

Bio-oil Product from Non-catalytic and Catalytic Pyrolysis of Rice Straw

Razi Ahmad, Nasrul Hamidin, Umi Fazara Md Ali

School of Environmental Engineering, Universiti Malaysia Perlis 02600 Arau, Perlis, Malaysia

Abstract: The study of catalytic pyrolysis on rice straw was carried out in a fixed-bed reactor. The objectives were to determine the effect of catalyst on the distribution of product yield and bio-oil characterization. The non-catalytic and catalytic process of rice straw was performed at the optimum conditions with zeolite ZSM-5 and dolomite catalyst. The highest bio-oil yield from the catalytic pyrolysis was 26.3% with zeolite ZSM-5, while the yield of bio-oil from non-catalytic pyrolysis was 27.6%. Elemental composition and spectroscopic methods were applied for the characterization of bio-oil. The chemical characterization studies of uncatalysed bio-oil derived from pyrolysis of rice straw reflect a considerable amount of carbonyl and oxygenated compound, resulting in higher oxygen content in elemental composition. In the presence of the catalyst, the yield of bio-oil was markedly reduced and so was the oxygen content of the bio-oil itself. The product yields and quality of the resultant bio-oil were significantly affected by the use of the catalyst.

Key words: biomass, pyrolysis, catalytic, bio-oil

INTRODUCTION

In recent years, there is a great concern with the environmental problems associated with the great CO₂, NO_x and SO_x emissions resulting from the rising use of fossil fuels. For this reason, more attention is being paid to renewable energy especially biomass energy (Mangut *et al.*, 2006). Biomass feedstock including wood, industrial and agricultural residue and by products (e.g., sawdust, wood chip, bagasse and rice husk) or dedicated energy crops (e.g., fast growing trees, shrubs and grass) usually applied as biomass fuels are significant interest because biomass is the fourth largest source of energy in the world, accounting for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in developing countries (Chen *et al.*, 2003).

There are three main thermal processes of converting solid wastes into energy; pyrolysis, gasification and combustion. Each process gives different range of products. The primary products from thermal conversion processes can be either gas, liquid or solid. These products can be used directly as raw fuel, or they can be subjected to further treatment and processes to produce secondary products such as higher value and quality fuel or chemical products. In pyrolysis process, when the components were quickly quenched, the volatile components condensed to bio-oil. The bio-oil can substitute for fuel oil in many static applications including boilers, combustion engines and turbine for the generation of electricity (Xiu *et al.*, 2005). Pyrolysis is generally described as the thermal decomposition of the organic component in biomass in the absence of oxygen to yield char (charcoal), tar (pyrolysis oil) and gaseous fraction (fuel gases).

The bio-oil derived from the pyrolysis of biomass can be highly oxygenated, viscous, corrosive, relatively unstable and chemically very complex (Bridgwater, 1996). The direct substitution of the biomass derived pyrolysis oil for conventional petroleum fuels may therefore be limited. Consequently, upgrading the bio-oil by catalytic treatment has received increasing attention. This catalyst is expected to improve the cracking reactions of the heavy molecules in pyrolysis products resulting in the production of lighter and less viscous bio-oil and to stimulate the reactions that involve the removal of the oxygenated species.

Rice straw is a lignocelluloses agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) (Hills and Robert, 1981). The estimation on annual production of rice by Food and Agriculture Organization (FAO) points to about 600 million tones per year in 2004. On the other hand, it has reported that every kilogram of grain harvested is accompanied by production of 1 to 1.5 kg of rice straw (Maiorella, 1985). Thus rice straw can cause a lot of environmental problems since it exists with enormous quantities and is not easy to handle or transport. Therefore, direct open burning in fields is a common option for disposal. This option causes serious air pollution, hence new economical methods for rice straw disposal and utilization must be developed.

This is where this study comes into picture, where the utilization of rice straw, a by-product of rice production which is available in abundance in the country, as a renewable energy source could be a value added entity and subsequently solve air pollution problems caused by open burning during paddy harvesting season.

In this study, the pyrolysis of rice straw was conducted under the optimum condition in a fixed-bed reactor. The effects of the catalyst on the pyrolysis product yield and bio-oil characterization were investigated.

