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# Slow pyrolysis of rice straw: Analysis of products properties, carbon and energy yields

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## HIGHLIGHTS

- Slow pyrolysis of rice straw was investigated for temperatures of 300–700 °C.
- Biochar had a mass yield of about 25% from the organic fraction above 500 °C.
- Biochar was the primary product containing 40% of energy and 45% of carbon.
- Bio-oil and light gases had about 60% of energy yield in total.
- Drying of raw material was crucial to efficiently utilize the gases for process heat.

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## ABSTRACT

Among many uses of rice straw, application of its biochar from pyrolysis to the soil is receiving greater interest for increased crop productivity and sequestration of $CO_2$. This study investigated slow pyrolysis of rice straw at 300–700 °C to characterize the yields and detailed composition of the biochar, bio-oil and non-condensable gases. Biochar was analyzed for pH, microscopic surface area and pore volume distribution. Although the mass yield for the organic fraction was only about 25% above 500 °C, biochar was the primary product of pyrolysis containing 40% of energy and 45% of carbon from the straw. The utilization of by-products (bio-oil and gases) as energy resources was essential, since the sum of energy yield was about 60%. The gases could be burned to produce the heat for an auto-thermal pyrolysis process, but the heat balance was significantly influenced by the moisture content of the raw material.

## 1. Introduction

Biomass is composed of organic polymers originally produced by photosynthesis. Based on the available forms, biomass can be categorized into forestry/wood residues, agricultural residues, organic fractions of municipal/industrial wastes, manures, energy crops, and macro/micro algae. Biomass is unique among renewable energy resources, because it can be converted into both energy and chemical feedstock. Various mechanical, biological and thermo-chemical conversion technologies have been developed for the use of biomass, and applied in industry to produce different types of energy, fuel and chemical products. The thermo-chemical conversion includes pyrolysis, gasification and combustion.

Rice straw a major agricultural residue, accounting for 731 Tg/yr in the world (average of 1997–2001), mostly generated in Asia (Kim and Dale, 2004). In developed countries, rice straw is densified into bales by harvesters at paddy fields for easy transport and storage. It has many competing uses, such as cattle feed, bedding for poultry, compost and energy/chemical production. In under-developed countries, however, rice is manually harvested, and the straw is often left in the field and burned. For a large-scale energy production from rice straw, combustion is the dominant technology used in industry with a typical scale of 5–12 MWe (Gadde et al., 2008). However, the high $SiO_2$ and alkali metal content in the rice straw often cause problems, such as erosion in size reduction equipment and slagging/fouling in the heat exchangers of a boiler. It is also difficult to feed or to reduce its size due to its fibrous form.

Pyrolysis is an alternative technology for utilization of rice straw for conversion into valuable products. It involves the thermal decomposition of organic polymers that release vapors of various molecular weight compounds leaving carbon-rich solid residue (char) (Jahirul et al., 2012). The pyrolytic vapors can be separated into condensable hydrocarbon compounds (oil, also known as tar) and non-condensable gases. For biomass, it can be used as a

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single-step conversion process dedicated to the production of biochar, bio-oil and gases for use as fuels or chemical feedstock. The process is also an initial step for further break-down of the organic polymers in an oxidative atmosphere during gasification or combustion processes. Pyrolysis characteristics (reaction kinetics, products yields and composition) are influenced by many parameters, such biomass types, temperature, heating rate, particle size, reaction atmosphere, and vapor residence time due to the complex chemical structures and reactions involved (Antal and Grønli, 2003).

Table 1 presents recent studies in literature for pyrolysis of rice straw. Fast pyrolysis technology has been investigated mainly for production of bio-oil. It is typically performed using a fluidized bed to increase the heating rate ($\sim 10^3$ °C/s) and at temperatures about 500 °C to maximize the bio-oil yield (Wannapeera et al., 2008; Jung et al., 2008; Zhang et al., 2013; Eom et al., 2013; Pattiya and Suttibak, 2012; Fu et al., 2011, 2012; Lou et al., 2010). Higher temperatures and increased vapor residence time cause thermal cracking of hydrocarbon compounds, decreasing bio-oil yield. Pyrolysis using radio frequency plasma has been also studied to increase the gas yields by fully converting the tar (bio-oil) compounds to CO and $H_2$ rich gases (Tu et al., 2009).

In contrast to fast pyrolysis, slow pyrolysis is performed at a heating rate of about 10 °C/m for a typical temperature range of 300–700 °C (Pütün et al., 2004; Xiao et al., 2010; Peng et al., 2011; Huang et al., 2012, 2013; Wu et al., 2012; Chatterjee et al., 2013). This requires about 1 h of particle residence time to reach the target temperature. Slow pyrolysis of rice straw is applied as pretreatment (Xiao et al., 2010; Huang et al., 2012), or for biochar production as a soil ameliorator (Peng et al., 2011; Wu et al., 2012). Pyrolysis at low temperatures (typically below 300 °C), also referred to as torrefaction, is used to upgrade its fuel quality, such as the heating value (energy density) and grindability, as a pretreatment of biomass for pelletization, bio-oil production, gasification or combustion processes (Meng et al., 2012; Batidzirai et al., 2013).

