

Factors Related to Minerals and Ingredients Influencing the Distribution of Pyrolysates Derived from Herbaceous Biomass

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Considerations related to minerals and the organic composition play a major role in biomass pyrolysis, determining the distributions and properties of pyrolysate. Thus, a correlation was developed to predict the influence of both the ingredients and minerals (additive NaCl) on the yield of pyrolysates. The feedstock was processed in a tubular reactor furnace at the temperature levels for 400, 450, 500, 550, 600, 700, 800, and 900 °C using fast pyrolysis method. The obtained pyrolysates were analyzed by a gas chromatograph-mass spectrometer (GC/MS). The results indicated that the ratio of addition 1% NaCl to bamboo had the greatest impact on the ingredients of bio-oil. A higher ash content and addition of NaCl can promote more generation of CO₂ and also make the char possess greater aromaticity. Therefore, de-ashing or removing minerals in the feedstock is indispensable for favorable conversion of biomass to bioenergy.

Keywords: Herbaceous biomass; Pyrolysis; Catalyst; Mineral; Ingredients

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INTRODUCTION

One of the most challenging tasks in utilizing biomasses as sustainable energy sources is to find technically and economically feasible methods of converting them into liquid fuels. The ideal process for lignocellulosic biomass conversion to liquid fuels would involve single-step conversion directly from solid biomass, and it also would involve short residence times. Fast pyrolysis is a vital pyrolysis technique, widely used in the solid biomass conversion. The lignocellulosic material is converted into hydrocarbon chemicals and fuels additives directly from the solid form. The process also is economical on a smaller scale, such that smaller distributed plants can be built close to the location of biomass (Bridgwater and Cottam 1992; Wright and Brown 2007; Ruane *et al.* 2010). However, bio-oil from biomass pyrolysis is of poor quality. If it is to be used as a transportation liquid fuel, it must be catalytically upgraded (Adam *et al.* 2006; Horne and Williams 1996; Nokkosmaki *et al.* 2000).

Factors such as biomass composition, pyrolysis temperature, and particle size, as well as pyrolysis conditions all have significant effects on the yields and compositions of bio-oil. In order to obtain optimal conditions for the desired products, more work needs to be done on the effects of process variables and products distribution. The effect of feedstock properties has recently been identified as one of the key research areas (Antal

1983), and the influence of composition on ash deformation and fusion temperatures for various biomass has been studied (Osman 1982; Kim *et al.* 2010). In addition, different kinds of biomass contain mineral matter in various proportions. Ganesh (1990) reported the influence of silica in rice husk and rice straw on their combustion and gasification characteristics and reported that silica in biomass traps carbon particles, making it unavailable for conversion above 1146 K. Thus, the catalytic role of mineral matter in char formation has also often been reported. Shafizadez *et al.* (1968) and Shao *et al.* (2010) found that inorganic salts suppress the formation of bio-oil and favour char-forming secondary reactions. Torren *et al.* (2009) pointed out that lower catalyst to feed ratios can lead to the formation of volatile oxygenates containing furans, acetic acid, and hydroxyacetaldehyde.

The properties of products are dependent on both the type and content of the catalyst and reaction temperature. Pyrolysis temperature to biomass has a significant influence on pyrolysis products, especially liquid product (Chen *et al.* 2001). Studies (Zuo *et al.* 2008) have shown that in the temperature range of 400 °C to 600°C, the variety of the distribution pattern and the yields of the compounds of pyrolysate are minor. However, the proportion of methoxyphenolic compounds decreases significantly and the proportion of phenol increases markedly when the temperature is up to the range 600 °C to 700 °C. At 700 °C, the relative content of phenol increases rapidly and the formation of aromatic hydrocarbons is enhanced, and small amounts of indene, naphthalene, and their derivatives are produced as well. The influence of pyrolysis temperature on phenolic products from lignin fast pyrolysis provides a theoretical basis on lignin fast pyrolysis for preparing phenolic chemicals. Therefore, the pyrolysis conditions are critical in maximizing the desired product. A promising option of upgrading bio-oil is to use a catalyst as part of the pyrolysis step to break down the macromolecules in biomass more completely.

EXPERIMENTAL

Materials

Feedstocks of bamboo and rice straw from Hunan Province, after leaf removal and oven drying, were milled and extracted for 48 h with acetone. The solid then was ground in a porcelain ball jar for 240 h with a rotation speed of 36 rpm, and micro-sized samples were prepared. The particles size of the raw material was distributed in the range 5 to 10 µm.

Feedstock characterization

Component analysis of feedstocks was completed according to the National standard methods and the literature (Shi *et al.* 2003); CHNS elemental analysis was performed with an elemental analyzer (Vario-I Germany), and metal-containing minerals were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

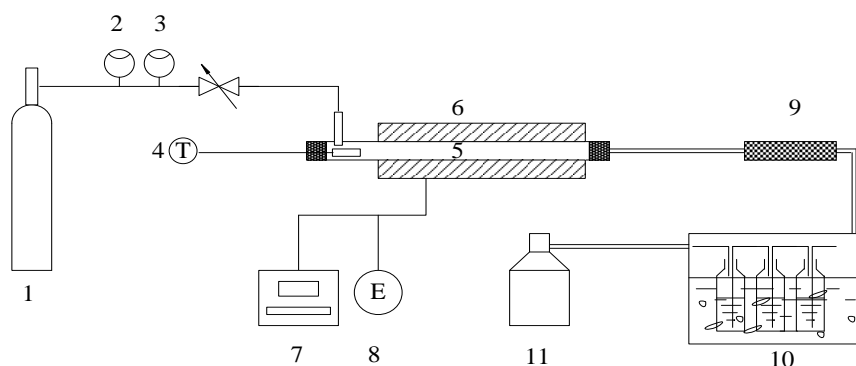
Catalyst

Before mixing the feedstocks and catalyst, NaCl was calcined to efficiently remove organic matter. Treatment conditions: a nitrogen atmosphere, a temperature of 800 °C, and an operating time of 6 h. NaCl was mixed well with feedstocks and used

once in the pyrolysis experiment. The related literature showed that impregnation of wood biomass with sodium hydroxide solution and direct mixing with NaOH pellets in a mortar resulted in the same effects upon pyrolysis (Domburg *et al.* 1976).

