasing pressure favoured the formation of low molecular weight gas, such as H_2. Maximum surface area of chars was obtained at atmospheric pressure and the surface areas decreased rapidly with increasing pressure. GC/MS results shows that the amount of fatty acids in bio-oils was increased by increasing pressure and bio-oils showed non-Newtonian behavior. Based on EDXRFS results, bio-oils and char contained lots of elements.

1. Introduction

Renewable energy sources are capable of providing a considerable fraction of World energy demand in this century. Biomass is one of the most abundant and utilized sources of renewable energy in the world. There are several available biomass conversion technologies, which can be classified as physical, thermal and biological. Among them, the most acceptable method seems to be the thermochemical processes. These processes are irreversible chemical processes that produce a number of products, like fuels (gases and liquids), chemicals and solid products, such as activated charcoal. Thermochemical conversion processes generally comprise gasification, liquefaction and pyrolysis. Among them, gasification and liquefaction processes are highly focused production of only one product. However, when pyrolysis used appropriately, this method is capable of producing useful solid, liquid and gas products simultaneously. Recently, pyrolysis studies have been diversified by changing the proportions of the liquid, solid and char. Of the primary pyrolysis products, bio-oil can be stored and transported, easily and can be utilized as a fuel in power stations. For producing these bio-oils moderate temperatures of 450–600 °C, high heating rates and short residence times are used. Char, solid pyrolysis product, is a carbon-rich product formed when biomass is heated in a reactor in the absence of oxygen. The physical features of char majorly depend on the biomass and pyrolysis system. This is because the original structure of raw materials is imprinted on the char product (Lehmann and Joseph, 2009). Pyrolysis gas product formation is high at higher temperatures with CO, H_2, CO_2, C_mH_n as main constitutions.

Because of the complexity of the pyrolysis process and the interactive effect of the pyrolysis parameters, there is still much development possible (Diebold and Bridgewater, 1999). Furthermore, the formation and quality of the products will significantly

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depend on the operating parameters (temperature, residence time, heating rate and pressure). Considerable work has been carried out to study the influences of parameters on pyrolysis technologies. In addition to the liquid, gas and char yields, the influences of these parameters on the characterization of products have also been examined (Kim et al., 2010; Mullen and Boateng, 2008). Pressure is one of the important parameters in thermal decomposition, because it affects the physical mass transfer of volatiles releasing at the given temperature (Lehmann and Joseph, 2009). However, little attention has been paid to influence of pressure on biomass pyrolysis. Melligan et al. (2011), studied the pressurized pyrolysis of Miscanthus. In their study the pressure was varied ranged from atmospheric to 26 bar, while pyrolysis temperature was 550 °C. Maguyon and Capareda (2013), considered the microalgae as biomass sample in a pressurized fixed-bed reactor with operating temperatures varying between 400 and 600 °C, while pressure was maintained at 6.9 bar. Mahinpey et al. (2009), pyrolyzed the wheat straw at various pressurized atmospheres (0.69, 1.38, 2.07 and 2.76 bar) at an operating temperature of 500 °C. In all these studies, the resulting pyrolysis products: bio-oil, char and gas were analyzed and it can be concluded that the operating pressure has significant influence on the quality of the pyrolysis products.

In this study, pyrolysis experiments were conducted on two biomass samples: canola seed press cake and DDGS (Dried Distillers Grains with Soluble). Also they have been examined by pressurized pyrolysis.

DDGS is cereal by-product discharged from the ethanol production process. It is currently used as a feed grain to livestock due to its high protein, fiber and oil content (Wang et al., 2012). A potential surplus of DDGS discharge has been observed in recent years. Therefore, treatment of DDGS will need to find some new areas developments. The recovery of DDGS as a fuel is an attractive method of treating this waste. The fuels generated can be used for power generation, since this material found to have high energy content of 27 MJ/kg (Alves et al., 2011). The energy content of DDGS is greater than that of the other biomass samples. For most agricultural residues, the energy content are even more uniform – about 15–17 MJ/kg; the values for most woody materials are 18–19 MJ/kg (cta.ornl.gov). This high energy content of DDGS can be recovered by storing into liquid, gas or char products. Canola, de-oiled seedcake biomass (press cake) has no use as animal feed, contain residual vegetable oils and possess sufficient calorific value. Thermal decomposition of canola and DDGS have been getting attention recently as the resulting products like gas, bio-oil and char are found of commercial importance (Wang et al., 2012; Alves et al., 2011; Mullen et al., 2010; Gudka et al., 2012; Giuntoli et al., 2011).

