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Applications of Chromatography Hyphenated Techniques in the Field of Lignin Pyrolysis

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1. Introduction

Due to the urgency of the current world energy supply-and-demand situation, the need for clean sources of energy is receiving an increasing attention. In the framework of a future sustainable development, biomass is one of the most often considered sources of renewable energy (Bridgewater et al., 1999). There are many ways of converting biomass into useful products and energy, such as direct combustion processes, thermochemical processes, biochemical processes, and agrochemical processes etc. Of these, pyrolysis forms the focus of this study (Bridgewater, 2004; Mohan et al., 2006). The pyrolysis of lignocellulose is very complex, primarily due to the inherent complexity of the substrate, which changes continuously both chemically and structurally throughout the decomposition process (Hosoya et al., 2007; Lv et al., 2010a).

The chemical structure and major organic components in biomass are extremely important in biomass pyrolysis processes. Knowledge of the pyrolysis characteristics of the three main components is the basis and thus essentially important for a better understanding of biomass thermal chemical conversion. Lignin is one of the main components of woody biomass, and the worldwide production of technical lignins as a by-product from chemical pulping processes stands at approximately 50 million t/yr (Harumi et al., 2010). However, it is merely used as fuel to recover energy in conventional pulping industry. Only recently, with the upcoming focus on biorefineries, lignin has gained new interest as chemical resources.

Analytical pyrolysis is a well-known technique to analyse lignin pyrolysis and various authors published different analytical methods to determine decomposition characteristics of lignin. Many researchers presented that the pyrolysis of lignin primarily occurred in a wide temperature range (200-600°C) by means of thermogravimetric analysis method (Domínguez et al., 2008; Lv et al., 2010b). Some researchers (Liu et al., 2008; Wang et al., 2009) also compared the pyrolysis behavior of lignin from different tree species using thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR). Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), which is an advanced pyrolysis methods combined with hyphenated separation and detection systems (i.e. GC-MS), is often used for studying degradation mechanisms of lignin because of its strong ability to identify the pyrolysis products (Atika et al., 2007; Windt et al., 2009).

On lignin pyrolysis, their product analysis, and further deriving the cracking mechanism, many researchers have done considerable works. For example, Baumlin et al. (2006) have reported the results of experiments performed on the flash pyrolysis of two types of lignins, i.e. kraft lignin and organocell lignin, to produce hydrogen. Nowakowska et al. (2010) presented an international study of fast pyrolysis of lignin. Jegers and Klein (1985) had reported that various catechol (1,2-dihydroxybenzene), o-cresol (2-methylphenol) and other phenols products go along with the formation of guaiacols during the course of lignin pyrolysis, the yields of those products are different corresponding to the different kinds of lignin and pyrolysis conditions. According to Britt et al. (1995), lignin pyrolysis occurred mainly by a free-radical reaction mechanism. The relative distribution of products is dependent on pyrolysis conditions, such as sources of raw materials, pyrolysis temperature, heating rate, pyrolysis atmosphere, and catalyst etc. (Garcia et al., 2008).

To sum up, there have already emerged lots of studies about lignin pyrolysis, and their focus and concerns were also varied. But so far, to our knowledge, limited information is available in the literature concerning the product generation and distribution regularities of lignin pyrolysis under the influence of parameters like temperatures and catalysts. Therefore, the objectives of this work were to attempt to carry out fast pyrolysis of several lignin samples (one enzymatic/mild acidolysis lignin and two technical lignins were used) and analyse the products by Py-GC/MS, in order to firstly establish the potential of this method for lignin processing and secondly to investigate the effects of temperature and catalysts on lignin pyrolysis.

2. Hyphenated techniques

In the case of samples originating in the real world, each of the techniques has a place, and often several must be used in order to obtain a complete overview of the nature of the sample.

The use of multiple techniques and instruments, which allow more than one analysis to be performed on the same sample at the same time, provide powerful methods for analyzing complex samples (Kealey & Haines, 2002). If the instruments are combined so that the analyses are done essentially at the same time, this is called a simultaneous approach and is often written with a hyphen, so that they may be referred to as hyphenated techniques, for example gas chromatography-mass spectrometry (GC-MS) and gas chromatography-infrared spectrometry (GC-IR). By using many techniques in combinations, the advantages to the analyst in the additional information, time saving and sample throughput are considerable.

2.1 Gas Chromatography-Mass Spectrometry (GC-MS)

The use of chromatographic techniques to separate mixtures is one of the most important analytical tools. The separated components may then be identified by other techniques. Mass spectrometry is the most important of these.

2.1.1 Separation

Gas chromatography, is a common type of chromatography used in analytic chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical

uses of GC include testing the purity of a particular substance, or separating the different components of a complex mixture, such as bio oil.

When used to prepare pure compounds from a mixture, GC can separate the volatile components of mixtures by differential migration through a column containing a liquid or solid stationary phase (Fu, 2008). Solutes are transported through the column by a gaseous mobile phase and are detected as they are eluted. Solutes are generally eluted in order of increasing boiling point, except where there are specific interactions with the stationary phase. An elevated temperature, usually in the range 50-350°C, is normally employed to ensure that the solutes have adequate volatility and are therefore eluted reasonably quickly.

2.1.2 Identification

Mass spectrometry (MS) is an analytical technique in which gaseous ions formed from the molecules or atoms of a sample are separated in space or time and detected according to their mass-to-charge ratio, m/z (Sparkman, 2000). It is usually used for determining masses of particles, for determining the elemental composition of a sample or molecule, and for elucidating the chemical structures of molecules, such as phenols, aldehydes, and other chemical compounds.

The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios. The numbers of ions of each mass detected constitute a mass spectrum. The spectrum provides structural information and often an accurate relative molecular mass from which an unknown compound can be identified or a structure confirmed.

2.1.3 Combination

Gas chromatography-mass spectrometry (GC-MS) is a common combined technique, comprising a gas chromatograph (GC) coupled to a mass spectrometer (MS), by which complex mixtures of chemicals may be separated, identified and quantified. A schematic diagram of a GC-MS is shown in Fig. 1. In this technique, a gas chromatograph is used to separate different compounds. This stream of separated compounds is fed online into the ion source, a metallic filament to which voltage is applied. This filament emits electrons which ionize the compounds. The ions can then further fragment, yielding predictable patterns. Intact ions and fragments pass into the mass spectrometer's analyzer and are eventually detected (Adams, 2007; Lee & Eugene, 2004).

This makes it becoming an ideal tool of choice for the analysis of the hundreds of relatively low molecular weight compounds found in biomass pyrolysis liquid products (bio oil). In order to make a compound be analysed by GC-MS, it must be sufficiently volatile and thermally stable. In addition, functionalised compounds may require chemical modification (derivatization) prior to analysis, to eliminate undesirable adsorption effects that would otherwise affect the quality of the data obtained (Wu, 2005). Bio oil samples are usually needed to be solvent extracted, and dehydrated before GC-MS analysis.