Pyrolysis Procedure

Pyrolysis experiments were carried out in a tubular reactor pyrolyzer, of which a schematic is shown in Fig. 1 (Lou and Wu 2010; Shen *et al.* 2010). Briefly, the reactor consisted of a temperature control device and quartz tube heated by a stainless steel block furnace. The carrier gas during pyrolysis runs was nitrogen at a flow rate 200 mL/min. A porcelain boat containing up to about 800 mg of feedstock, spread as a thin layer, was placed in middle from the downstream end of the tube. The furnace initially was heated over an empty portion of the tube and was equilibrated at a series of desired temperatures, *i.e.* 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 700 °C, 800 °C, and 900 °C. After the desired temperature was reached, the sample was rapidly moved into the furnace to initiate pyrolysis reaction. The runs were carried out at a series of desired temperatures and atmospheric pressure under approximately the constant heating rate. Pyrolysis reaction time was retained constant for 4 min, and the heating rate was constant for 1×10^4 °C/min at each temperature. The gaseous products passed through an ice-water condenser before being vented into a hood airbags. The isopropanol was fed into the condenser to absorb the condensed liquid product (bio-oil). The pyrolysis and evolution of most components were generally completed as soon as possible. This run duration also ensured that no significant decomposition occurred during the cooling of the sample. At the end of the run, the solid product (char) was allowed to cool to ambient temperature before being recovered, and it was stored over dry silica gel under vacuum until analysis.



1. Nitrogen cylinder. 2,3. Flow meters. 4. Thermocouple and porcelain. 5. Quartz tube. 6. Tubular furnace. 7. Temperature controller. 8. Electric power. 9. Filter. 10. Cooling system. 11. Gas collecting unit.

Fig. 1. Experimental schematic of biomass pyrolyzing reactor

Pyrolysate Characterization

After being dehydrated and filtered with a Millipore apparatus to eliminate ash residue, bio-oil was diluted to a suitable concentration for GC/MS analysis on an Agilent 7890 A GC equipped with an Agilent 5975 C mass selective detector (MSD, USA) under He carrier gas. The type of GC column was DB-5 (30 m × 0.25 mm, film thickness 0.25 μm). Carrier gas was highest purity helium with a flow rate of 0.8 mL/min. The oven was programmed to hold 40 °C for 2 min, ramp to 100 °C at a heating rate of 10 °C/min, then heated to 120 °C at a heating rate of 4 °C/min, after which it was heated to 230 °C for 5

min at a heating rate of 20 °C/min. The injector temperature was set at 250 °C, and the injector split ratio was set at 5/1 with a flow rate of 1 mL/min. Data processing was in compliance with Perkin Elmer NIST 08.

Surface morphology of char was analyzed with a scanning electron microscope coupled with energy dispersive spectrometer (SEM-EDS). After slicing and Au-ion plating, the dealt samples were evaluated with the SEM (S-3700N Hitachi, Japan).

Infrared spectra of char were recorded on an infrared spectrometer (FT-IR Nexus series, Thermo Nicolet Company, USA). The samples were pressed with chromatography grade KBr on a type Tianjin Fw-4 press machine, then the pressed transparent films were determined. Due to differences in the IR signal from various samples and to optimize the IR signal from each sample, the amount of sample used in IR could not be kept constant. The spectra were analyzed to compare the relative intensities of a functional group in different chars. However, since the amount of sample used in different analyses was not the same, only the relative ratios of the various functional groups in different chars were contrasted.

RESULTS AND DISCUSSION

Feedstock Analysis

Characteristics analysis and inorganic elemental composition of the feedstocks are presented in Tables 1 and 2, respectively. By comparison with its composition on a dry basis (see Table 1), bamboo contained a great amount of cellulose and lignin, whereas rice straw was found to be higher in hemicellulose and ash. Besides, the contents of carbon and oxygen were higher in bamboo than that of rice straw. Potassium was the most abundant in the inorganic fraction of the bamboo and rice straw, and other important minerals including calcium and magnesium were present at significant concentrations in the feedstock (see Table 2).

Table 1. Characteristics of the Feedstock

		Bamboo	Rice straw
Ultimate Analysis (wt%, db)	C	49.16	40.24
	H	5.85	5.44
	N	3.32	3.40
	S	0.09	0.17
	O/C	0.62	0.69
	H/C	1.43	1.62
	HHV (MJ/kg)	19.77	15.69
Empirical formula		$\text{CH}_{1.43}\text{N}_{0.06}\text{O}_{0.62}$	$\text{CH}_{1.62}\text{N}_{0.07}\text{O}_{0.69}$
Chemical Analysis (wt%, db)	Cellulose	43.19	34.38
	Hemicellulose	17.50	19.61
	Lignin	27.23	22.91
	Acetone-extractive	2.73	3.72
	Holocellulose	70.67	58.93
	Ash	0.62	13.53

Table 2. Inorganic Elemental Composition of the Feedstock

Content (mg kg ⁻¹)	Bamboo	Rice straw	Content (mg kg ⁻¹)	Bamboo	Rice straw
Al	0.29	24.78	Mn	118.67	373.56
Ca	158.01	1452.38	Na	20.35	528.19
Cu	1.04	1.95	Ni	0.59	599.86
Fe	32.16	189.99	Zn	47.28	203.47
K	1219.01	1676.61	P	47.27	82.70
Mg	134.56	530.05	Si	17.09	203.77

Effect of Feedstock Composition on Pyrolysate Yield

Different compositions of the materials contribute to a diversity of behaviours for biomass pyrolysis, and the properties of biomass have certain direct influence on its conversion into biofuels and biochemicals (Buranov and Mazza 2008; Lou and Wu 2010). During biomass pyrolysis, these inorganics, especially potassium and calcium, catalyze biomass decomposition and char forming reactions (Agblevor and Besler 1996). Studies on wood and 12 other types of biomass showed that de-ashing improved the volatile yield and increased initial decomposition temperature and rate of pyrolysis. The content of ash ranges from less than 1 wt% in softwoods to 15 wt% in herbaceous biomass or agricultural residues. On de-ashing, liquid yield increased and gas yield decreased for all the biomass samples studied (Raveendran *et al.* 1995; Matjaz *et al.* 2010). Thus, the low content of ash made the volatile yield and liquid yield increase, and it decreased gaseous yield for the feedstock in this experiment. An increase in char yield was attributed on a high content of potassium and zinc; thus rice straw had a high char yield, while bamboo had a high conversion to the liquid bio-oil. Pyrolysates were classified in terms of three phases, *i.e.* the gaseous, the liquid (bio-oil), and the solid (char). Table 3 presented the production yields from bamboo and rice straw pyrolysis.