Corresponding Author: Razi Ahmad, School of Environmental Engineering, Universiti Malaysia Perlis 02600 Arau, Perlis, Malaysia
E-mail: razi@unimap.edu.my,

MATERIALS AND METHODS

Material:

The biomass used in this research was rice straw. The material is widely available in Perlis and Kedah because the states are considered as the largest rice straw producers in Malaysia. The samples were dried under the sun and separated from physical impurities. The dried rice straw was grounded in a rotary cutting mill and screened into a fraction between 0.6 mm to 1.18 mm in size. The sample was analyzed for carbon, oxygen, hydrogen, nitrogen and sulfur compositions by using a CHN-S elemental analyzer. The proximate and ultimate analysis is shown in Table 1.

The dolomite used in this study was supplied by the School of Material Engineering, Universiti Malaysia Perlis. The dolomite was originated from Tasuh Kuari, Perlis. The diameter of the dolomite was 300 μm . This catalyst was activated by calcination to a temperature of 900°C for 8 hours. The zeolite ZSM-5 catalyst was also used for upgrading the pyrolysis derived oil from the rice straw. The catalyst employed in the study was purchased from A.R Alatan Sains Sdn. Bhd. For its activation, the zeolite ZSM-5 was calcined in a furnace at 550 °C for 1 hour.

Table 1: Proximate and Ultimate Analysis of Rice Straw

Characteristics	Values (wt %)
Proximate analysis ^a	
Moisture	10.8
Volatile matter	66.89
Fixed carbon	14.57
Ash	7.56
Ultimate analysis ^a	
Carbon	39.98
Hydrogen	2.45
Nitrogen	4.43
Sulfur	0.53
Oxygen ^b	52.61

^a As received

^b By different

Pyrolysis Process and Methods:

The fixed-bed pyrolysis experiments were performed in a vertical tubular reactor with an internal diameter of 1 cm and 37 cm in length. It was constructed using 316-stainless steel tube. Approximately 4.5 g of rice straw was placed inside the reactor tube. The reactor was heated externally by an electric furnace, with the temperature being measured by a thermocouple inside the reactor tube. The outlet of the pyrolysis reactor was connected to a condenser via a connecting tube. Following the condenser was a liquid collector on the bottom of condenser. Nitrogen gas is passed through the system serving as purge gas and protective gas to avoid coking occurring on the surface of the reactor. The constant nitrogen flow rate was precisely metered to the experimental system using mass flow controller.

The experimental conditions in the pyrolysis system were designed as follows: pyrolysis temperature at 450 °C, heating rate at 77.63 °C/min, holding time at 2.61 min and nitrogen flow rate at 100 cm³/min. These pyrolysis parameters were chosen from the optimization process in the previous study (Ahmad and Isa, 2010). In the last set of samples, the experiments were performed with zeolite ZSM-5 and dolomite catalyst. The quantity of catalyst used were 10 wt % of the biomass. The purpose of this experiment is to evaluate the effect of catalyst on pyrolysis product yields. The average yields from at least three experiments were presented within the experimental error of less than 0.5 weight percent.

The char and liquid product were collected and weighed after completion of the pyrolysis process. The yields of the resulting products were calculated based on mass of rice straw fed. The gas yield was calculated from the material balance. The bio-oil product was analyzed by CHN-S Analyzer for elemental composition and by Fourier Transform Infrared (FTIR) spectroscopy to identify the basic compositional groups.

RESULTS AND DISCUSSION

The Effect of Catalyst on the Yields of Pyrolysis Product:

As seen from Figure 1, for the pyrolysis of rice straw in the absence of catalyst, the derived liquid yield was 27.6%. However, by catalytic pyrolysis of rice straw, the bio-oil yield reduced to 26.3% and 23.2% respectively, with zeolite ZSM-5 and dolomite.

Samolada *et al.*, (2000) studied catalytic flash pyrolysis with the commercial catalysts Fe/Cr, alumina, and H-ZSM-5 at 500 °C in a piston reactor and called the catalyst mixing with raw material as “inbed mode” and

used the catalyst bed in the system in “ex-bed mode”. They found that the use of catalyst in biomass pyrolysis resulted in the reduction of the liquid yield and increased of the gas yield. The finding is similar compared to this study.

In the presence of the catalyst the yield of bio-oil was markedly reduced, and the oxygen content of the oil was reduced with the formation of coke on the catalyst. The influence of the catalyst was to convert the oxygen in the pyrolysis oil to largely H₂O at the lower catalyst temperature and to largely CO and CO₂ at the higher catalyst temperature (Williams and Nugranad, 2000).