The prepared sample solution is injected into the GC inlet where it is vaporized and swept into a chromatographic column by the carrier gas. The sample flows through the column and the compounds comprising the mixture of interest are separated by virtue of their

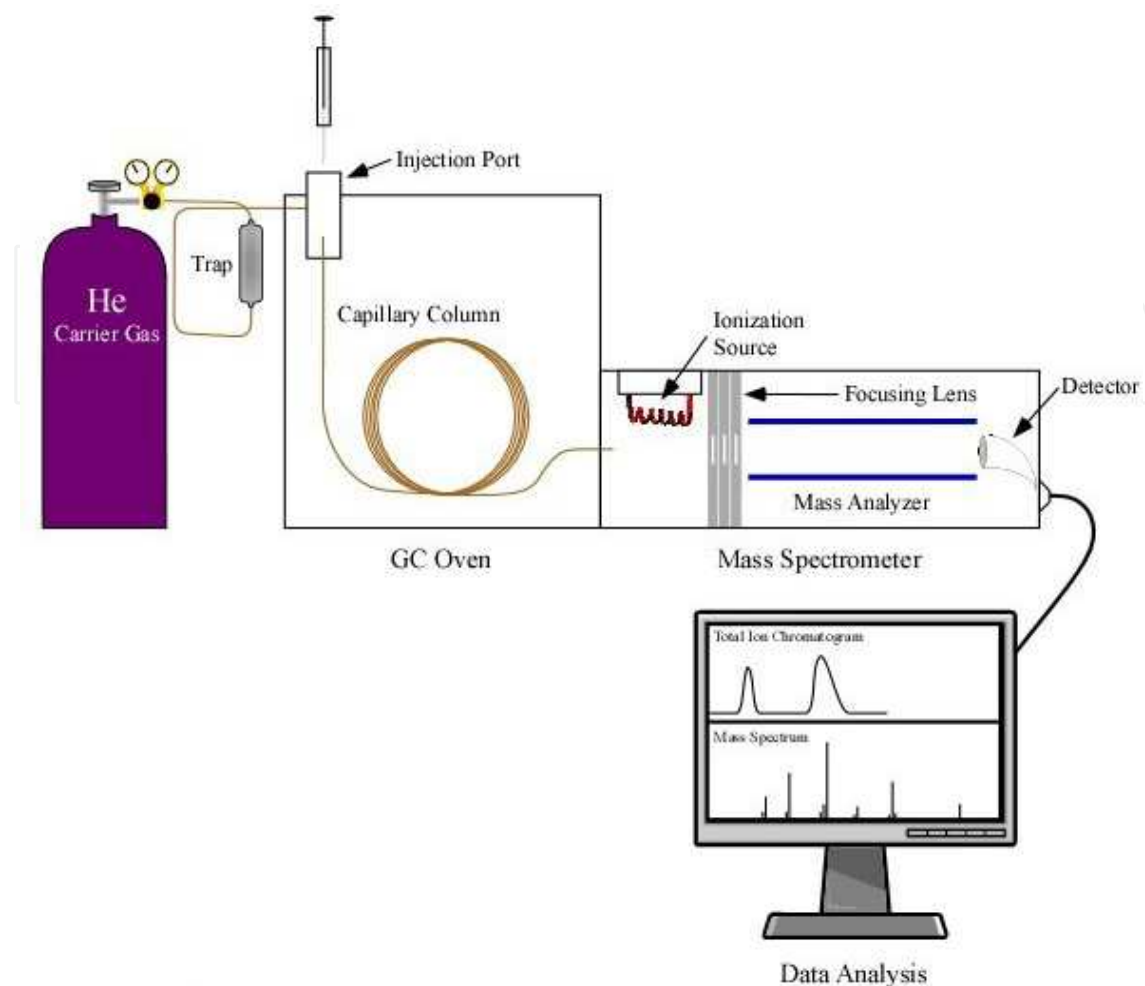


Fig. 1. Schematic of a GC-MS system

relative interaction with the coating of the column (stationary phase) and the carrier gas (mobile phase). The latter part of the column passes through a heated transfer line and ends at the entrance to ion source (Fig. 1) where compounds eluting from the column are converted to ions. Then the ions are separated in a mass analyser (filter). After that, the ions enter a detector the output from which is amplified to boost the signal. The detector sends information to a computer that records all of the data produced, converts the electrical impulses into visual displays and hard copy displays. In addition, the computer also controls the operation of the GC-MS system.

2.2 Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), which extends the combination to include three distinct techniques, is an instrumental method that enables a reproducible characterisation of the intractable and involatile macromolecular complexes found in virtually all materials in the natural environment (Bull, 2005). It differs from GC-MS in the type of sample analysed and the method by which it is introduced to the GC-MS system. Instead of the direct injection of a highly refined organic solution, a few amount (usually <math>< \text{mg}</math>) of the original natural material (e.g. soil, sediment, biomass etc.) is analysed directly (Jin et al., 2009).

When analyzed, the samples are first inserted into a quartz chamber in a pyrolysis unit (Fig. 2) that is then heated resistively in an oxygen free environment at a pre-set temperature for a number of seconds (e.g. 600°C for 10s). This results in a heat mediated cleavage of chemical bonds within the macromolecular structures of interest producing a suite of low molecular weight chemical moieties, which is indicative of specific types of macromolecule (e.g. lignin, cellulose, hemicelluloses etc.). This mixture of compounds is then swept into the analytical column of the GC and GC-MS proceeds as normal.