Table 3. Production Yield from Bamboo and Rice Straw Pyrolysis

Temperature (°C)	Pyrolysate yield from bamboo (wt%)			Pyrolysate yield from rice straw (wt%)		
	Char	Gas	Bio-oil	Char	Gas	Bio-oil
400	30.41	14.60	54.99	38.63	18.69	42.68
450	22.29	18.13	59.58	32.36	20.26	47.38
500	18.20	19.39	62.41	32.18	24.10	43.72
550	19.13	26.75	54.12	30.68	26.00	43.32
600	19.81	21.35	58.84	30.75	24.32	44.93
700	18.19	29.21	52.60	30.77	29.48	39.75
800	15.12	31.62	53.26	30.70	33.70	35.60
900	15.47	37.36	47.17	27.18	35.62	37.20

Table 3 shows that the pyrolysis temperature had an obvious impact on the yield of products. As pyrolysis temperature increased, the gaseous yield generally continued to increase, and the gas was produced more rapidly from rice straw pyrolyzing than that of bamboo. In contrast to the char yield from rice straw, that of bamboo was far less, and it showed that the bamboo was pyrolyzed more thoroughly and generated more of the volatiles. The bio-oil yield from bamboo and rice straw reached a maximum at 500 °C and 450 °C, respectively, as pyrolysis temperature increased, and the secondary reaction intensified, causing the bio-oil yield to decline. Supposing the goal is to obtain bio-oil,

the pyrolysis temperature for the two biomass products needs to be chosen near to 500 °C. From the above analysis it is apparent that higher carbon and lower ash content of bamboo resulted in higher conversion to the volatiles or biofuel. Biomass containing more holocellulose and lignin produced much more bio-oil in the course of pyrolysis. Based on these considerations, bamboo is more suitable than rice straw for biomass pyrolysis when the purpose is conversion into biofuels or biochemicals.

A distribution of the gaseous production

The detected components of the gas contained hydrogen (H₂), carbon monoxide (CO), methane (CH₄), carbon dioxide (CO₂), and hydrocarbon (C₂H_x, x = 4, 6). Except for carbon dioxide, the other species together can be defined as total combustible gas (TCG). The unit of amount (mL/g) based on each gram raw materials to pyrolysis can be used to calculate the gas volume. The distribution of gaseous production was dependent on the temperature, as depicted in Fig. 2.

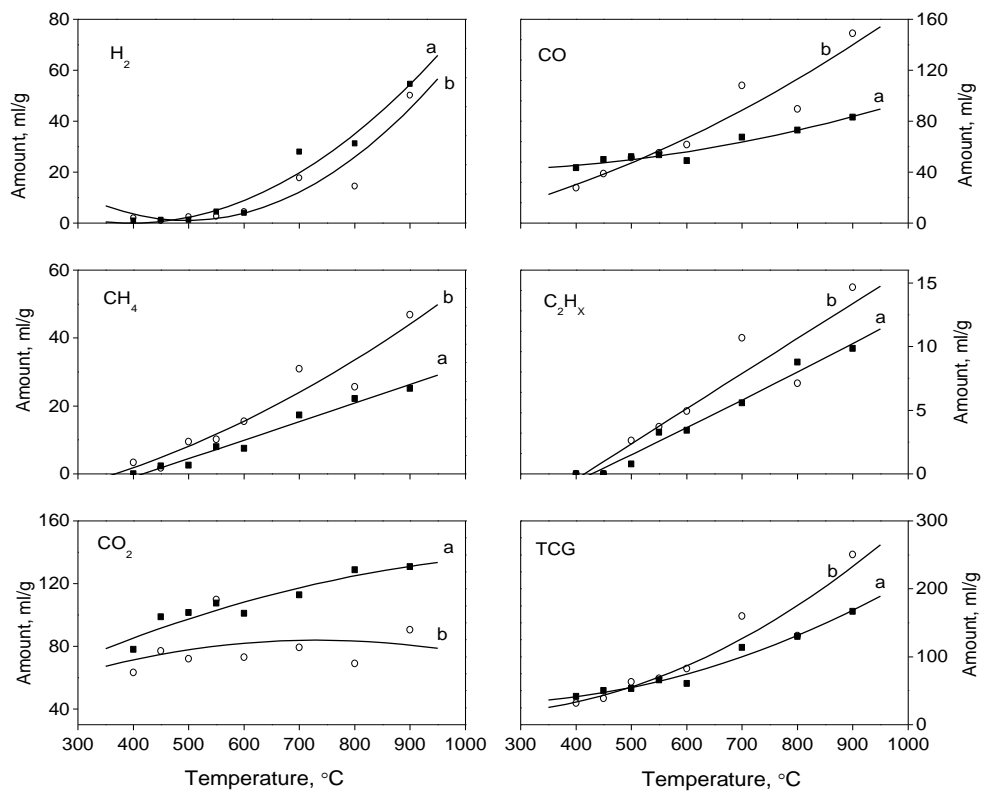


Fig. 2. Distribution of the gaseous products with temperature (a-rice straw, b-bamboo)

We can be seen from Fig. 2, the amount of gas products gradually increased with an increase of pyrolysis temperature. At low temperatures carbon dioxide was produced. Its amount from rice straw significantly increased as temperature increased, but not for bamboo. Carbon monoxide was generated much abundantly from bamboo pyrolysis. Moreover, the amounts of methane and hydrocarbon derived from bamboo pyrolysis far exceeded that from rice straw. Comparing bamboo and rice straw, the level of hydrogen was nearly equal. Generally, the amounts of TCG derived from bamboo were higher than that from rice straw in the temperature range from 550 °C to 900 °C, but the low temperature results did not follow the same rule.

Ingredients of bio-oil

The detected compounds present in bio-oil derived from bamboo and rice straw are respectively given in Table 4 (a) and Table 4 (b), and changes of ingredients yield in bio-oil varying with temperature are presented in Fig. 3.

