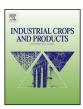
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Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products

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ABSTRACT

In this work, pyrolysis of sugarcane bagasse was conducted in a semi batch reactor. Pyrolysis experiments were carried out to study the effect of temperature (350-650 °C), heating rate (10 and 50 °C/min), biomass particle size (< 0.25 to 1.7 mm) and nitrogen flow rate (50-200 cm³/min) on the pyrolysis product yields. The maximum bio-oil yield of 45.23 wt% was obtained at temperature of 500 °C, heating rate of 50 °C/min, particle size of 0.5 to 0.6 mm and nitrogen flow rate of 100 cm³/min. The characterization of pyrolysis products (bio-oil, bio-char) have been made through different instrumental methods like Fourier transform infrared spectroscopy (FTIR), Gas chromatography-mass spectrometry (GC–MS), Nuclear magnetic resonance spectroscopy (11 NMR), X-ray powder diffraction (XRD), Field emission scanning electron microscope (FESEM) and Brunauer–Emmett–Teller (BET) surface area analysis. Bio-oil is found to have H/C molar ratio of 1.27, empirical formula of CH_{1.27}O_{0.30}N_{0.004} and heating value of 27.75 MJ/kg. It is dark brownish color acidic liquid with complex mixture of chemical compounds including acids, alcohols, aldehydes, furfural, furan, phenols and some aromatics. The results show that the bio-oil can be potentially valuable as a renewable fuel after upgrading and can be used as a chemical feedstock. The properties of bio-char reveal that it can be used as solid fuels, as a cheap adsorbent, as feedstock for activated carbon production and for agricultural application.

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1. Introduction

Global demand of energy is increasing rapidly due to population growth and economic development. Now a days, around 85% of world energy demand is fulfilled by fossil fuels. The continuous use of fossil fuels such as coal, petroleum and natural gas raise various economic and environmental issues. The release of greenhouse gases (GHG) by consumption of fossil fuels is warming the planet earth, which has potentially serious future environmental and social consequences. The renewable energy resources have potential to diminish the GHG emissions and improve energy security. Therefore, during last few years there has been a remarkable growth and development in renewable energy production and consumption. Among various alternative renewable energy sources, biomass is the most valuable, since it is available worldwide and can be transformed into solid, liquid and gaseous products from which fuels and other valuable chemicals/products can be derived (Nilsen et al., 2007). In addition, utilization of biomass is carbon neutral and it does not emit harmful gases into the atmosphere

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http://dx.doi.org/10.1016/j.indcrop.2016.11.039 0926-6690/© 2016 Elsevier B.V. All rights reserved. (Brand et al., 2014). Main types of biomass are wood, forest and agricultural residue, herbaceous species, manures, aquatic biomass etc. (McKendry, 2002).

Sugarcane is the largest agricultural crop in the world and bagasse is a major byproduct of the sugar industry (Islam et al., 2010a). Bagasse is a lignocellulosic residue of the sugar industry, which consists of around 40-50% cellulose, 20-30% hemicellulose, 20-25% lignin and 1.5-3% ash. It has high energy content (Drummond and Drummond, 1996). It plays an important role to fulfill the energy requirement for developing countries like India, Brazil etc, where large amount of sugarcane are produced. After Brazil, India is second major producer of sugarcane in the world. In year 2011–2012 around 342.20 million tons of sugarcane was produced on 5.03 million hectares of land, with an average yield of 70 tons/ha (Chouhan et al., 2016). Generally, one ton of raw sugarcane produces around 100 kg of sugar, 270 kg of dry bagasse and 35 kg of molasses (Garcià-Pèrez et al., 2002a).Usually, bagasse is used as a fuel source for boiler in sugar mills. But this is not fully used as a source of energy in sugar mills, because it creates the waste management problem at mill site. In addition, the direct combustion of bagasse in boilers has efficiency of only 26%, as well as the burning of bagasse in the boilers form airborne fly ash, which is responsible for major health hazard. It can be used as renewable

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A.K. Varma, P. Mondal / Industrial Crops and Products xxx (2016) xxx-xxx

Pyrolysis type	Reactor type	Temperature (°C)	Heating rate (°C/min)	Key results	Reference
Fast	Induction-heating	400-800	100-500	Products yields; properties of bio-oil	Tsai et al. (2006)
Slow	Fixed bed tubular	400-550	25	Products yields; properties of bio-oil	Parihar et al. (2007)
Slow	Fixed bed	300-600	50	Products yields; properties of bio-oil	Asadullah et al. (2007)
Slow	Fixed bed	600 & 800	10	Char yield; properties of char	Bonelli et al. (2007)
Fast	Fluidized bed	400-500	100	Products yields; properties of bio-oil	Islam et al. (2010a)
Vacuum Slow	Quartz tube	350–530 261–570	9–23 5–29	Products yields; properties of char	Carrier et al. (2011)
Vacuum	Quartz tube	460	17	Properties of char	Carrier et al. (2012)
Slow	Fixed bed	500	10	Products yields; properties of char	Lee et al. (2013)
Slow	Batch	400-600	-	Products yields; properties of bio-oil	Mantilla et al. (2014)
Fast	Fluidized bed	500 & 550	-	Products yields	Montoya et al. (2015)
Slow	Fixed bed tubular	350–550	-	Products yields; Analysis of gaseous products	Parthasarathy and Narayanar (2015)

energy source for high density biofuels production through energy efficient and cost effective thermochemical conversion processes.