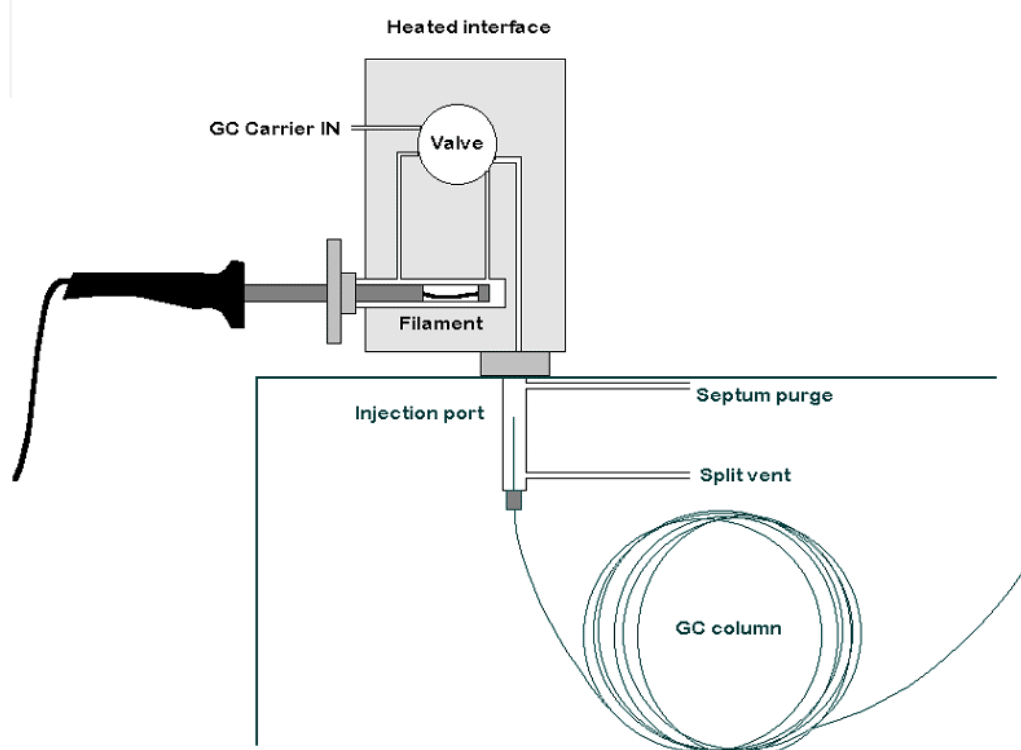


Fig. 2. Schematic of a Pyroprobe combined with GC-MS system

Because of its high sensitivity, a rapid analysis time, and less sample pretreatments, the analytical technique of Py-GC/MS is widely used to research chemical structure and pyrolysis characteristics of biomass and its three main components (i.e. lignin, cellulose, and hemicellulose), to examine reaction products of biomass thermal degradation (Meier & Faix, 1999), and to investigate fast pyrolysis of biomass and on-line analysis of the pyrolysis vapors (Fahmi et al., 2007; Nowakowski & Jones, 2008)

3. Experimental

3.1 Materials

The enzymatic/mild acidolysis lignin (EMAL) was isolated from Moso bamboo by means of enzymatic/mild acidolysis method previously described (Wu & Argyropoulos, 2003; Lou & Wu, 2011), and the so called enzymatic/mild acidolysis lignin was obtained.

Technical alkali lignin (AL) and acid hydrolysis lignin (AHL) were isolated from bagasse black liquor and bagasse respectively, according to our previous reports (Wu et al., 2008; Tan, 2009).

Elemental analysis of three types of lignin was implemented in a Vario EL elemental analyzer and an ICP inductively coupled plasma emission spectrometer. Table 1 lists the results of the elemental analysis, from which the O content can be calculated by difference.

	Organic Elements / wt%				Inorganic elements / ppm								
	C	H	N	S	Al	Ca	Na	Mg	Mn	K	Zn	Cu	Fe
EMAL	58.74	5.72	2.58	0.06	5.73	1.26	80.19	0.37	-	12.50	14.45	3.79	109.10
AL	62.20	7.37	0.07	0.65	-	381.79	226.70	26.13	3.56	806.27	9.87	32.81	89.81
AHL	49.64	5.78	2.52	0.17	8.55	189.68	47.22	16.95	1.23	19.13	0.46	26.70	116.37

Table 1. Elemental analysis of the lignin samples

3.2 Analytical pyrolysis

Fast pyrolysis of prepared samples was carried out in a Py-GC/MS system, which includes a JHP-3 model Curie-point pyrolyzer (CDS5200, USA) and a Shimadzu QP2010 Plus gas chromatograph-mass spectrometer (Japan). The pyrolyzer consisted of an inductive heated coil to heat the samples and was capable of maintaining up to 1200°C temperature with a heating rate of approximately 10°C · ms⁻¹ from room temperature to the terminal temperature, with helium as both purge gas and carrier gas.

On the basis of the thermal behaviors of EMAL (Lou & Wu, 2008), the pyrolysis temperature of EMAL samples was set at 320°C, 400°C, 600°C, and 800°C, respectively. Approximately 0.1mg of each sample was pyrolyzed. Pyrolysis reactions were carried out with an event time of 10s, and the obtained pyrolysis products were then analyzed by GC-MS.

The pyrolysis products were separated in a DB-5MS (Agilent Technologies, USA) capillary column (30m×0.25mm×0.25µm). The split ratio of 70/1 and linear velocity of 40.0cm · s⁻¹ was used. The GC oven was heated from 50°C to 250°C at a heating rate of 10°C/min, and then maintained for another 2min. The injector temperature was 250°C. The mass spectrometer was operated in the EI mode using 70eV of electron energy. The mass range m/z 45-500 was scanned. Identification of the pyrolysis compounds was achieved by comparison of their mass fragment with Perkin Elmer NIST 05 mass spectral library. For qualitative and quantitative analysis of the pyrolysis products, a more detailed explanation based on a practical example will be given.

3.3 Catalytic pyrolysis

In order to study the effect of catalysts on EMAL pyrolysis, sodium chloride (NaCl) of metal salt and permutite of zeolite were selected to serve as the catalyst. The catalysts were previously subject to high temperature treatment under N₂ atmosphere at 800°C for 6h to ensure the decomposition reaction of catalysts did not happen during lignin pyrolyzing. The additive amount of each catalyst was set to be 5%, 10%, and 20% based on weight, and the catalyst and lignin were ground and mixed together evenly before used for experiment. As lignin pyrolysis reaction was complete at 800°C, so the catalytic pyrolysis temperature of EMAL was set at 800°C to better investigate the impact of the additive catalysts on products.

4. Results and discussion

4.1 Identification of pyrolysis products

According to the previous introduction of GC-MS, both qualitative and quantitative analysis of the pyrolysis compounds can be achieved with GC-MS easily. For example, Fig. 3 shows TIC chromatogram of Bamboo lignin pyrolysis at 600°C, in which each peak shown a compound produced during lignin pyrolysis process. An effective and efficient way to qualitative identify these peaks is to compare its experimental mass spectrum against a library of computerized mass spectra (Mistrik, 2004).