Table 4(a). Bio-oil Compounds from Bamboo Pyrolysis at Various Temperatures

Compounds class		Relative area to tetracosane							
		400 °C	450 °C	500 °C	550 °C	600 °C	700 °C	800 °C	900 °C
Furans	Furfural	2.31	1.76	1.75	1.88	2.83	2.29	2.75	1.65
	5-methyl-2-Furancarboxaldehyde	0.16	0.16	0.18	-	0.21	-	0.20	-
	2-Furanmethanol	2.35	2.94	3.18	2.68	2.21	1.69	1.49	0.94
	2,3-dihydro-Benzofuran	5.92	10.65	11.44	16.53	7.22	7.41	6.87	6.26
	2(5H)-Furanone	0.44	0.41	0.44	0.51	1.19	0.34	0.72	-
	5-(hydroxymethyl)-2-Furancarboxaldehyde	0.67	-	-	-	0.41	0.43	0.43	-
	1-(2-furanyl)-Ethanone	0.61	0.37	0.42	-	0.30	-	-	-
Acids	Acetic acid	9.18	12.80	14.33	14.91	11.49	9.37	11.09	5.73
	Propanoic acid	1.03	1.94	1.98	0.87	0.51	1.10	0.54	0.38
	4-hydroxy-Butanoic acid	-	-	-	1.19	-	-	-	-
	4-hydroxy-3-methoxy-Benzeneacetic acid	0.28	1.00	-	-	3.90	6.39	-	-
	Pterin-6-carboxylic acid	0.51	2.04	0.38	0.41	1.87	-	-	-
	Cycloserine	0.72	-	-	-	-	-	0.41	-
Ketones	1-hydroxy-2-Propanone	2.43	4.49	4.42	4.35	2.94	3.01	2.83	2.15
	Hydroxy-2-butanone	2.43	1.27	1.31	0.79	0.93	0.89	0.93	0.67
	Cyclopenten-1-one	0.31	2.61	5.75	2.38	1.67	2.42	2.00	0.98
	Butyrolactone	0.32	1.24	1.82	-	0.60	0.80	-	-
	1,2-Cyclopentanedione	1.80	2.59	3.20	3.79	2.02	1.46	1.47	1.50
	3-ethyl-2-hydroxy-2-Cyclopenten-1-one	2.33	0.61	1.13	0.82	1.63	1.61	0.71	-
	1-(2-hydroxy-5-methylphenyl)-Ethanone	-	-	-	1.09	-	0.52	-	-
	3,3-dimethyl-2-Butanone	-	0.22	0.91	0.28	-	-	-	-
	4(1H)-Pyridone	-	-	0.42	-	-	-	-	0.39
3,4-dimethyl-Sydnone	0.18	-	-	-	-	-	-	-	
Phenols	2-methoxy-Phenol	1.63	2.16	2.09	2.07	0.94	0.37	0.59	0.26
	4-methyl-Guaiacol	0.97	0.49	0.49	0.47	0.54	-	0.43	-
	4-ethyl-Guaiacol	0.66	0.71	0.65	0.74	0.47	-	-	-
	4-vinyl-Guaiacol	2.24	2.24	2.84	3.06	1.67	1.20	1.54	1.15
	Phenol	1.09	3.55	4.75	4.06	3.09	4.20	3.93	4.55
	2,6-dimethyl-Phenol	3.15	2.69	0.22	-	0.24	0.33	0.29	-
	2- or 4-ethyl-Phenol	0.80	2.18	2.65	4.16	3.50	5.00	3.56	3.46
	3- or 4-methyl-Phenol	0.57	1.41	2.95	3.74	2.59	3.61	3.34	3.76
	2,6-dimethoxy-Phenol	3.15	-	2.56	2.99	1.73	0.88	1.14	0.57
	2-methoxy-4-(1-propenyl)-Phenol	2.73	1.14	1.07	1.54	1.29	0.69	1.08	0.67
	2,6-dimethoxy-4-(2-propenyl)-Phenol	2.92	1.86	0.27	1.65	2.62	0.30	1.56	0.77
PAH	(E)-Stilbene	1.95	1.88	1.85	1.82	1.19	-	-	-
	4-ethyl-Biphenyl	-	-	-	-	-	-	0.46	0.64
	Naphthalene	-	-	-	-	-	-	0.39	1.63

Note: "-" — Not detected, the same below

Table 4(b). Bio-oil Compounds from Rice Straw Pyrolysis at Various Temperatures

Compounds class		Relative area to tetracosane							
		400 °C	450 °C	500 °C	550 °C	600 °C	700 °C	800 °C	900 °C
Furans	Furfural	1.06	1.95	1.72	1.40	2.17	1.94	1.53	1.66
	tetrahydro-2-Furanmethanol	0.85	-	0.49	-	-	-	-	-
	2-Furanmethanol	1.80	3.53	2.82	2.29	1.92	1.80	1.38	1.16
	2,3-dihydro-Benzofuran	2.38	5.13	5.96	6.47	4.12	3.99	5.26	5.14
	2(5H)-Furanone	- b	0.51	0.51	0.36	0.37	-	-	-
	5-Hydroxymethyl dihydrofuran-2-one	-	0.53	0.44	0.59	-	-	-	-
	1-(2-furanyl)-Ethanone	-	-	-	0.37	0.31	0.22	-	0.52
	2,3-dihydro-2-methyl-Benzofuran	-	-	-	-	-	0.28	-	0.31
Acids	Acetic acid	5.12	9.76	8.88	6.71	6.39	5.61	2.98	2.91
	Propanoic acid	0.55	1.15	1.06	0.80	0.74	0.73	0.41	0.41
	2-methyl-anhydride-Propanoic acid	-	-	1.16	-	-	-	-	-
	4-hydroxy-Butanoic acid	-	-	-	1.43	1.24	-	-	-
	2-Pyrone-5-carboxylic acid	-	-	-	0.40	-	-	-	-
	Pterin-6-carboxylic acid	-	-	-	0.24	-	-	-	-
Ketones	1-hydroxy-2-Propanone	5.08	9.11	6.97	5.16	5.13	4.44	2.82	3.36
	Hydroxy-2-butanone	1.05	1.91	1.54	2.87	1.46	1.33	0.74	1.09
	l-2-Cyclopenten-1-one	0.53	2.44	3.63	4.43	1.41	3.52	2.56	4.03
	Butyrolactone	0.89	1.76	1.63	-	-	1.35	0.99	0.90
	1,2-Cyclopentanedione	1.94	3.98	3.19	5.36	4.01	2.40	0.97	1.94
	3-ethyl-2-hydroxy-2-Cyclopenten-1-one	0.53	1.27	2.63	2.47	1.66	1.30	1.52	1.17
	1-(2-hydroxy-5-methylphenyl)-Ethanone	-	4.27	4.35	-	-	-	-	-
	Cyclopentanone	-	-	0.24	0.30	0.31	-	-	0.22
	2-Acetylcyclopentanone	-	-	0.47	-	-	-	-	-
	tetrahydro-2H-Pyran-2-one	-	0.42	0.43	-	-	-	-	-
	2,3-dihydro-1H-Inden-1-one	-	-	0.35	0.40	0.27	0.31	0.39	0.48
Phenols	2-methoxy-Phenol	1.55	2.89	2.91	2.13	1.39	0.44	0.75	0.44
	4-methyl-2-methoxy-Phenol	0.00	0.35	0.54	0.47	0.30	-	-	-
	4-ethyl-2-methoxy-Phenol	0.41	0.87	1.01	0.97	0.58	-	0.54	0.27
	4-vinyl-2-methoxy-Phenol	2.02	-	-	3.94	2.32	0.64	1.92	1.40
	Phenol	1.11	1.62	4.00	4.76	3.68	4.74	6.72	5.58
	2,6-dimethyl-Phenol	-	-	0.84	0.63	0.68	0.55	0.38	0.80
	2- or 4-ethyl-Phenol	0.66	1.15	2.60	3.49	2.18	3.38	6.18	5.22
	3- or 4-methyl-Phenol	-	-	2.38	3.77	1.97	3.11	5.37	5.41
	2,6-dimethoxy-Phenol	0.87	1.89	2.00	1.94	1.07	0.50	0.91	0.49
	4-(1-propenyl)-Guaiacol	-	0.91	0.84	0.96	0.44	-	0.51	0.39
	3-hydroxy-4-methoxy-Benzaldehyde	0.28	0.64	0.63	0.86	0.33	-	-	-
Others	4-(2-propenyl)-Syringol	-	0.40	0.37	0.29	-	-	-	-
	D-glucopyranose	-	-	0.59	0.76	0.37	0.31	0.41	0.41
	Naphthalene	-	-	-	-	-	0.42	0.91	1.91