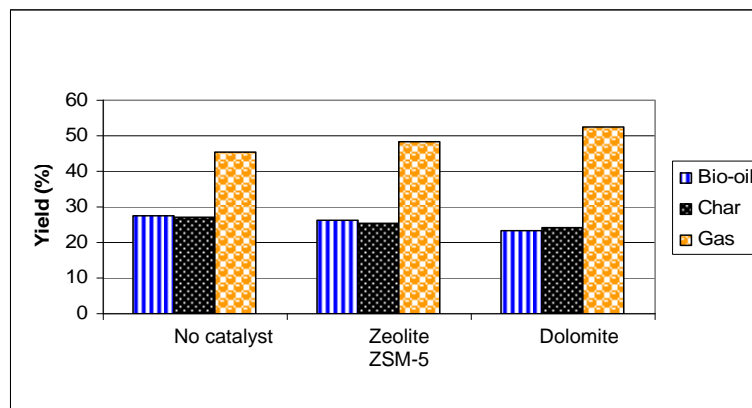


Fig. 1: Effect of catalyst on product distribution

Effect of Elemental Composition:

The elemental composition of the characterized oils is listed in Table 2. Compared with non-catalytic pyrolysis, the bio-oil obtained with catalytic pyrolysis had higher carbon and hydrogen value and lower oxygen, nitrogen and sulphur content. The action of the catalyst in removing the oxygen from the pyrolysis oil was noticeable. After catalytic pyrolysis, the oxygen content of bio-oil was found to be less than those for non-catalytic pyrolysis. The oxygen content of non-catalytic pyrolysis oil was 68.98 % and decreased to 57.79 % and 58.78 % with zeolite ZSM-5 and dolomite respectively. Even as oxygen levels in the catalysed oil are reduced, the oxygen was not totally eliminated.

Table 2: Elemental composition of bio-oil obtained by non-catalytic and catalytic pyrolysis of rice straw

Compound	Non-catalytic pyrolysis (%)	Catalytic pyrolysis	
		Zeolite (%)	Dolomite (%)
C	20.69	30.72	30.10
H	9.36	11.32	10.85
N	0.57	0.09	0.18
S	0.40	0.08	0.09
O ^a	68.98	57.79	58.78

^a By different

Functional Group Analysis:

Functional group analysis was determined by Fourier transform infra-red (FTIR) spectrometry and the results are shown in Figure 2 and 3 for comparison between non-catalytic pyrolysis and catalytic pyrolysis. The uncatalysed rice straw pyrolysis oil shows the presence of oxygenated groups. For example, peaks representing O–H vibrations between 3200 and 3600 cm⁻¹, C=O stretching vibrations between 1640 and 1750 cm⁻¹ and C–O stretching and O–H bending between 950 and 1300 cm⁻¹ are all present in the uncatalysed oil. However, these oxygenated peaks are also present in the catalysed oil suggesting that the zeolite ZSM-5 and dolomite catalyst does not completely remove the oxygenated species, as has already been shown by the significant oxygen content in the oils shown in Table 2.

The oxygenated compounds represented by the functional groups discussed are represented by a wide range of oxygenated compounds which have been identified in biomass pyrolysis oils. These include primary, secondary and tertiary alcohols such as methanol, propanol, butanol and furfuryl alcohols, carboxylic acids for example, formic, acetic, propionic, benzoic and butyric acids and their derivatives, ketones and aldehydes including, acetaldehyde, benzaldehydes, acetone, pentanone, indanone and alkylated derivatives, phenol, alkylated phenols and oxyphenols etc (Nokkosmaki *et al.*, 1998; Williams and Horne, 1994).

Also present in the uncatalysed and catalysed oils were peaks representative of non-oxygenated compounds. For example, the C–H stretching vibrations between 2800 and 3000 cm⁻¹ and C–H deformation vibrations between 1325 and 1490 cm⁻¹ indicate the presence of the chemical functional groups, –CH₃, –CH₂ and –CH

which are characteristic of alkane groups. The absorption peaks between 655 and 900 cm^{-1} and 1500 and 1650 cm^{-1} are characteristic of single ring aromatic compounds and polycyclic aromatic compounds. Alkanes, single ring aromatic compounds and polycyclic aromatic hydrocarbons have been detected in biomass pyrolysis oils but at low concentration (Williams and Horne, 1994). Therefore, the presence of these peaks in the uncatalysed oil are perhaps more likely to represent the presence of alkyl groups attached to oxygenated compounds and complex oxygenated compounds with attached aromatic groups, which have been detected in wood pyrolysis oils (Desbene *et al*, 1991).