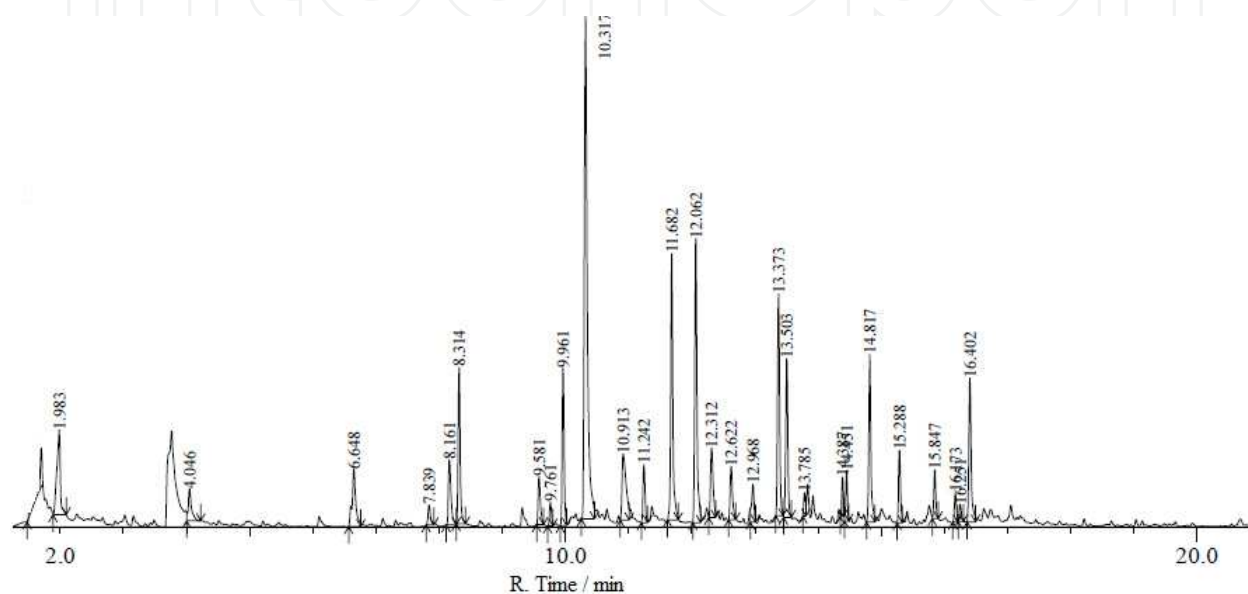


Fig. 3. Total ion chromatograms of Bamboo EMAL pyrolyzed at 600°C

In our experiment analysis, identification of the pyrolysis compounds was achieved by comparison of their mass fragment with Perkin Elmer NIST 05 mass spectral library. Fig. 4 shows examples of identified peaks of some major pyrolysis products by searching computerized spectra library. In addition, by means of spectral libraries, more information about identified compounds can be obtained, such as compound name, molecular formula, structural formula, and molecular weight, etc.

Quantitative analysis of lignin pyrolysis products can be obtained in terms of peak areas or peak heights, both of which are known as semi-quantitative method. Although it can not be accurately determined the content of a certain compound without standard samples, it does can be used to compare the relative content of each or each kinds of compounds, and get the increase or decrease tendencies of a certain kinds of compound with pyrolysis parameters by their peak area percentage. This is why many researchers have been studying biomass pyrolysis by using Py-GC/MS. Of course, for precise quantification of certain components of bio-oil derived from pilot laboratory equipment or factory, it is recommended to use internal or external standards, or by standard addition or internal normalization. However, at present, in order to study the trends or regularities of lignin pyrolysis products with the experimental conditions, quantitative information obtained from integrated peak areas are the most reliable and convenient.

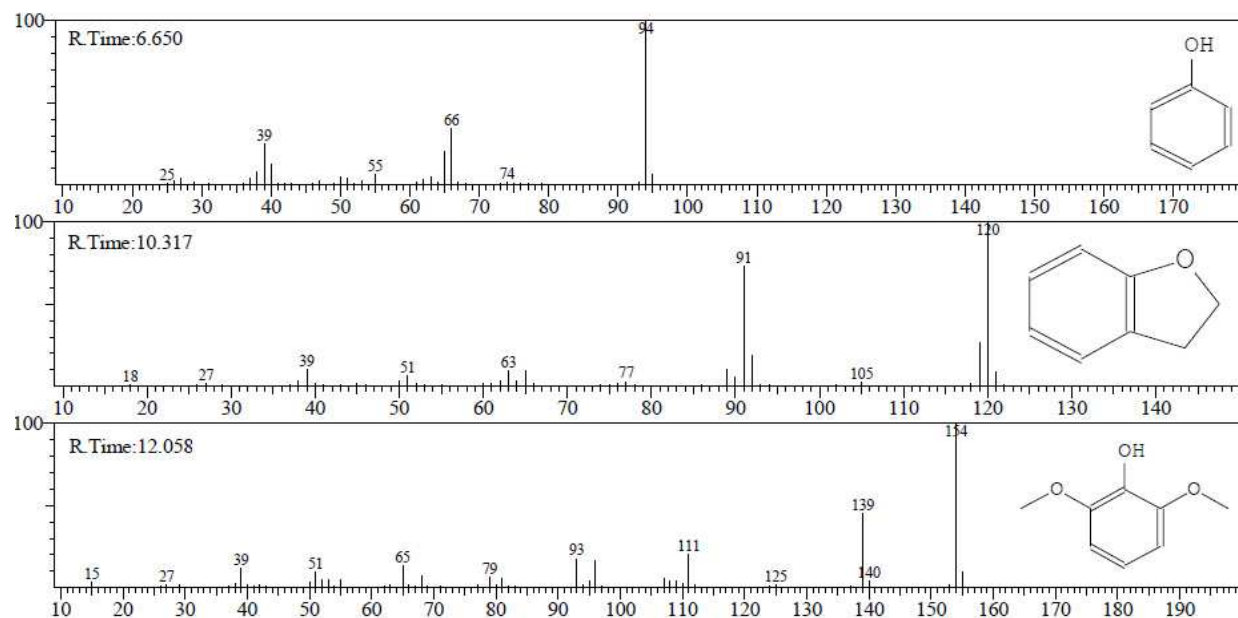


Fig. 4. Some examples of mass spectra identified by searching libraries

4.2 Effect of temperature on EMAL pyrolysis

Based on the analysis method described earlier, quantitative information of bamboo EMAL pyrolysis products at different temperatures are presented in Table 2. As can be seen from Table 2, The major compounds derived from p-hydroxyphenylpropanoid, guaiacylpropanoid, and syringylpropanoid of lignin units during pyrolytic reactions, were mainly classified as the heterocycles (2,3-dihydrobenzofuran), phenols, and a small amount of acetic acid. The yield of phenolic compounds increased with an increase of pyrolysis temperature, and the highest fraction of phenols was 56.43% at 600°C.

Among these pyrolysis products, the small molecule compounds of vanillin and acetic acid generated as a result of the bond cracking of interlinkage C_{α} - C_{β} of lignin phenylpropane, and the breakage of C_{α} - C_{β} can induce the production of carboxylic acid and carbon dioxide (Yang et al., 2010). Bond breakage of the side chains of lignin structural units can lead to generate degradation products with the new hydroxyl and carbonyl groups. Thus, with the contents of the hydroxyl and carbonyl groups increasing, the side chains of aromatic compounds connected to α -carbonyl, α -carboxyl or ester groups appeared (Lou et al., 2010a).

In all the identified products, 2, 3-dihydrobenzofuran (DHBF) accounted for the largest quantity, in addition, other compounds such as ethenylguaiacol, 2, 6-di-tert-butyl-p-cresol (DTBC), 3, 5-dimethoxyacetophenone (DMAP), methoxyeugenol etc. also account for considerable amount. Some of these selected compounds with higher yields during lignin pyrolysis and their chemical structures are shown in Fig. 5, and their yield distributions varying with pyrolysis temperature are presented in Fig. 6. The yields of obtained compounds possessing the syringyl unit structure (methoxyeugenol, syringol, and syringaldehyde) and 2, 3-dihydrobenzofuran (DHBF) are shown in Fig. 6(a) and the yield of compounds possessing guaiacyl unit structure (ethenylguaiacol, vanillin, E-isoeugenol, and sinapylaldehyde) are shown in Fig. 6(b).

