

PYROLYTIC PRODUCTS FROM RICE STRAW AND ENZYMATIC/MILD ACIDOLYSIS LIGNIN (EMAL)

Rui Lou, Shu-bin Wu,* Gao-jin Lv, and Da-liang Guo

A pyrolysis tube furnace system was designed to assess the impact of different components on pyrolysis characteristics under nitrogen atmosphere, and pyrolysis temperature (400 to 900°C) as important factors acting on the samples during pyrolysis. The obtained pyrolysate was classified into three groups, i.e. the condensed liquid product (bio-oil), solid product (bio-char), and light gas. Gas chromatography (GC) was used to analyze ingredients of the light gas released during pyrolysis, and a gas chromatography/mass spectrometer (GC/MS) was used to analyze bio-oil. The results revealed that the volatiles from rice straw pyrolysis exceeded that from lignin at temperatures below 700°C as a result of the higher char generation from lignin pyrolysis. With an increase of pyrolysis temperature, the yield of char decreased and light gas persistently increased, and the yield of bio-tar was maximized at 500°C. In the gas product, H₂, CO, CO₂ and some light hydrocarbons (CH₄, C₂H₄ and C₂H₆) could be found, and H₂ and CO were abundant. Compounds of bio-oil derived from lignin were simple and consisted of aromatic hydrocarbons, chain hydrocarbon, monoaromatics, and a minor amount of ketones. Phenolic compounds, which comprised 50 to 60%, can be converted easily to obtain high-value chemicals and high quality biofuels.

Keywords: Rice straw; Lignin; Pyrolysis; Gas chromatography; Bio-oil; Bio-char; Gaseous

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INTRODUCTION

Biomass from herbaceous crops is the largest renewable source for the production of bioproducts and biofuels. The available information about lignins in straw of herbaceous crops is scattered, and the available reviews generally address wood lignins (Buranov and Mazza 2008). Lignin in herbaceous plants is receiving increasing attention for two primary reasons: (a) annual renewability and (b) herbaceous plants have the largest annual biomass stock (1549 million tons/year worldwide) (Kim and Dale 2004). Lignin is a major constituent of all woods (typically 15 ~ 30wt %) and of many other biomass materials. The pyrolysis of lignin, cellulose, and other biomass materials has been studied extensively (Theodore 1985; Dieboid 1981; Ferdous 2002; Tan 2005). The increased interest in the conversion of wood and its components for producing alternative fuels and chemicals necessitates a fundamental understanding of processes involving pyrolysis of biomass (Demirba 1998). Biomass is converted to liquid fuels to increase the volumetric heat content and to decrease transportation costs, and conversion of biomass to liquid products is based on early research.

Fast- and flash-pyrolysis appear as the most promising methods for fuel-oil-substitute production from biomass (Beckman 1985; Radlein 1991). It has been verified that the highest liquid yields from novel biomass can be produced with flash pyrolysis (Scott 1982).

Plants that differ in their chemical composition have different pyrolytic properties, and these properties have direct influences on the thermochemical conversion of plants into biofuel and chemicals. Thus, in the present study, rice straw and lignin derived from rice straw are contrasted to study their pyrolysis characteristics, and the conversion of lignin into value-added products is addressed.

EXPERIMENTAL

Materials

Rice straw (RS) without leaves was collected from Hunan Province. After being dried, milled, and finally extracted for 48 hrs with acetone, the obtained powder was milled in a porcelain ball jar for 240 hrs at a rotation speed of 36 rpm, and then was used to prepare lignin by means of enzymatic/mild acidolysis method (Wu 2003; Wang 2006; Lou 2008; Zheng 2009; Yang 2010). Finally, the enzymatic/mild acidolysis lignin (EMAL) from rice straw with particle size of about 5 μm was obtained. The lignin and the rice straw were then separately subjected to pyrolysis, as described below.