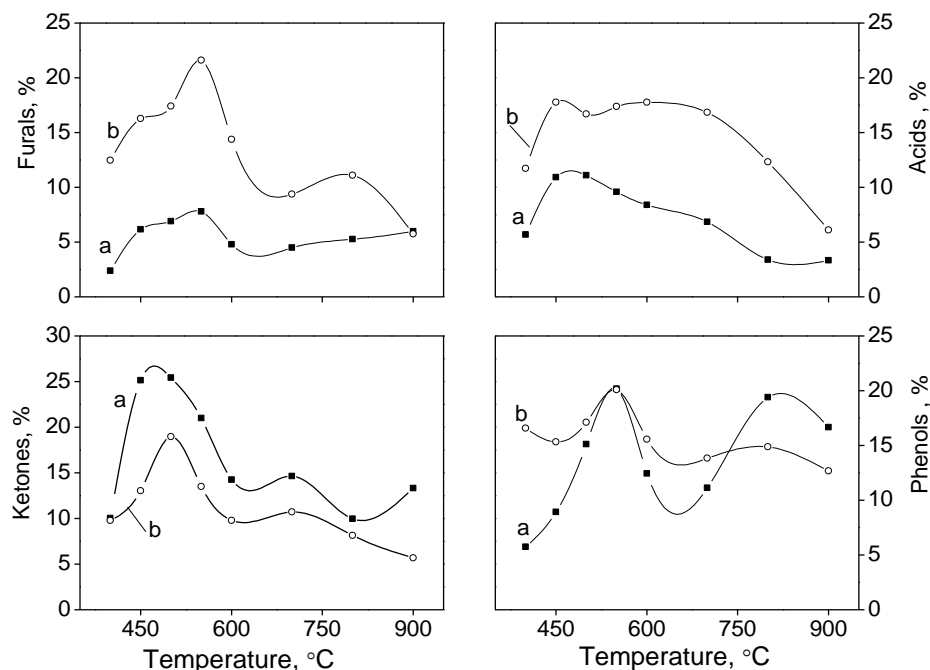


Fig. 3. Changes of ingredients yield in bio-oil varying with temperature (a – rice straw, b – bamboo, % – relative area to tetracosane)

Compounds of bio-oil from feedstock pyrolysis include mainly phenols, ketones, furans, organic acids (mainly acetic acid), and small portions of naphthalene. Major furans were 2,3-dihydro-benzofuran, 2-furanmethanol, and furfural. Among them the highest content of 2,3-dihydro-benzofuran (16.53 %) was formed at 550 °C, and it was derived from bamboo pyrolysis much more than that from rice straw owing to the different lignins structure. Ketones were derived from hemicellulose pyrolysis that mainly contained 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 3-ethyl-2-hydroxy-2-cyclopenten-1-one, and 2-cyclopentanedione, *etc.* Lignin was pyrolyzed to form bio-oil mainly containing aromatic compounds and a small amount of acid alcohol, *etc.*, and aromatic compounds were mostly phenol, guaiacols, syringols, and alkyl-phenols.

Figure 3 shows that the formation rate of products had two extreme values with an increase of temperature. One extreme value was at around 500 °C around, while the other was at approximately 750 °C. Substantial quantities of phenols, ketones, and furans were generated, owing to the fact that cellulose and hemicellulose undergo pyrolysis to produce a large amount of furans, ketones, and acids at 500 °C, while simultaneously the lignin also begins to undergo a degradation reaction to generate phenolic compounds, as pyrolysis temperature increases. The producing phenols and furans were involved in a secondary decomposition reaction and were metabolized into simple phenols and furan through microbial decarboxylation and dehydroxylation, and therefore there was an extreme value at approximately 750 °C.

The compositions and its content of biomass pyrolysis had a significant influence on the products production and ingredients. Compared to rice straw, bio-oil derived from bamboo pyrolysis contained relatively more phenols, furans, organic acids, and less ketones because of bamboo containing higher cellulose and lignin and rice straw containing more hemicellulose. However, it is worth mentioning that organic acids in

bio-oil are considered unfavourable for bio-oil quality, and possible measures to reduce acids content need further study.

Effect of Additive NaCl on Pyrolysate Yield

In the case of bamboo, since the obtained bio-oil derived from bamboo pyrolysis was the highest at 500 °C, NaCl was added to bamboo as catalyst and pyrolysis temperature was set at 500 °C. Three levels of additive NaCl were respectively 1 %, 5 %, and 10 % (based on mass ratio).

The fast pyrolysis of bamboo with the catalytic NaCl was carried out in a tubular reactor pyrolyzer at 500 °C. The obtained productions of gas, bio-oil (also called tar), and char are presented in Fig. 4. It is apparent that the production changed with the additive amount of NaCl.

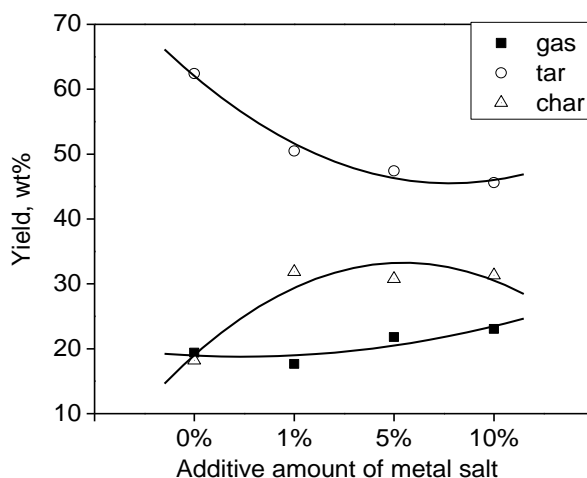


Fig. 4. Effect of catalyst-to-bamboo for catalytic fast pyrolysis (Reaction conditions: final reaction temperature for 500 °C; NaCl catalyst)

Compared with no-catalyst, the yield of the gas derived from catalyst-to-bamboo pyrolysis increased from 19.39 wt% to 23.4 wt%, and char yield also increased from 18.20 wt% to 31.35 wt%, while bio-oil yield decreased from 62.41 wt% to 45.61 wt%. From the added amount of catalyst, it is apparent that the increase of NaCl improved the gas and char productions yet reduced bio-oil production. When NaCl catalyst added to bamboo was 1%, the catalyst had a noticeable effect on pyrolysate production, so the contrasting materials of alkali and salts in biomass pyrolysis would have different degrees of inhibition, restraining the cracking reaction for lignin, cellulose, and hemicellulose, and inhibiting the biomass pyrolyzed thoroughly. Thus lower minerals content in biomass was found to be favourable for cracking.