Compound class	Compounds	Yield, Area percent (%) ^a			
		320°C	400°C	600°C	800°C
p-Hydroxyphenols	Phenol	- ^b	-	1.61	2.99
	o-Cresol	-	-	-	1.68
	p-Cresol	-	-	1.01	3.58
	2,6-Di-tert-butyl-p-cresol (DTBC)	6.91	5.89	2.10	1.67
	2,4-xylenol	-	-	-	0.88
	p-Ethylphenol	-	-	0.74	1.59
	2-Allylphenol	-	-	-	1.84
Guaiacols	Guaiacol	-	-	3.78	1.08
	p-Methylguaiacol	-	-	1.45	1.72
	Ethenylguaiacol	8.18	9.22	7.23	3.16
	Vanillin	-	2.76	2.64	2.51
	E-isoeugenol	-	1.99	2.66	2.00
	Sinapylaldehyde	-	1.50	1.96	2.01
	Coniferylalcohol	-	5.34	9.49	-
Syringols	Syringol	-	3.57	9.69	4.53
	Methylsyringol	-	-	2.98	3.01
	Syringaldehyde	-	2.36	2.42	1.45
	Methoxyeugenol	4.65	5.67	5.06	2.39
	Acetosyringone	-	-	-	1.23
Heterocycles	2,3-Dihydrobenzofuran (DHBF)	66.26	56.62	36.05	19.15
Others	Acetic acid	-	-	-	0.97
	3,7-Dimethylnonane	-	-	-	-
	3,5-Dimethoxyacetophenone (DMAP)	4.09	5.10	6.63	2.20
	m-Phthalic acid	-	-	-	9.69
	p-p'-Isopropylidenebisphenol (IPBP)	-	4.46	5.72	7.89
	Allylphthalate	0.89	0.97	1.37	2.69
	Tetracosane	-	-	-	3.65
	2-Phenylbutyrophenone	-	-	-	2.61
Dipropylene glycol dibenzote	-	-	-	1.63	
	Dotriacontane	-	-	-	4.89

^a based on the integrated areas; ^b not detected.

Table 2. Products identification from bamboo EMAL pyrolysis

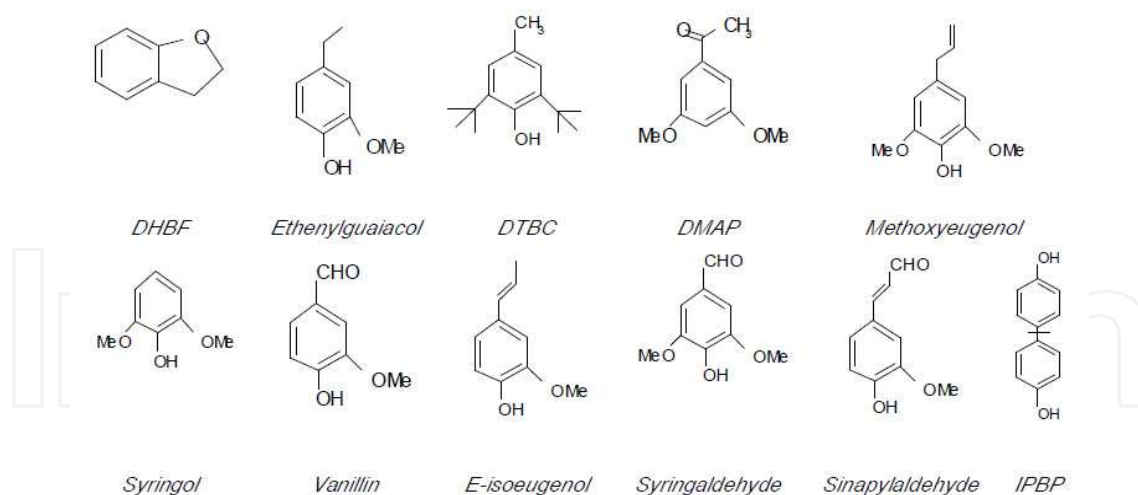


Fig. 5. Products with higher yields in EMAL pyrolysis

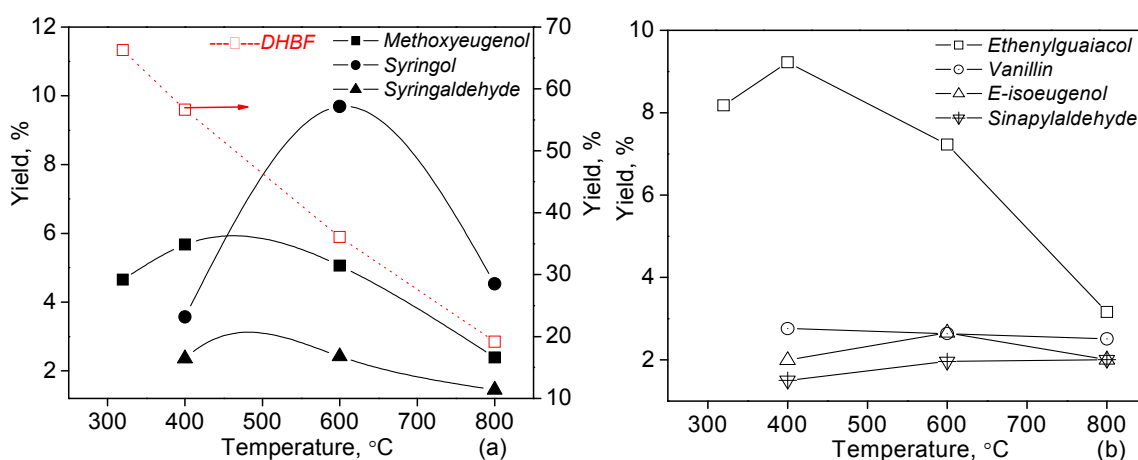


Fig. 6. Product Yields distribution varied with pyrolysis temperature

It can be seen from Fig. 6 that almost all of the compounds derived from EMAL pyrolysis appeared at 400°C, except for *DHBF*, methoxyeugenol, and ethenylguaiacol emerged earlier at about 300°C. The formation fraction of methoxyeugenol, syringaldehyde, ethenylguaiacol, and vanillin reached a maximum at 400°C, then, the yields of these compounds decreased with the increment of temperature, which may be because the secondary decomposition took place at high temperatures. The highest yield of 2, 3-dihydrobenzofuran (*DHBF*) was 66.26% at 320°C, as pyrolysis temperature increased to 800°C, the yield of *DHBF* decreased rapidly to 19.15%. This confirms that in lignin pyrolysis process, the maximum formation of *DHBF* occurred at around 300°C (Lou et al., 2010b). The yield of *E-isoeugenol* and sinapylaldehyde increased slowly because their chemical structures possessed the double bonds of side chain and the benzene rings formed conjugated system, thus became more stable even at high temperature.