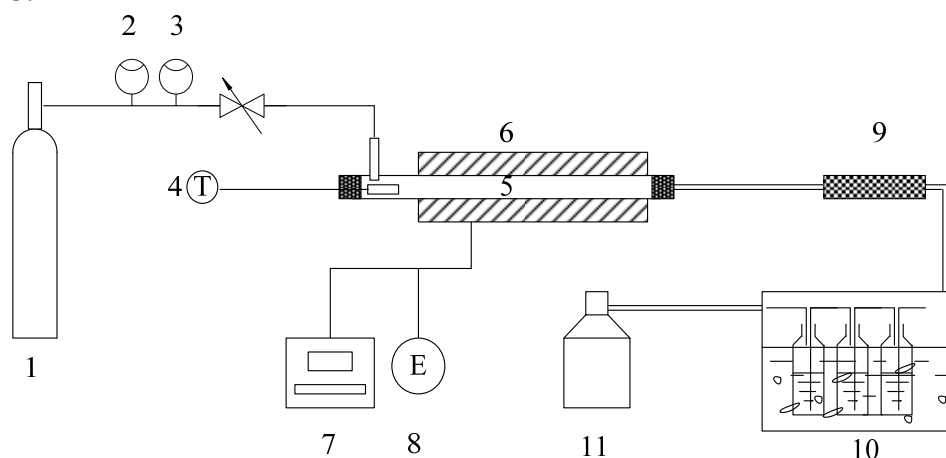
Methods

Pyrolysis was carried out in a tubular reactor at the following six levels of temperature: 400, 500, 600, 700, 800 and 900 °C. Figure 1 shows a schematic of the pyrolysis reactor (Lou 2010). Briefly, the reactor consisted of a cylindrical quartz glass tube heated by a stainless steel block furnace. The carrier gas was nitrogen in pyrolysis runs at a flow rate 200 mL/min. A porcelain boat containing 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 the desired temperature. After the desired temperature was reached, the sample was rapidly moved into the furnace to initiate pyrolysis. The runs were made at atmospheric pressure and at the desired temperature range from 400 to 900 °C under approximately isothermal conditions. Reaction time for pyrolysis was kept constant (240s) at each temperature, assuming that the heating rate (1×10^4 °C/min) was constant. The gas products were the released volatiles that passed through an ice-water condenser before being vented into the gas collecting unit. The isopropanol was set in a condenser to absorb the condensed liquid products (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 (bio-char) was allowed to cool to ambient temperature before being recovered. It was stored over dry silica gel under vacuum until analyzed.

Gaseous products released from pyrolysis were analyzed by GC analyzer (GC-20B SHIMADZU) with a thermal conductivity detector (TCD), and the C-RID area method was used to detect gaseous component. Mixed standard gas (H_2 9.08 %, CH_4 2.12

%, CO 10.3 %, CO₂ 3.31 %, C₂H₄ 1.01 %, C₂H₆ 1.02 %, C₂H₂ 1.12 %, O₂ 1.10 %, N₂ 70.94 %, mol/%) was used as external standard under following conditions: carrier gas, Ar (99.9995%) with a flow rate of 25 mL/min; injector temperature: 50 °C; column temperature: 50 °C; TCD temperature: 100 °C with TCD current of 70 mA.

GC/MS analysis for liquid samples was performed with an Agilent 7890 A gas chromatograph and mass selective 5975 C with Triple-Axis detector; a DB-INNO WAX MS capillary column (30 m × 0.25 mm, 0.5 μm film thickness), and a 7683 B Series Autosampler injector was supplied. Carrier gas was highest purity helium with a flow rate of 0.8 mL/min. The temperature program was 40 °C for 5 min, followed by 5 °C/min heating rate to 200 °C, then heated up to 250 °C with 20 °C/min and kept it for 5 min. Electron energy with EI⁺ ionization mode was 70 eV, and interface temperature was held at 250 °C.



1.Nitrogen cylinder 2, 3.Flowmeter 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

RESULTS AND DISCUSSION

Composition Analysis

The chemical components of rice straw were analyzed according to National Standards Methods and the literature (Shi 2003). Component and ultimate analyses of materials are summarized in Table 1.

The data showed that lignin in rice straw accounted for 22.9 % of the mass; in composition of lignin, carbon accounted for a large part, and hydrogen was 6.24 wt%. The contents of carbon and hydrogen in EMAL were higher than that in rice straw, so that the conversion for EMAL to fine chemicals and biofuels would be more advantageous.