The trends of products derived from bamboo pyrolysis agreed with an earlier report (Zhang *et al.* 2009). The oil yield was markedly reduced with catalyst added, although the oxygen content in the oil reduced with the formation of coke. The influence of catalyst causes the oxygen in the pyrolysis oils to be converted into H₂O at lower catalysis temperatures and largely into CO and CO₂ at higher catalysis temperatures (Williams and Nugranad 2000).

Ingredients of bio-oil from bamboo with NaCl

From the above pyrolysates yield, it was known the NaCl dosage of 1% had a marked catalytic action. However, with the NaCl dosage increased to 10%, the catalysis

gradually weakened, so it was possible to detect only the ingredients of bio-oil at the NaCl dosage of 1% and 5%, which was in contrast to the results with no catalyst in bamboo. The detected ingredients of bio-oils at 500 °C are listed in Table 5, whereas Fig. 5 shows the distribution of phenols, ketones, acids, and furan derivatives when the catalyst was introduced.

Table 5. Ingredients of Bio-oil from Bamboo Pyrolysis with NaCl Catalyst

Compounds class		Relative area to tetracosane		
		0%	1%	5%
Furans	Furfural	0.96	3.08	2.53
	5-methyl-2-Furancarboxaldehyde	0.10	0.21	0.53
	2-Furanmethanol	1.75	4.45	3.90
	2,3-dihydro-Benzofuran	6.29	14.65	15.59
	2(5H)-Furanone	0.24	0.75	0.71
	1-(2-furanyl)-Ethanone	0.23	0.57	0.52
Acids	Acetic acid	7.88	20.36	18.52
	Propanoic acid	1.09	0.98	0.91
	Pterin-6-carboxylic acid	0.21	-	-
Ketones	1-hydroxy-2-Propanone	2.59	8.66	7.35
	1-Hydroxy-2-butanone	1.22	1.61	1.46
	Cyclopenten-1-one	3.16	2.98	2.96
	Butyrolactone	1.00	1.23	1.30
	1,2-Cyclopentanedione	1.76	2.28	3.59
	3-ethyl-2-hydroxy-2-Cyclopenten-1-one	0.62	5.11	0.81
	4(1H)-Pyridone	0.23	0.26	0.30
Phenols	2-methoxy-Phenol	1.15	3.02	2.80
	2-methoxy-4-methyl-Phenol	0.27	0.59	0.58
	4-ethyl-2-methoxy-Phenol	0.36	0.86	0.90
	2-methoxy-4-vinyl-Phenol	1.56	3.54	3.37
	Phenol	2.61	3.57	4.92
	4-ethyl-3-methyl- Phenol	0.12	0.22	0.73
	4-ethyl-Phenol	1.46	1.89	1.93
	3- or 4-methyl-Phenol	1.62	0.94	2.13
	2,6-dimethoxy-Phenol	1.41	3.40	3.67
	2-methoxy-4-(1-propenyl)-Phenol	0.59	1.71	1.72
	2,6-dimethoxy-4-(2-propenyl)-Phenol	0.47	1.49	1.50
	5-tert-Butylpyrogallol	-	1.16	-
	4-Methyl-2,5-dimethoxybenzaldehyde	0.28	-	-
Others	(E)-Stilbene	1.02	-	-
	1,2,3-trimethyl-Benzene	-	1.14	1.30
	Indane	-	-	1.06
	3-oxo-Butanoic acid, propyl ester	0.24	1.25	1.10
	Propanoic acid, 2-oxo-, ethyl ester	0.64	1.34	1.24
	9,10-dihydro-Phenanthrene	-	2.37	2.31
	Styrene	1.98	-	-
	4-tert-Butoxystyrene	-	0.95	0.47

Research results revealed that while the introduction of catalyst generally restrained the generation of bio-oil, nevertheless a small amount of catalyst can cause a big change in the chemical composition of bio-oil. Compared with the no-catalytic experiment, the monofunctional phenols, furans, and acetic acid increased, and the ketones and acids were maximized with a NaCl addition of 1%. A similar result has been

reported by Zhang *et al.* (2009), who investigated catalytic fast pyrolysis of corncob with fluidized catalytic cracking (FCC) catalysts in a fluidized bed, which indicated that the use of the FCC catalyst led to an increase of the total acetic acid yield.

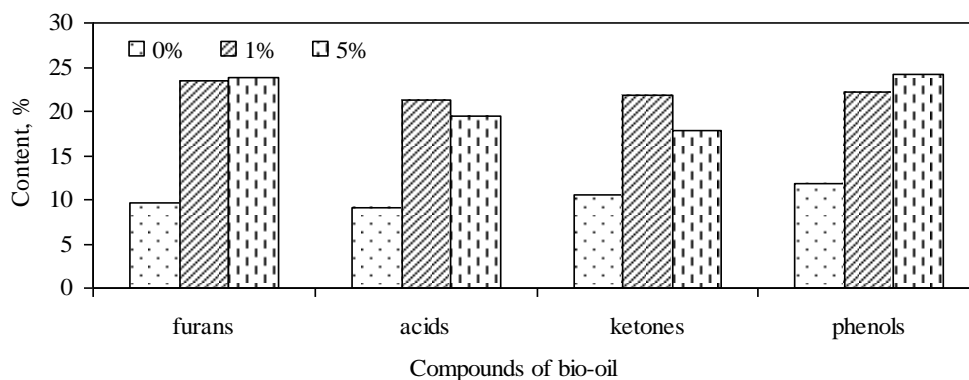


Fig. 5. Distribution of bio-oil ingredients from bamboo pyrolysis with NaCl catalyst at 500 °C

The phenols derived from the polymerization precursors of lignin increased with an increase of added NaCl. For instance, the following substances were increased: 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol, phenol, 2-methoxy-4-vinyl-phenol, 2,6-dimethoxyphenol, 2-methoxy-4-(1-propenyl)-phenol, and 2,6-dimethoxy-4-(2-propenyl)-phenol. The ketones, such as 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, and 1,2-cyclopentanedione increased remarkably in the presence of NaCl. The most abundant furan derivatives detected in bio-oil were 2,3-dihydro-benzofuran, 2-furanmethanol, furfural, 2(5H)-furanone, 5-methyl-2-furancarboxaldehyde, and 1-(2-furanyl)-ethanone. The peak area percentages of furan derivatives increased from 9.57% to 23.78%. In particular, that of 2,3-dihydro-benzofuran increased significantly with the additive amount of NaCl catalyst increasing, but sugar was not detected in the collected bio-oil. Research results showed that NaCl added to feedstock managed to change the pyrolysis behaviors of biomass and pyrolysate distribution, especially affecting the composition of bio-oil and gas.