Recent interest on slow pyrolysis of rice straw is for the application of biochar to soil to increase the soil fertility and to sequestrate carbon. Biochar increases the retention of nutrients and water in soil and provides habitats for symbiotic micro-organisms, which reduces the need for chemical fertilizers and increases crop productivity (Spokas et al., 2012). Biochar can also sequestrate carbon for many years due to the strong resistance of its aromatic carbon structure to biological decomposition (Lehmann et al., 2006). As listed in Table 1, detailed properties of rice straw biochar as a soil ameliorator were presented by Wu et al. (2012) for pyrolysis temperature of 300–700 °C. In pot trials for maize, using 1% mix of rice straw biochar with soil increased the growth of the crop by 64% (without fertilizer) and 146% (with fertilizer) (Peng et al., 2011). Application of wheat straw biochar to paddy fields achieved a significant increase in the rice yield and reduction in the overall greenhouse gas emission from the soil, especially in the second year of field experiment (Zhang et al., 2012).

In order to realize the potential benefits of biochar, it is essential to maximize its economic and environmental efficiency, including the production process of biochar. One important factor for the efficiency is how to utilize the by-products of biochar production. The amount of the bio-oil and non-condensable gas products in terms of mass and energy is considerably larger than that for biochar (Lee et al., 2013a). Bio-oil is a renewable fuel or chemical feedstock, but its chemical properties are not as good as biochar due to its high water content and numerous inhomogeneous compounds resulting in acidity and toxicity (Mohan et al., 2006). The pyrolytic gas is composed largely of CO and $CO_2$ that lead to poor fuel quality. Therefore, efficient use of the by-products should be considered together with biochar production, especially for large-scale production and application of biochar. This requires comprehensive information for mass yields and properties of the three pyrolysis products, including the distribution of carbon and chemical energy between products. However, such information is rare in slow pyrolysis studies in the literature, including those summarized in Table 1.

This study presents the slow pyrolysis characteristics of rice straw to provide comprehensive information for the chemical properties, carbon distribution and energy yields of the three pyrolysis products (biochar, bio-oil and gases). The mass yield, elemental composition and other key properties of the products were analyzed for pyrolysis temperatures of 300–700 °C. The carbon and energy yields of the products were calculated using analytical data. Based on these results, considerations required for application of the slow pyrolysis technology to rice straw were discussed.

## 2. Methods

### 2.1. Rice straw sample

The straw sample used in this study was from long grain rice delivered from Indonesia after air drying. Table 2 lists the chemical properties of the sample. Details of the analytical methods are presented in Section 2.3. The ash content was higher compared to the values in the literature (9.7–16.6%). Also, the volatile matter (VM) to fixed carbon (FC) ratio was lower in this sample, which can lead to larger char yields. However, the C, H, O, and N contents in the

**Table 1**
Recent studies on pyrolysis of rice straw reported in literature.

| Refs. | Pyrolysis type | Reactor type | Temp. (°C) | Heating rate | Key results for products |
|---|---|---|---|---|---|
| Wannapeera et al. (2008) | Fast | Drop-tube, fixed-bed | 200–850 | $>10^3$ °C/s | Properties of char and gas; effect of holding time |
| Jung et al. (2008) | Fast | Fluidized | 414–542 | | Product yields; properties of char, oil and gas |
| Zhang et al. (2013) | Fast | Fluidized; catalytic | 550 | | Properties of oil |
| Eom et al. (2013) | Fast | Fluidized | 350–500 | | Product yields; properties of oil |
| Pattiya and Suttibak (2012) | Fast | Fluidized | 375–500 | | Product yields; properties of bio-oil |
| Fu et al. (2011, 2012) | Fast, slow | Quartz tube | 600–1000 | 300 °C/s, 10 °C/min | Product yields; properties of char and gas |
| Lou et al. (2010) | Fast | Quartz tube | 400–900 | $\sim 10^4$ °C/min | Product yields; properties of bio-oil and gas |
| Tu et al. (2009) | Plasma | | 467–603 | | Product yields; properties of char and gas |
| Pütün et al. (2004) | Slow | Fixed bed | 400–650 | 5 °C/min | Product yields; properties of oil |
| Xiao et al. (2010) | Slow | Fixed bed | 300–700 | 5 °C/min | Product yields; properties of char and oil |
| Peng et al. (2011) | Slow | Muffle furnace | 250–450 | | Properties of biochar |
| Huang et al. (2012) | Slow | Microwave | 237–423 | 13–31 °C/min | Properties of char (torrefaction) |
| Wu et al. (2012) | Slow | Tube furnace | 300–700 | 5 °C/min | Properties of biochar |
| Chatterjee et al. (2013) | Slow | Fixed bed | 500 | 10 °C/min | Properties of bio-oil (toxicity) |
| Huang et al. (2013) | Slow | Microwave | <550 | $\sim$100 °C/min | Product yield; properties of gas |