Table 1. Characteristics of RS and EMAL

	EMAL	Rice straw
<i>Ultimate analysis (wt%, db)</i>		
C	50.42	40.24
H	6.24	5.44
O ^a	40.10	37.22
N	0.35	3.40
S	0.09	0.17
O/C	0.60	0.69
H /C	1.49	1.62
HHV (MJ/kg)	20.35	15.69
Empirical formula	CH _{1.49} O _{0.60}	CH _{1.62} N _{0.07} O _{0.69}
<i>Chemical analysis (wt%, db)</i>		
NE Cellulose		34.4
Hemicellulose		19.6
Lignin		22.9
Acetone-extractive		3.72
Holocellulose		58.9
Ash	2.8	13.5

^a Calculated by difference.

Pyrolytic Property

Pyrolysis conversion

Pyrolysis conversion of rice straw (RS) and EMAL varied with the levels of temperature, as shown in Fig. 2. When the pyrolysis temperature was below 700 °C, the volatiles in the rice straw were able to escape to a great extent than with EMAL isolated from rice straw. The conversion was generally about 69 wt%, and the amount of volatiles from rice straw varied with temperature (600, 700, and 800 °C). The conversion of EMAL increased from 55 to 73 wt% with temperature (400 to 900 °C). Lignin gave a higher char yield than biomass (Overend 1985).

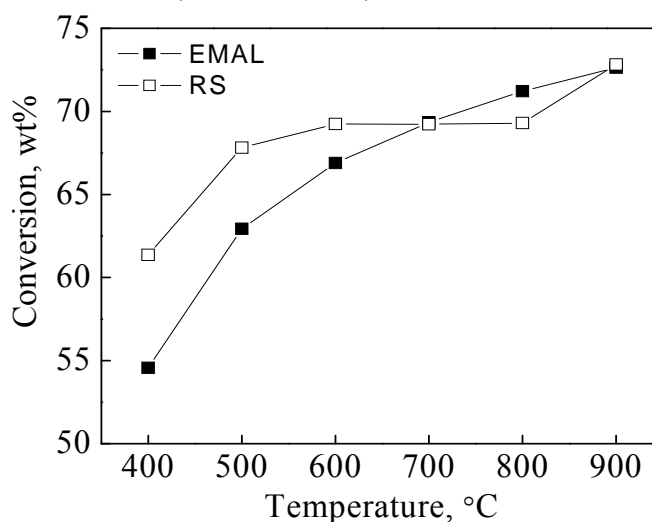


Fig. 2. Conversion of rice straw (RS) and enzymatic mild hydrolysis lignin (EMAL) during pyrolysis

Products yields

The products obtained from rice straw and EMAL pyrolysis were the condensed liquid (bio-oil), the solid (bio-char), and a mixture of light gases (syngas). Figure 3 shows that the temperature had an effect on product yield, and the trend of products was similar between rice straw and EMAL. The highest yield of bio-oil was 44% and 46%, respectively, obtained from RS and EMAL at 500 °C, but at higher temperatures the yield of bio-oil began to decrease slightly with temperature. This decrease was due to secondary decomposition occurring at higher temperature. From RS and EMAL, gaseous yield separately increased gradually with increasing temperature up to 37.6% and 39.5%, but bio-char yield decreased to 27.2% and 27.4%.

For product yield from RS pyrolysis, when the temperature was lower than 700 °C, gaseous and bio-oil yields were higher and bio-char yield was less than that from EMAL pyrolysis. The result was caused by cellulose and hemicellulose pyrolyzing at low temperature (≤ 600 °C), thus, the amount of gas escape from lignin pyrolysis was far below rice straw. Figure 3 also shows that the yields of bio-char, bio-oil, and gaseous became more closer between rice straw and EMAL as temperature increased from 700 to 900 °C because pyrolysis reaction of lignin occurred at higher temperature.