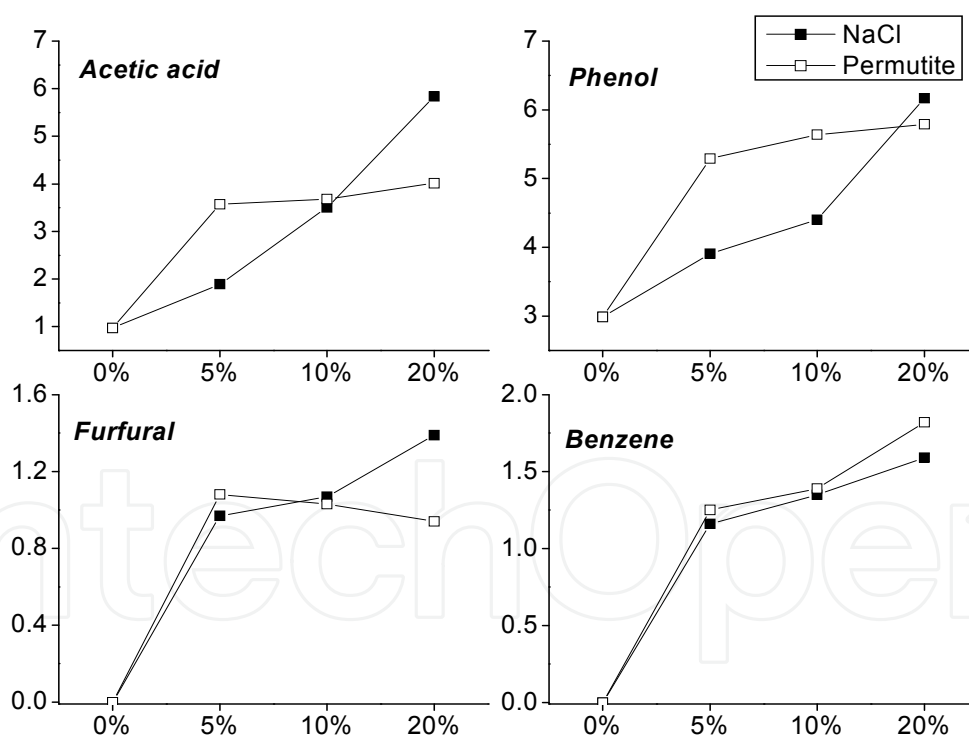
4.3 Effect of catalysts on EMAL pyrolysis

The effects of catalysts on the yield of products from EMAL pyrolysis were studied in detail. The quantitative analysis of pyrolysis product based on the integrated areas is shown in Table 3, and the yield distributions of valuable product are present in Fig. 7.

Compound class	Compounds	Yield, Area percent (%)						
		EM AL	EMAL +xNaCl			EMAL +xPermutite		
			5%	10%	20%	5%	10%	20%
Gas	Carbon dioxide	-	-	5.18	2.96	15.21	15.83	18.31
Benzenes	Benzene	-	1.16	1.35	1.59	1.25	1.39	1.82
	Toluene	-	1.83	1.40	2.62	2.13	2.24	2.02
	m-Xylene	-	0.72	0.74	1.25	0.83	1.27	0.94
	Styrene	-	0.95	-	-	0.81	-	-
	Phenol	2.99	3.91	4.40	6.17	5.29	5.64	5.79
p-Hydroxyphenols	o-Cresol	1.68	1.59	2.04	3.20	1.83	2.27	1.89
	p- Cresol	3.58	3.20	3.96	6.03	4.31	5.26	4.65
	o-Allylphenol	-	0.90	2.05	1.11	1.52	2.27	1.35
	m-Xylenol	0.88	1.10	1.71	2.50	1.60	2.07	2.14
	p-Ethylphenol	1.59	2.53	3.15	4.76	2.17	2.78	2.89
	Butylated hydroxytoluene	-	1.04	1.63	1.44	1.00	1.04	1.09
	Guaiacols	o-Guaiacol	1.08	0.85	1.85	1.76	1.77	1.27
	Methoxyl phenol	1.72	3.31	5.70	6.37	1.51	0.81	1.35
	2-Dihydroxytoluene	-	2.60	3.20	4.66	1.74	2.97	1.98
	p-Vinylguaiacol	-	3.84	4.20	4.04	5.15	2.39	4.84
	Vanillin	2.51	0.86	1.20	1.10	1.54	1.99	1.59
	<i>E(Z)</i> -isoeugenol	2.00	2.23	2.55	3.11	2.37	2.22	1.97
	γ -Hydroxyisoeugenol	-	0.85	0.90	0.92	0.66	1.00	1.23
	Acetoguaiacone	-	-	-	-	0.62	0.65	0.83
	Ferulic acid	-	8.40	4.93	3.65	0.60	0.48	0.37
Syringols	Syringol	4.53	1.32	1.99	1.18	5.25	4.94	4.34
	3,4- Dimethoxyphenol	-	1.07	1.70	1.86	-	-	-
	Methoxyeugenol	2.39	1.35	1.02	0.81	2.29	1.66	1.63
	Syringaldehyde	1.45	9.32	2.44	1.25	0.36	0.44	1.51
	Acetosyringone	1.23	-	-	-	0.82	0.86	1.42
	Guaiacylacetone	-	1.56	-	-	-	-	-
	Catechols	4-Ethylcatechol	-	-	1.07	1.04	1.11	0.84
	3-Mmethyl-1,2- benzenediol	-	2.28	3.54	3.77	-	-	-
Heterocycles	2,3- Dihydrobezofuran (DHBF)	19.15	16.30	15.43	13.08	21.54	23.78	24.19
Others	Acetic acid	0.97	1.89	3.50	5.84	3.57	3.68	4.01
	Furfural	-	0.97	1.07	1.39	1.08	1.03	0.94
	1,2,4- Trimethoxybenzene	-	1.07	2.01	1.32	2.87	2.34	2.26
	3,5- Dimethoxyacetophen one (DMAP)	2.20	3.55	2.52	1.96	3.12	2.22	2.15

Compound class	Compounds	Yield, Area percent (%)						
		EM AL	EMAL +xNaCl			EMAL +xPermutite		
			5%	10%	20%	5%	10%	20%
	p-p'- Isopropylidenebisph enol (<i>IPBP</i>)	7.89	2.91	1.38	1.00	-	-	-
	Dibutyl phthalate	1.63	0.90	1.41	0.77	-	-	-
	4-Hydroxy-3,5- dimethoxybenzohydr azide	-	3.62	1.14	0.78	-	-	-

Table 3. Products identification from EMAL pyrolysis with catalysts at 800°C



(a)