Recent studies on purolusis of sugarcane bagasse reported in literature

Pyrolysis is the most promising thermochemical conversion process for conversion of biomass/organic materials into biofuels. Pyrolysis process is advancing at a rapid rate and has promising potential for commercialization. It is also the first step in combustion and gasification processes (Bridgwater et al., 2008; Gao et al., 2013), which converts biomass/organic materials into liquid product (bio-oil), solid char (bio-char) and non-condensable gases (NCGs) by heating in inert atmosphere (Demirbas and Arin, 2002). On the basis of heating rate and residence time, pyrolysis is classified as slow and fast pyrolysis. Slow pyrolysis, termed as carbonization is mainly used for charcoal production due to the long residence time, with low temperature (200–400 °C) and lower heating rate $(5-10 \circ C/min)$ and it uses wide range of particle sizes (5-50 mm) (Demirbas and Arin, 2002). For this process target product is often the char, but this is always be accompanied by liquid and gas products. Fast pyrolysis typically involves moderate temperature (450-650 °C), higher heating rate (10-200 °C/s) for particle size of less than 2 mm and short residence time (0.5-10s, typically <2s) (Demirbas and Arin, 2002). The compositions and yield of pyrolysis products are highly dependent on nature of feedstock, maximum temperature, heating rate, reactor types and other parameters (Yang et al., 2006). Liquid product produced during pyrolysis is termed as bio-oil/pyrolysis-oil/bio-crude/wood-oil (Kan et al., 2016). It is a dark brownish color organic liquid mixture, it usually contains water (15-35 wt%) and hundreds of organic compounds (Isa et al., 2011; Rezaei et al., 2014). Generally, bio-oil has calorific value in the range of 15–38 MI/kg (Asadullah et al., 2007). The solid char is also termed as bio-char/coke/charcoal has high carbon content with calorific value in the range of 17-36 MJ/kg, due to this, it can be used as source of energy and to internally provide heat for pyrolysis process (Garcia-Perez et al., 2002b). In addition, it can also be utilized as a precursor for activated carbon production (Williams and Besler, 1993). In recent years, application of bio-char has gained enormous attention as it can be used as a fertilizer when mixed with soil (Lehmann, 2007). It also enhances the quality of soils through increases the retention and availability of water and nutrients in soil, as well as in many cases it also increases the crop growth (Chan and Xu, 2009). The gaseous product of pyrolysis is generally synthesis gas or syngas. It mainly contains CO₂, CO, CH₄ and H₂ with gross calorific value of 6.4-9.8 MJ/kg. It can be used to

provide the process heat for pyrolysis, and used as a carrier gas or for drying of biomass in pyrolysis process (Islam et al., 2010b).

Sugarcane bagasse (SB) has high energy content and available abundantly in India. So, it has potential to utilized as feedstock for pyrolysis. Table 1 summarizes the recent studies for pyrolysis of sugarcane bagasse. From Table 1, it seems that different types of pyrolysis such as slow, fast and vacuum of SB have been studied. Most of the study focus on effect of pyrolysis temperature on product yields and mainly describes the properties of bio-oil or bio-char or gas. However, a comprehensive study of the pyrolysis of SB in semi batch reactor and the effect of process parameters such as temperature, heating rate, particle size and nitrogen (N₂) flow rate on the product yields as well as characterization of pyrolysis products (bio-oil, bio-char, pyro gas) to asses their utilization potential as valuable products are hardly available.

In present study, pyrolysis of SB is done in a semi batch reactor. The effects of pyrolysis temperature, heating rate, particle size range and nitrogen flow rate on the pyrolysis product yields are investigated. In addition, it provides comprehensive information about the various physical, chemical and fuel characteristics of

Table 2

Proximate, ultimate analysis and lignocellulosic composition of SB.

Characteristics	SB
Proximate analysis (%)	
Moisture	5.4
Volatile matter	80.2
Fixed carbon [*]	11.3
Ash content	3.1
Ultimate analysis (%)	
Carbon (C)	44.86
Hydrogen (H)	5.87
Nitrogen (N)	0.24
Sulfur (S)	0.06
Oxygen (O) [*]	48.97
O/C molar ratio	0.82
H/C molar ratio	1.57
Empirical formula	CH _{1.57} O _{0.82} N _{0.005}
HHV (MJ/kg)	18.0
Lignocellulosic composition (%)	
Cellulose	47.6
Hemicellulose	39
Lignin	11.2
Extractives	2.2
* By difference	

* By difference.

2

Table 1

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