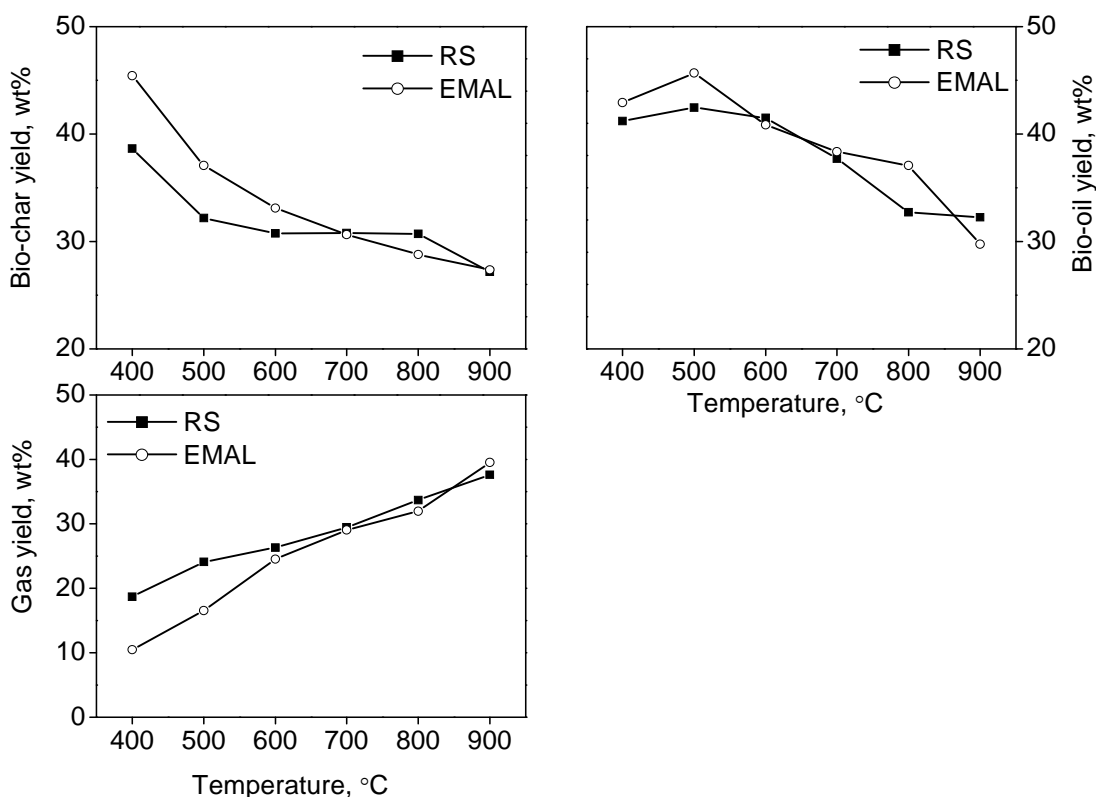
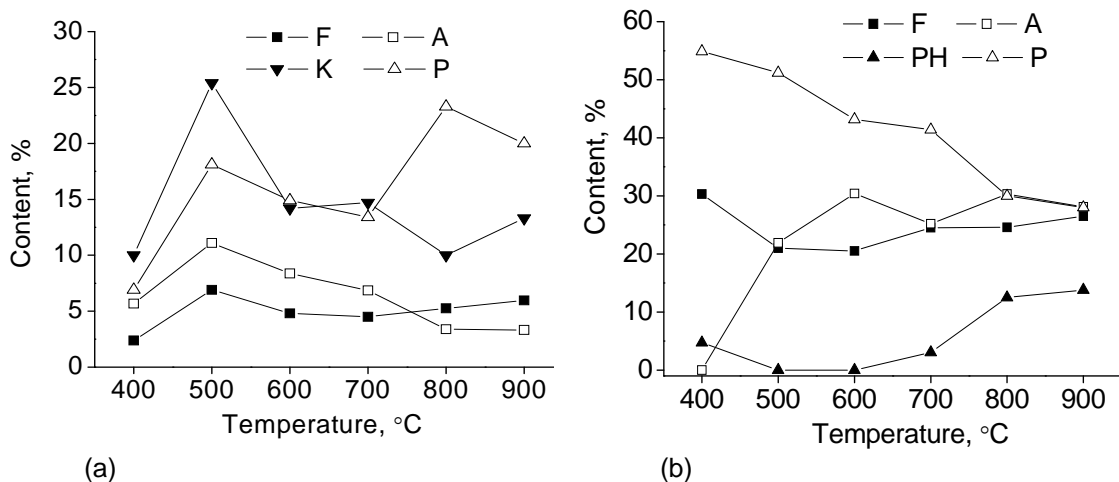


Fig. 3. Yields of bio-char, bio-oil, and gaseous products

The detected compounds from rice straw and EMAL pyrolysis are listed in Table 2 (a) and (b).