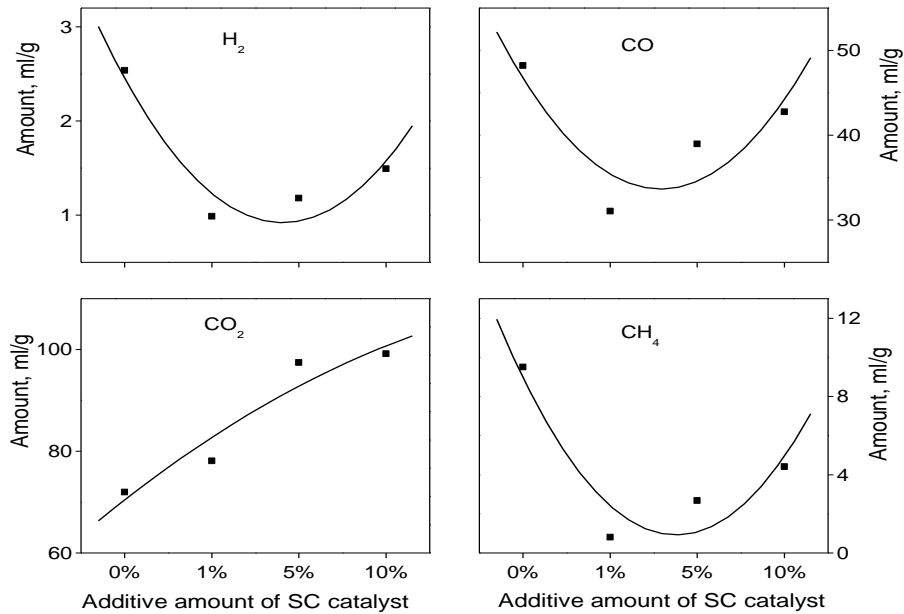
A distribution of gaseous production with NaCl catalyst

The distributions of gas with NaCl catalyst are presented in Fig. 6. The total yield of gas with varying amounts of NaCl added is listed in Table 6. Except for C₂H₄, the ingredients of H₂, CO, CO₂, and CH₄ produced 2.45 mL/g in catalytic pyrolysis of NaCl. It was observed that a lower catalyst percentage led to more change of gaseous amount. The amount of CO₂ increased linearly as the percentage of NaCl catalyst increased. However, the presence of NaCl lowered the amount of H₂, CO, and CH₄, and the amount of H₂, CO, and CH₄ were minimum with a NaCl level of 1%. The amount then increased with the increase of NaCl up to 10%.

During the catalytic pyrolysis experiments, more carbon was converted to CO and CO₂. The increase of oxygen transferred into coke in the catalytic experiments can be attributed to the increase of the coke yield. NaCl contributed more catalytic activation in converting oxygen into CO and CO₂. Converting oxygen into CO and CO₂ was an ideal route to decrease the oxygen content of bio-oil (tar). Gas increased from 19.39 % in the noncatalytic experiment to 23.40 % in the catalytic experiments with a NaCl level of 10%.

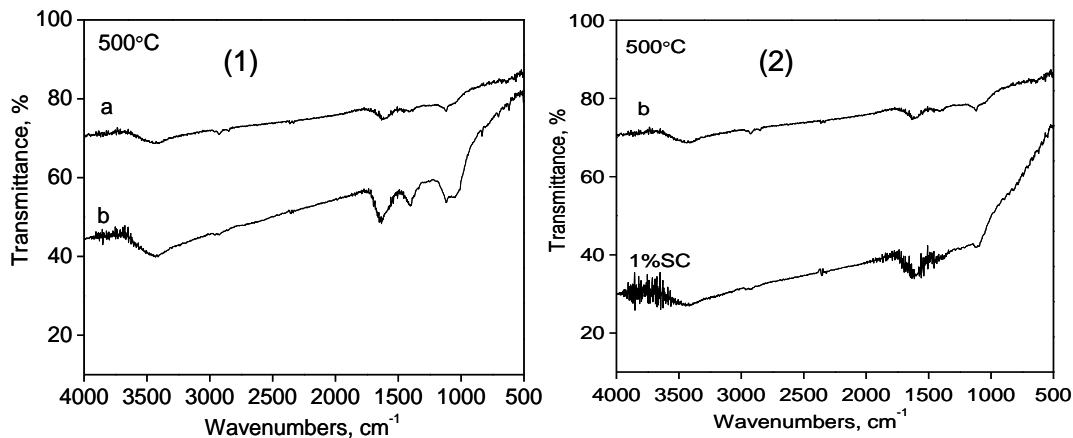
Table 6. Total Yield of Gas from Bamboo Pyrolysis with NaCl Catalyst at 500 °C

Catalyst amount	Mass fraction (wt %)	Volume yield (ml/g)
No catalyst	19.39	154.67
1%	17.67	110.93
5%	21.80	139.21
10%	23.04	147.82

**Fig. 6.** Distribution of gas yield from bamboo with NaCl catalyst at 500°C

FT-IR Characteristics of Char

FT-IR spectra of char from rice straw and bamboo, with a NaCl addition of 1% to bamboo pyrolysis are given in Fig. 7.

**Fig. 7.** FT-IR spectra of char samples (a-rice straw; b-bamboo; 1%SC - NaCl of 1%to bamboo)

Compared to the char of rice straw, the char of bamboo had a stronger absorbance in the range of wave numbers from 1000 to 1600 cm⁻¹, and the peaks in the wavenumbers range were attributed to absorption from aromatic rings. Therefore, the aromatic quality

of char from bamboo pyrolysis became more intense than that from rice straw because of the high lignin content in bamboo. Also the aromatic quality of char with a level of 1% NaCl to bamboo was more intense than that from bamboo by itself, which is because NaCl markedly improved the yield of bio-oil yet suppressed the formation of char. The solid product led to a gradual accumulation of inorganic crystals on the exposed surface during pyrolysis process, and some constituents also melted, resulting in the formation of bubbles by the evolving gas (Sharma *et al.* 2002).