Fig. 7. Continued

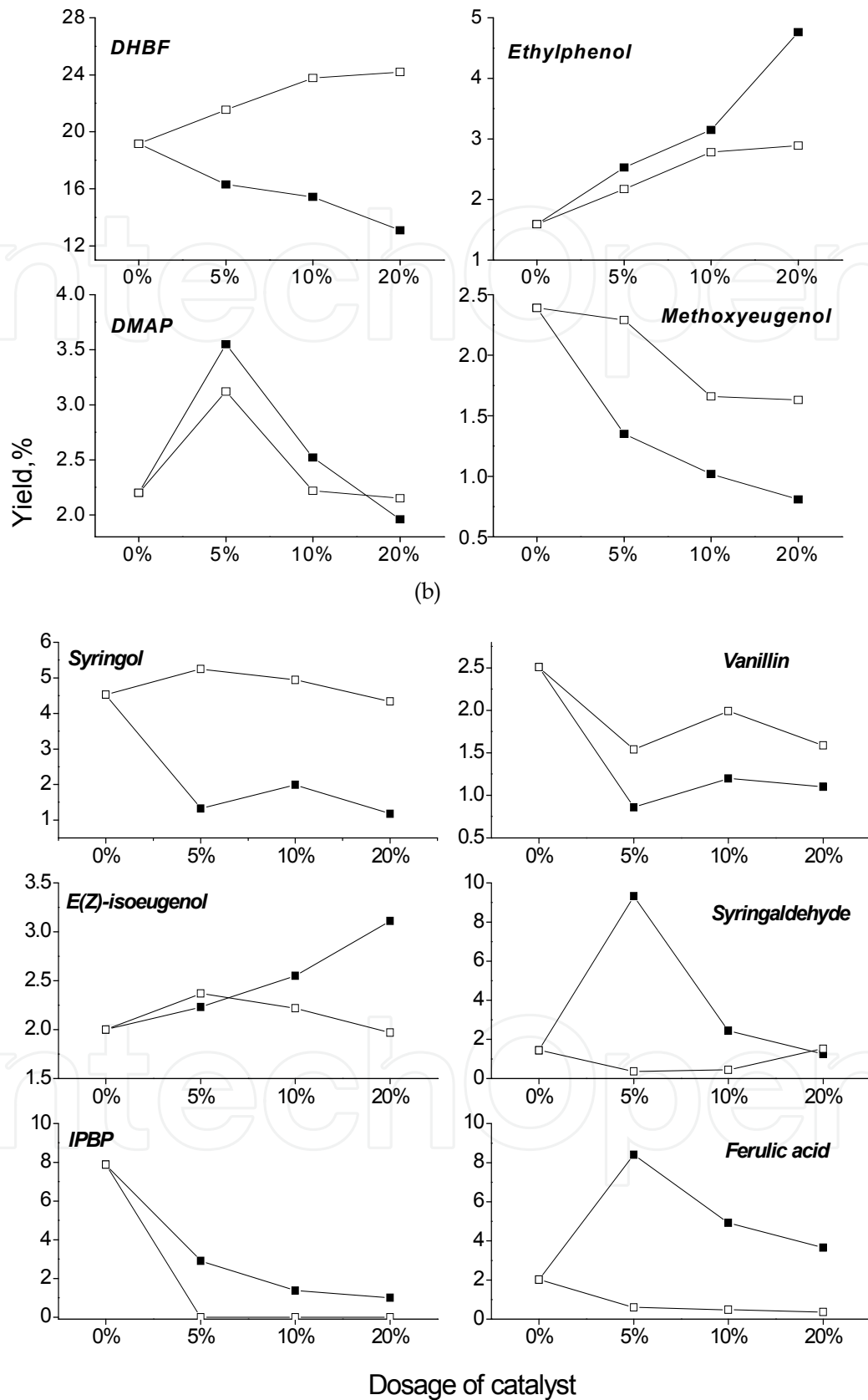


Fig. 7. Product Yields distribution varied with different dosages of catalyst

Additive Na-salt and permutite promoted the formation of small molecules. The amount of acetic acid, phenol, furfural, and benzene varying with dosage of catalyst is shown in Fig. 7(a). It revealed that yields of acetic acid, phenol, furfural, and benzene increased with an increase of the dosage of two catalysts, and the two catalysts in EMAL pyrolysis promoted the generation of benzene and furfural. When the dosage of permutite was 5%, the formation rate of acetic acid, phenol, and furfural were the most distinct, as the amount of permutite further increased, the increase in yield of them was not obvious. However, as the amount of NaCl increased, the yield enhanced considerably. In short, the addition of two catalysts promoted the cleavage of lignin and the generation of small molecule compounds.

It can be obtained, from Fig. 7(b), that with the additive catalyst increasing from 5% to 20%, permutite has a significant role in promoting the formation of *DHBF* from 19.15% to 24.19%, however, NaCl catalyst was effective to reduce the production of *DHBF* from 19.15% to 13.08%. On the yields of ethylphenol, *DMAP*, and methoxyeugenol during EMAL catalytic pyrolysis, the catalysts of permutite and NaCl had the same impact. Compared with permutite, NaCl catalyst had more pronounced effect to improve or suppress the generation of ethylphenol, *DMAP*, and methoxyeugenol.

Fig. 7(c) shows that when NaCl catalyst was 5%, product of syringaldehyde and ferulic acid reached their maximum yield, while with further increase in the amount of catalyst, the yield decreased. This was similar to that of *DMAP* shown in Fig. 7(b).

Two kinds of phenols' generation trends (i.e. guaiacols and syringols) affected by variations of temperature and catalysts are shown in Fig. 8. Both guaiacols and syringols reached their maximum yields at 600°C. The catalytic effects of NaCl and permutite for improving guaiacols were the most prominent at dosage of 5%, however, the catalytic effect of permutite for syringols was not obvious.

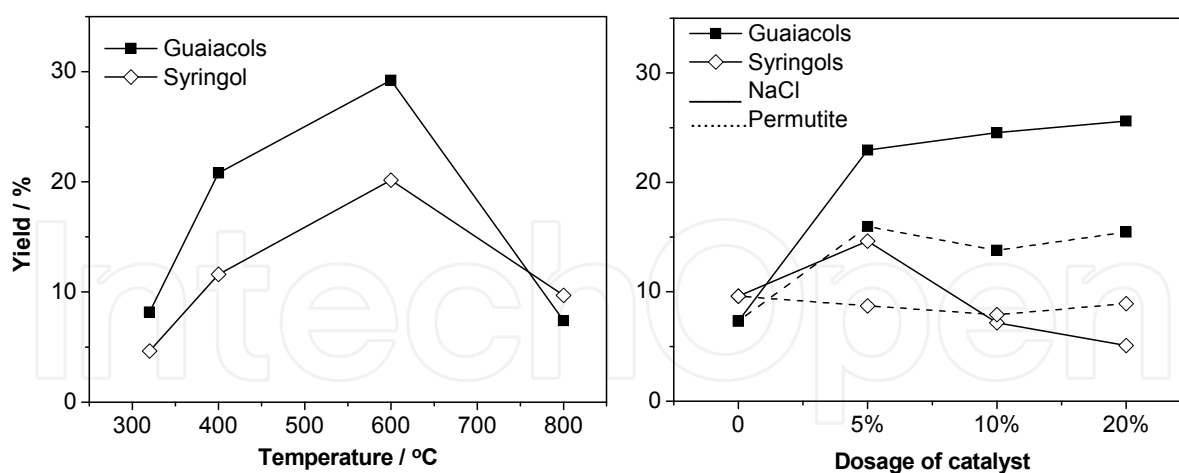


Fig. 8. The total amount of guaiacols and syringols with pyrolysis conditions

To sum up, the impact of different catalysts on the selectivity of pyrolysis products is different. Compared with permutite, the effect of catalyst NaCl was considered to be more significant. Two types of catalysts added to EMAL can promote the generation of small molecule compounds, such as carbon dioxide, acetic acid, benzene series, furfural, and phenol etc. Meanwhile, add catalysts to EMAL made macromolecular lignin degrade to small molecule compounds more thoroughly.

4.4 Effect of temperature on technical lignin pyrolysis

Pyrolysis studies of two types of technical lignin were also started by means of Py-GC/MS analysis. The pyrolysis temperature selection was based on their thermal degradation behaviors (Tan et al., 2009; Wu et al., 2008), respectively.