There were approximately 40 kinds of identifiable substances in the bio-oils, and the essential bio-oil constituents from them were mainly higher alkanes, alcohols, ketones, phenols, and organic acid. Compounds of bio-oil from rice straw were classified into furans, phenols, aromatics, alcohols, ketones, acids, and pyranoglucose. Among them, monocyclic aromatics, containing toluene and styrene, represented a huge proportion, 48%; the yield of ketones including 1-hydroxy-2-propanone, butyrolactone, 1,2-cyclopentanedione, and 1-(2-hydroxy-5-methylphenyl)-ethanone was 19%; the compounds of phenols were phenol, 2- or 4-ethyl-phenol, 2-methoxy-phenol, 2,6-dimethyl-phenol, 2,6-dimethoxy-phenol, 3- or 4-methyl-phenol, and 4-ethyl-2-methoxy-phenol. Moreover, alcohols and pyranoglucose were derived from cellulose, and ketones came from hemicellulose pyrolysis. Compared to compounds obtained from rice straw, bio-oil from EMAL was comprised of phenols, furans, acids, and polycyclic hydrocarbons. Phenols included the compounds 2-methoxy-phenol (7.9 %), phenol (9.6 %), 4-ethyl-phenol (5.2 %), 2-methoxy-4-vinylphenol (6.8 %), 4-methyl-phenol (4.0 %), 2,6-dimethoxy-phenol (4.4 %), etc. Acids and esters included 1,2-benzenedicarboxylic acid, diisooctyl ester, and 1-phenanthrene-carboxylic acid methyl ester.

From Table 2, compound classes of bio-oil from RS mainly consisted of furans, acids, ketones and phenols; accordingly, bio-oil from EMAL contained furans, acids, phenols and polycyclic hydrocarbons. The distribution of ingredients of bio-oil with temperature is presented in Fig. 4. Figure 4 (a) shows that the content of acids, furans, and ketones from RS was the highest at 500 °C, except for phenols, and then decreased with temperature. At the low temperature (400 – 600 °C), bio-oil product was derived from cellulose and hemicellulose pyrolyzing in RS, and hence the highest yield was for ketones, followed by phenols, acids, and furans. As temperature increased, the content of phenols increased and reached a maximum at 800 °C; based on this result the phenolic compounds and 2,3-dihydro-benzofuran were derived from lignin pyrolysis at high temperature.



F --- Furans; A--- Acids; K--- Ketones; P--- Phenols; PH--- Polycyclic hydrocarbons.

Fig. 4. Distribution of ingredients of bio-oil with temperature ((a)---RS, (b)---EMAL)

Table 2 (a). Compounds Content of Bio-oil From RS Pyrolysis (Area, Pct%)