CONCLUSIONS

1. The different compositions of bamboo and rice straw contributed to different behaviors during the course of their pyrolysis. Higher cellulose and lower ash contents in bamboo led to the production of more volatiles and higher thermal conversion. The obtained bio-oil consisted of phenols, ketones, furans, and organic acids derived from bamboo pyrolysis, and it had a higher yield. Ketones and carbon dioxide had a higher production in rice straw pyrolysis due to the higher content of hemicellulose and ash present in rice straw.
2. A lower ash in biomass increased the volatiles production, yet decreased the char yield. Moreover, biomass having a lower-ash content to pyrolysis led to a higher yield of bio-oil and a lower yield of gas. On the side, added NaCl decreased bio-oil yield yet improved the gas and char yields. The NaCl dosage of 1% caused the composition of bio-oil to undergo a big change.
3. The products distributions were closely linked with the dosage of NaCl catalyst, which improved gas and char yields yet decreased bio-oil yield. Simultaneously, it increased the relative content of phenols, ketones, acids, and furans. In summary, the use of mineral or metal salt during pyrolysis reaction advanced the char formation and carbon dioxide production, and enhanced the aromatic quality of char. Therefore, de-ashing or removing minerals in the feedstock would be indispensable for biomass conversion into the most widely sought after forms of bio-energy or biochemicals by use of the fast pyrolysis technique.

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REFERENCES CITED

- Adam, J., Antonakou, E., Lappas, A., Stoecker, M., and Nilsen, M. (2006). "In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials," *Microporous Mesoporous Mater* 96, 93-101.
- Antal, M. J. J. (1983). In: *Advances in Solar Energy*, Vol. 2, Boer, K. W., and Duffie, J. A. (eds.), American Solar Energy Society, New York, pp. 175-239.

- Aglevor, F. A., and Besler, S. (1996). "Inorganic compounds in biomass feedstocks. 1. Effect on the quality of fast pyrolysis oils," *Energy Fuels* 10, 293-298.
- Buranov, A. U., and Mazza, G. (2008). "Lignin in straw of herbaceous crops," *Industrial Crops and Products* 28, 237-259.
- Bridgwater, A. V., and Cottam, M. L. (1992). "Opportunities for biomass pyrolysis liquids production and upgrading," *Energy Fuels* 6, 113-120.
- Chen, C. A., Pakdel, H., and Roy, C. (2001). "Production of monomeric phenols by thermchemical conversion of biomass: A review," *Bioresource Technology* 79, 277-299.
- Domburg, G., Kirsbaums, I., Dobele, G., and Sergeeva, V. N. (1976). "Influence of basic additives on the formation of phenols in lignin pyrolysis," *Khim. Drev.* 5, 73-80.
- Ganesh, A. (1990). *Studies on Characterisation of Biomass for Gasification*, Ph.D Thesis, Indian Institute of Technology, New Delhi.
- Horne, P.A., and Williams, P. T. (1996). "Upgrading of biomass-derived pyrolytic vapours over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields," *Fuel* 75, 1043-1050.
- Kim, S. J., Jung, S. H., and Kim, J. S. (2010). "Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds," *Bioresource Technology* 101, 9294-9300.
- Lou, R., and Wu, S. B. (2010). "Effect of conditions on fast pyrolysis of bamboo lignin," *J. Anal. Appl. Pyrol.* 89, 191-196.
- Lou, R., and Wu, S. B. (2010). "Products properties from fast pyrolysis of enzymatic/mild acidolysis lignin," *Applied Energy* 88, 316-322.
- Matjaz, O., Bogomir, M., and Vindis, P. (2010). "Biogas production from maize hybrids," *Biomass and Bioenergy* 34, 1538-1545.
- Nokkosmaki, M. I., Kuoppala, E. T., and Leppamaki, E. A. (2000). "Catalytic conversion of biomass pyrolysis vapours with zinc oxide," *J. Anal. Appl. Pyro.* 55, 119-131.
- Osman, E.A. (1982). "A study of the effects of ash chemical composition and additives on fusion temperature in relation to slag formation during gasification of biomass," Ph.D Thesis, University of California.
- Raveendran, K., Ganesh, A., and Khilar, K. C. (1995). "Influence of mineral matter on biomass pyrolysis characteristics," *Fuel* 74, 1812-1822.
- Ruane, J., Sonnino, A., and Agostini, A. (2010). "Bioenergy and the potential contribution of agricultural biotechnologies in developing countries," *Biomass and Bioenergy* 34, 1427-1439.
- Shafizadez, F.A. (1968). "Pyrolysis and combustion of cellulosic materials," *Carbohydrate Chem.* 23, 419-474.
- Shi, S. L., and He, F. W. (eds.) (2003). *Analysis of Pulp and Papermaking*, China Light Industry Press, Beijing.
- Sharma, R. K., Wooten, J. B., and Baliga, V. L. (2002). "Characterization of char from the pyrolysis of tobacco," *J. Agr. Food Chem.* 50, 771-783.
- Shao, J. G., Yan, R., Chen, H. P., Yang, H. P., and Dong, H. L. (2010). "Catalytic effect of metal oxides on pyrolysis of sewage sludge," *Fuel Processing Technology* 91, 1113-1118.
- Shen, D. K., Gua, S., Luo, K. H., Wang, S. R., and Fang, M. X. (2010). "The pyrolytic degradation of wood-derived lignin from pulping process," *Bioresource Technology* 101, 6136-6146.

- Torren, R., Carlson, G. A., and Tompsett, W. C. C. (2009). "Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks," *Top Cata.* 52, 241-252.
- Wright, M., and Brown, R. C. (2007). "Comparative economics of biorefineries based on the biochemical and thermochemical platforms," *Biofuels Bioproc. Bioref.* 1, 49-56.
- Williams, P. T., and Nugranad, N. (2000). "Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks," *Energy* 25, 493-513.
- Zhang, H. Y., Xiao, R., and Wang, D. H. (2009). "Catalytic fast pyrolysis of biomass in a fluidized bed with fresh and spent fluidized catalytic cracking (FCC) catalysts," *Energy Fuels* 23, 6199-6206.
- Zuo, S. L., Yu, J., and Che, S.W. (2008). "Effect of pyrolysis temperature on pyrolysate during fast pyrolysis of industrial lignin made by acid precipitation," *Journal of Fuel Chemistry and Technology* 36, 144-148.

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