In the literature, among various pyrolysis parameters, the influence of pressure on product yield and quality was least evaluated. For this purpose, in this study investigation of the influence of operating pressure of pyrolysis on char morphology, gas and bio-oil compounds at various operating temperatures was evaluated. Experiments were conducted in a pressurized fixed bed reactor with pressure ranging from 1 to 10 bar, at a pyrolysis temperature of 400, 500 and 600 °C.

2. Methods

2.1. Raw materials and TG analysis

Two kinds of biomasses have been used in this work as raw materials: dried distillers grains with soluble (DDGS) and canola seed press cake. Raw materials were provided by a company in Istanbul. Prior to the pyrolysis experiments, biomass samples were grounded in a high-speed rotary cutting mill and screened to give the fractions of $0.224 < \varnothing D < 0.425$; $0.425 < \varnothing D < 0.85$; $0.85 < \varnothing D < 1.25$ and $1.25 < \varnothing D < 1.8$ mm in particle sizes. We used samples with particle size of $0.425 < \varnothing D < 1.25$ mm particle size. Table 1 shows proximate analysis, elemental properties and calorific values of both raw materials. Both raw materials have quite similar moisture (7.2% (DDGS) and 8.6% (canola)) and ash content (5.6% (DDGS) and 6.0% (canola)). Further, higher fixed carbon (14.8%) and lower volatile matter (70.6%) content was measured in case of canola, than DDGS. Results of ultimate analysis demonstrate that canola has higher carbon, hydrogen and even nitrogen, while its oxygen content was lower than that of the DDGS. Owing to these higher carbon and hydrogen content the caloric value of canola sample (23.6 MJ/kg) was also higher than that of DDGS (23.3 MJ/kg).

Regarding DDGS raw material, it contains potassium, iron, sulfur, nitrogen, chlorine and phosphorous, while zinc, copper, calcium, was also involved in this sample, but lower concentration than 0.1%. Canola has calcium, phosphorous, chlorine, sulphur, potassium, manganese, iron and zinc. It is well shown that the canola raw material contains significantly lower amount of the before listed elements, exception of calcium. The calcium content in canola raw material was more than twenty times higher than that of the DDGS raw material. Our result was similar with experimental work of others, who found similar elements in products of agriculture. E.g. high levels of calcium, potassium, phosphorous, magnesium or sodium, furthermore lower concentration of aluminum, iron, manganese, cupper or zinc were found in canola sample in experimental work of Miller-Cebert et al., 2009. They investigated the mineral composition of canola and other cruciferous leafy greens.

TG analysis of raw materials was carried out in a Linseis Thermowaage L81 thermo-gravimetric analyzer coupled with differential thermal analyzer (DTA). For this, 25 mg of sample was heated to 1000 °C at a heating rate of 10 °C/min. Analysis was conducted with a carrier gas (N_2) flow rate of 50 cm^3/min.

Weight loss can be understood in three distinguished sections. Initially, up to 200 °C is referred in general as drying stage. During this stage, a weight loss of 10.8% and 12.7% has occurred for DDGS and canola samples, respectively. The weight loss in biomass samples can be due to the loss of moisture and some volatile compounds. Afterwards, the complex thermal chemical reactions occurred. The TG curve dropped sharply between 200 and 400 °C

Table 1
Proximate and ultimate analysis and the elemental composition of raw material.

		DDGS	Canola
Proximate analysis (%)	Moisture	7.2	8.6
	Volatile matter	75.3	70.6
	Fixed carbon	11.9	14.8
	Ash	5.6	6.0
Ultimate analysis (% daf)	C	49.8	51.3
	H	6.4	7.2
	N	3.4	5.5
	S	0.9	0.9
	O[a]	39.5	35.1
EDXFS (%)	P	0.121	0.080
	K	1.413	0.595
	Cl	0.552	0.173
	Ca	0.037	0.933
	Mn	n.d.	0.006
	Fe	0.295	0.079
	Cu	0.062	n.d.
	Zn	0.014	0.009
Caloric value (MJ/kg)		23.3	23.6

daf: dry ash free.
[a] By difference.