Compounds class	Area pct.% at each temperature						
	400	500	600	700	800	900	
Furans	Furfural	1.06	1.72	2.17	1.94	1.53	1.66
	tetrahydro-2-furanmethanol	0.85	0.49	-	-	-	-
	2-furanmethanol	1.80	2.82	1.92	1.80	1.38	1.16
	2,3-dihydro-Benzofuran	2.38	5.96	4.12	3.99	5.26	5.14
	2(5H)-furanone	-	0.51	0.37	-	-	-
	5-hydroxymethyldihydrofuran-2-one	-	0.44	-	-	-	-
	1-(2-furanyl)-ethanone	-	-	0.31	0.22	-	0.52
	2,3-dihydro-2-methyl-benzofuran	-	-	-	0.28	-	0.31
	Total	2.38	6.91	4.80	4.49	5.26	5.97
Acids	Acetic acid	5.12	8.88	6.39	5.61	2.98	2.91
	Propanoic acid	0.55	1.06	0.74	0.73	0.41	0.41
	2-methyl-anhydride propanoic acid	-	1.16	-	-	-	-
	4-hydroxy-butanolic acid	-	-	1.24	-	-	-
	2-pyrone-5-carboxylic acid	-	-	-	-	-	-
	Pterin-6-carboxylic acid	-	-	-	-	-	-
	Glycine	-	-	-	0.52	-	-
	Total	5.67	11.1	8.38	6.86	3.39	3.32
Ketones	1-hydroxy-2-propanone	5.08	6.97	5.13	4.44	2.82	3.36
	Hydroxy-2-butanone	1.05	1.54	1.46	1.33	0.74	1.09
	l-2-cyclopenten-1-one	0.53	3.63	1.41	3.52	2.56	4.03
	Butyrolactone	0.89	1.63	-	1.35	0.99	0.90
	1,2-cyclopentanedione	1.94	3.19	4.01	2.40	0.97	1.94
	3-ethyl-2-hydroxy-2-cyclopenten-1-one	0.53	2.63	1.66	1.30	1.52	1.17
	1-(2-hydroxy-5-methylphenyl)-Ethanone	-	4.35	-	-	-	-
	Cyclopentanone	-	0.24	0.31	-	-	0.22
	2-Acetylcyclopentanone	-	0.47	-	-	-	-
	tetrahydro-2H-pyran-2-one	-	0.43	-	-	-	-
2,3-dihydro-1H-Inden-1-one	-	0.35	0.27	0.31	0.39	0.48	
Total	10.0	25.4	14.2	14.7	10	13.3	
Phenols	2-methoxy-phenol	1.55	2.91	1.39	0.44	0.75	0.44
	4-methyl-2-methoxy-phenol	-	0.54	0.30	-	-	-
	4-ethyl-2-methoxy-phenol	0.41	1.01	0.58	-	0.54	0.27
	4-vinyl-2-methoxy-phenol	2.02	-	2.32	0.64	1.92	1.40
	Phenol	1.11	4.0	3.68	4.74	6.72	5.58
	2,6-dimethyl-phenol	-	0.84	0.68	0.55	0.38	0.80
	2- or 4-ethyl-phenol	0.66	2.60	2.18	3.38	6.18	5.22
	3- or 4-methyl-phenol	-	2.38	1.97	3.11	5.37	5.41
	2,6-dimethoxy-phenol	0.87	2.00	1.07	0.50	0.91	0.49
	2-methoxy-4-(1-propenyl)-phenol	-	0.84	0.44	-	0.51	0.39
	3-hydroxy-4-methoxy-benzaldehyde	0.28	0.63	0.33	-	-	-
	2,6-dimethoxy-4-(2-propenyl)-phenol	-	0.37	-	-	-	-
Total	6.91	18.1	14.9	13.4	23.3	20	
Others	D-glucopyranose	-	0.59	0.37	0.31	0.41	0.41
	Naphthalenes	-	-	-	0.42	0.91	1.91

Table 2 (b). Compounds Content of Bio-oil From EMAL Pyrolysis (Area, Pct%)