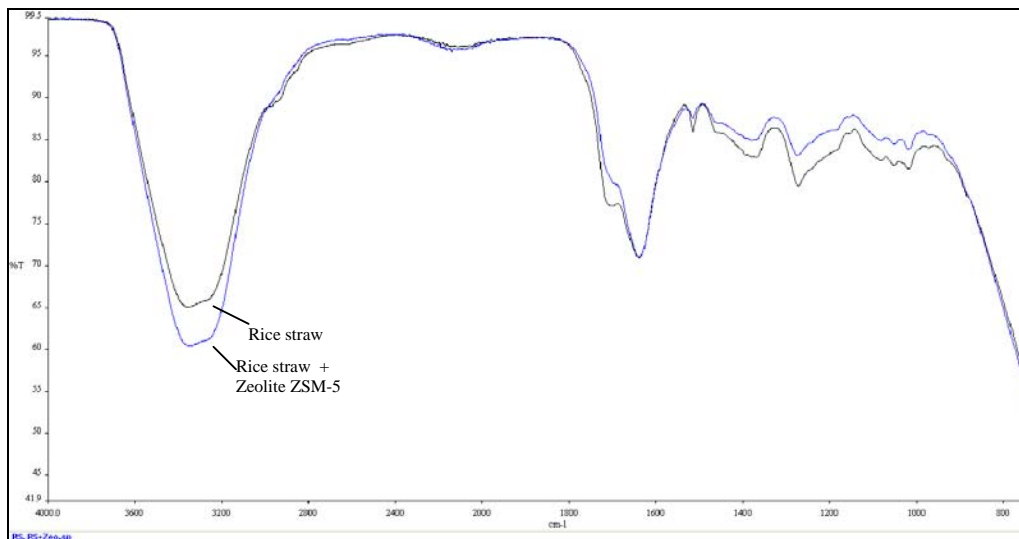


Fig. 2: FTIR spectra comparison between non-catalytic pyrolysis and catalytic pyrolysis with zeolite ZSM-5

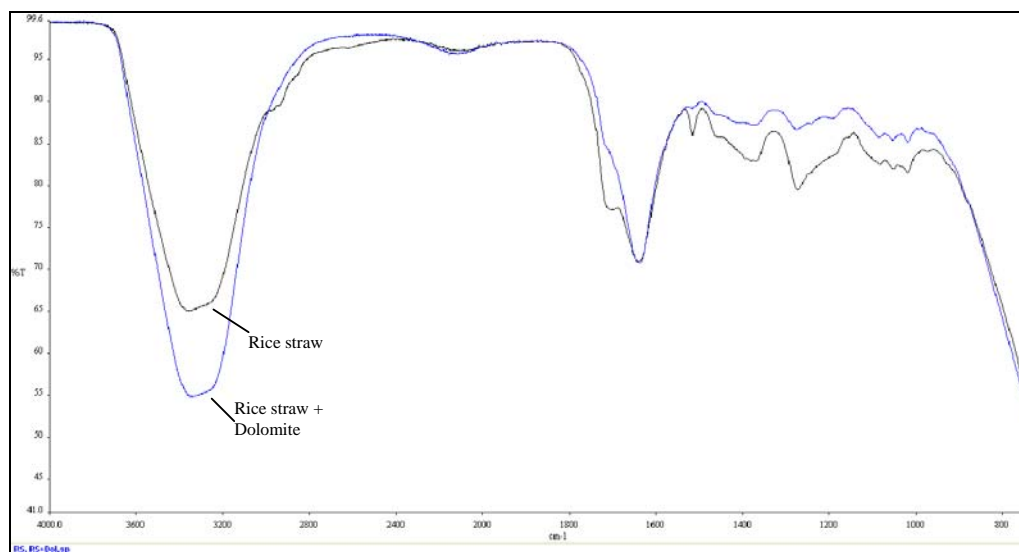


Fig. 3: FTIR spectra comparison between non-catalytic pyrolysis and catalytic pyrolysis with dolomite

Conclusion:

The pyrolysis of rice straw in a fixed bed reactor have been examined with dolomite and zeolite ZSM-5 catalytic upgrading. This study involved the used of catalyst to improve either the yield or quality of liquids obtained from pyrolysis of rice straw. The used of zeolites ZSM-5 and dolomite caused an increased in gas yields and a decreased in liquid yields. For the non-catalytic pyrolysis, there was a high conversion of the rice straw to highly oxygenated liquid. Conversely, in catalytic pyrolysis, the yield of bio-oil reduced after catalysis and the oxygen content of the bio-oil was also noticeably reduced.

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