Compounds class	Area pct.% at each temperature						
	400	500	600	700	800	900	
Furans	Furfural	5.48	5.29	3.68	3.70	3.72	3.02
	2,3-dihydro-benzofuran	24.8	15.7	16.8	20.8	20.9	23.5
	Total	30.3	21	20.5	24.5	24.6	26.5
Acids	1-Phenanthrenecarboxylic acid	^b	2.15	-	-	-	-
	dl-3-aminobutyric acid	-	-	0.83	-	-	-
	diisooctylester 1,2-benzenedicarboxylic acid	-	19.7	29.6	25.2	30.3	28.1
	Total	-	21.9	30.4	25.2	30.3	28.1
Phenols	2-methoxy-phenol	9.60	7.88	3.44	0.97	-	-
	4-methyl-2-methoxy-phenol	3.75	2.93	1.61	0.60	-	-
	4-ethyl-2-methoxy-phenol	3.57	2.72	1.70	0.64	-	-
	4-vinyl-2-methoxy-phenol	13.7	6.79	4.20	4.05	2.20	-
	Phenol	4.61	9.56	9.85	10.5	9.86	9.24
	2,6-dimethyl-phenol	-	-	0.63	0.60	-	-
	2- or 4-ethyl-phenol	3.75	5.22	7.77	7.41	5.72	6.40
	3- or 4-methyl-phenol	1.68	5.35	5.90	7.52	7.02	6.92
	3-ethyl-5-methyl-phenol	-	-	0.53	0.45	-	1.28
	2-(1-methylethyl)-phenol	-	1.55	0.96	1.09	1.07	1.34
	2,6-dimethoxy-phenol	7.59	4.39	3.04	1.29	0.86	-
	2-methoxy-4-(1-propenyl)-phenol	3.60	1.87	1.01	0.95	-	-
	2-Allylphenol	-	-	0.83	1.32	1.04	1.65
	3-hydroxy-4-methoxy-benzaldehyde	-	1.60	-	-	-	-
	4-(2-propenyl)-phenol	-	-	-	0.98	0.87	1.17
	4-Amino-2,3-xyleneol	0.95	-	-	-	-	-
	N-(4-guaiacyl)-2-hydroxyimino-acetamide	2.15	-	-	0.84	-	-
	5-tert-butylpyrogallol	-	1.36	-	-	-	-
	1-ethyl-4-methoxy-benzene	-	-	1.70	1.73	1.36	-
	2-hydroxy-benzaldehyde	-	-	-	0.47	-	-
Total	54.9	51.2	43.2	41.4	30	28	
Polycyclic hydrocarbons	4-Ethylbiphenyl	2.38	-	-	-	-	-
	Biphenylene	-	-	-	-	2.02	2.77
	cis-stilbene	2.33	-	-	-	-	-
	Naphthalene	-	-	-	1.70	2.72	3.28
	2-methyl-naphthalene	-	-	-	1.33	1.94	2.08
	2-ethenyl-naphthalene	-	-	-	-	1.0	1.05
	Indene	-	-	-	-	1.20	1.12
	Fluorene	-	-	-	-	1.56	1.76
	Phenanthrene	-	-	-	-	2.06	-
	Anthracene	-	-	-	-	-	1.72
Total	4.71	-	-	3.03	12.5	13.8	
Others	2,4(1H,3H)-dihydro-pyrimidinedione	2.30	1.96	-	-	-	-
	(1-acetyl-2-methyl-4-imidazolyl)-acetamide	4.59	3.44	-	-	1.56	-
	2,4,7(1H,3H,8H)-pteridinetriene	-	1.04	0.72	-	-	-
	1,2,4,5-tetramethyl-benzene	-	-	-	0.97	-	1.45
	1-ethenyl-4-methyl-benzene	-	-	-	-	-	1.01

^b – Not detected.

However, the trends of bio-oil compounds were significantly different in single-component lignin pyrolyzed independently in comparison to pyrolysis of full compositions. The content of phenols decreased with temperature, but polycyclic hydrocarbons increased. The reduction of oxygenated compounds and the increase of hydrocarbons helps to improve the quality of bio-oil. Therefore, the best advantage of rice straw pyrolysis to produce bio-fuel was to be pyrolyzed at 600 -700 °C, and the amount of gaseous output also was considerable within this temperature range. Moreover, it was best for lignin pyrolysis to produce bio-fuels at high-temperature (800 - 900 °C).

Evolved amounts of H₂, CO, CO₂ and some light hydrocarbons (CH₄, C₂H₄ and C₂H₆) as ingredients of gas products are shown in Fig. 4. It was revealed that a large amount of CO and CO₂ escaped from rice straw pyrolysis, especially at low temperature (400 to 600 °C) due to pyrolysis of cellulose and hemicellulose. Among the gaseous products, the highest yield was for carbon dioxide, followed by carbon monoxide, hydrogen, and methane. The yields of hydrogen increased sharply above 600 °C, and the yields of light hydrocarbons increased slowly with increase of temperature. In gaseous product from EMAL pyrolysis, the yield of CO₂ reached a maximum at 600 °C, and each yield of H₂, CH₄, and C₂H₄ was higher than that from RS pyrolysis distinctly, because lignin possessed abundant aromatic rings and methoxyl groups. At high temperature, the release of CO exceeded that from RS due to high content of carbonyl and carboxyl groups present in lignin (Caballero 1997; Tan 2009).

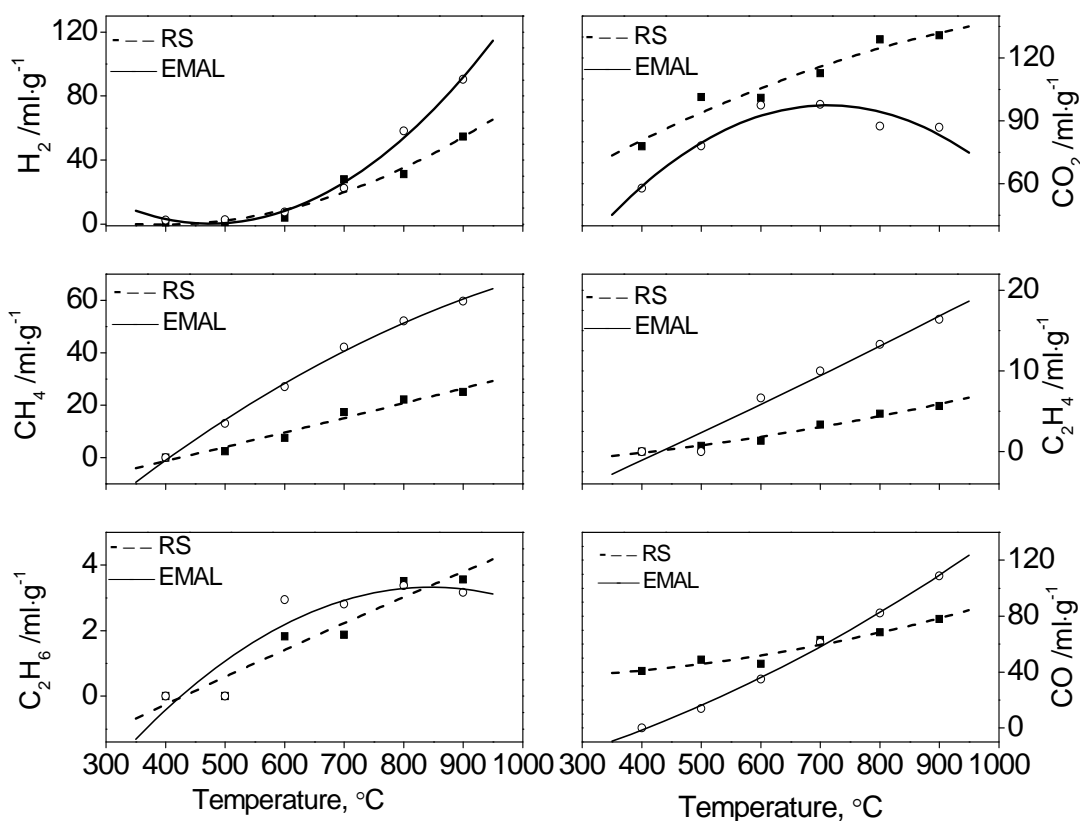


Fig. 4. Released amounts of gas ingredient with increasing temperature

CONCLUSIONS

Products from rice straw and EMAL pyrolysis consisted of bio-oil, bio-char, and gaseous compounds. Pyrolysis temperature had an obvious effect on products yield. The yield of gaseous increased gradually with increasing temperature, but the yield of bio-char decreased, and the maximum of bio-oil was obtained at 500°C or so.

The essential constituents of bio-oil mainly consisted of furans, ketones, phenols, organic acid, and higher alkanes. Alcohol and pyranoglucose were the representative products of cellulose pyrolysis, and ketones mainly came from hemicellulose pyrolysis. The trend of bio-oil compounds was significantly different in single-component lignin in comparison to full compositions, when pyrolysis was carried out independently. For bio-oil from EMAL, the content of phenols decreased with temperature, but polycyclic hydrocarbons increased. On the other hand, for RS pyrolysis at low temperature (400 to 600 °C), bio-oil products were mainly derived from the pyrolysis of cellulose and hemicellulose, and hence the highest yield was for ketones, followed by phenols, acids, and furans.

Comparing the pyrolysis characteristics between rice straw and EMAL, it was known that bio-char is derived from lignin pyrolysis, whereas cellulose and hemicellulose pyrolysis mainly generates carbon dioxide, carbon oxide, and methane, and the carbon monoxide primarily came from lignin pyrolysis. The conversion of EMAL increased with pyrolysis temperature, but the conversion of rice straw remained constant within the range 500 to 800°C.

Summing up, the best advantage of rice straw pyrolysis to produce bio-fuel was to be pyrolyzed at 600 to 700 °C, and the amount of gaseous output also was considerable within this temperature range. Moreover, it was best to carry out lignin pyrolysis at high temperature (800 - 900 °C) to produce bio-fuels.

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