According to preciously introduced method, identification information of pyrolysis products at different temperatures for two types of technical lignin is presented in Table 4 and 5. Pyrolysis products from technical lignin can be classified into benzenes, phenols, aromatic heterocyclics (mainly 2, 3-Dihydrobenzofuran), esters and trace acids. The lignin derived phenols can be further classified into molecules with guaiacyl, syringyl, and p-hydroxyphenyl aromatic moieties, and were defined as guaiacols, syringols, p-hydroxyphenols, respectively. Yields distribution of each type of product changed with pyrolysis temperature are plotted in Fig. 9.

As the pyrolysis temperature rise, the heterocyclics reduced, while phenolic compounds content increased. The maximum content of 2, 3-Dihydrobenzofuran emerged at about 375°C-400°C. At 600°C, the highest yields of phenols for AL and AHL were 57.91% and 52.11%, respectively. As the temperature increased further, both of their yields were reduced. This characteristic is consistent with that of EMAL.

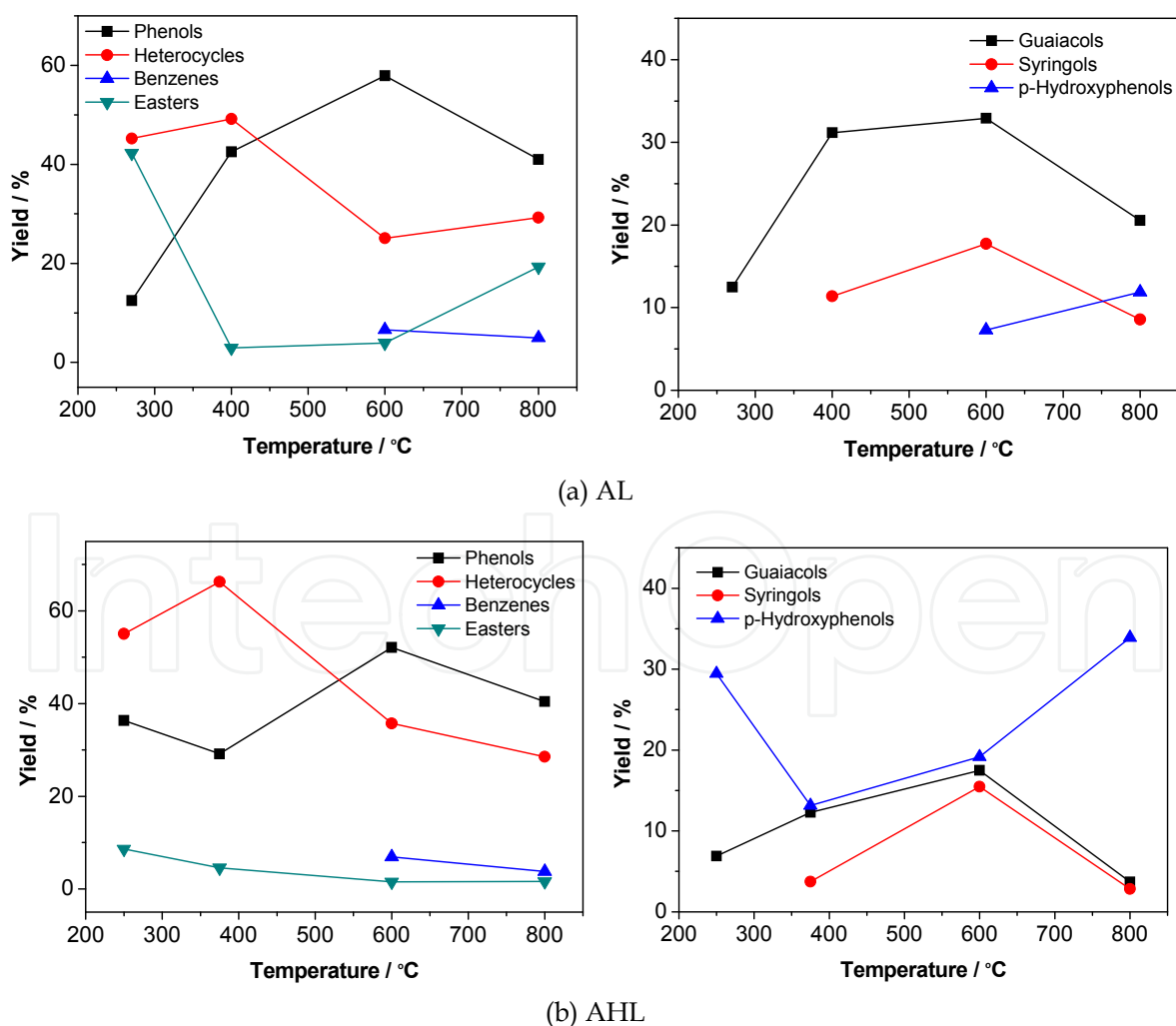


Fig. 9. Product Yields distribution varied with pyrolysis temperature

Compound class	Compounds	Yield, Area percent (%)			
		270°C	400°C	600°C	800°C
Benzenes	Benzene	-	-	-	0.99
	Toluene	-	-	-	1.06
	1,2,4-Trimethoxybenzene	-	-	6.58	2.89
p-Hydroxyphenols	Phenol	-	-	1.42	3.49
	2-Methylphenol	-	-	1.79	4.49
	4 (or 3)-Ethylphenol	-	-	1.81	2.31
	4-(2-Allyl)-phenol	-	-	2.26	1.58
Guaiacols	2-Methoxyphenol	-	-	6.12	1.58
	2-Methoxy-4-methylphenol	-	-	-	1.44
	3-Methoxycatechol	-	-	3.74	-
	4-Ethyl-2-methoxyphenol	-	-	1.84	0.80
	2-Methoxyl-4-vinylphenol	12.49	27.74	13.60	12.86
	Vanillin	-	-	1.58	-
	2-Methoxy-3-(2-allyl)-phenol	-	3.43	6.04	1.82
	Coniferylalcohol	-	-	-	2.06
Syringols	2,6-Dimethoxyphenol	-	2.22	7.43	4.87
	Syringaldehyde	-	-	0.95	-
	2,6-Dimethoxy-4-(2-allyl)-phenol	-	9.15	8.00	2.77
	4-Hydroxy-3,5-dimethoxyacetylbenzene	-	-	1.33	0.93
Heterocycles	2,3-Dihydrobenzofuran (<i>DHBF</i>)	45.23	49.19	25.09	29.27
	Phenyl glyoxylate-2 'acetyl	42.28	2.94	1.76	7.27
Esters	benzene ester	-	-	2.18	10.34
	Benzoic acid, phenylmethyl ester	-	-	-	1.72
	1,2-Benzenedicarboxylic acid, 1,2-diisooctyl ester	-	-	-	1.72
Others	3,5-Dimethoxy acetophenone	-	5.32	6.77	4.66
	Palmitinicacid	-	-	-	0.80

Table 4. Products identification from AL Pyrolysis

Aromatic esters decreased with temperature increasing, while benzenes compound only emerged at high pyrolysis temperature, with a little increase. Heterocyclic compounds and esters decrease with temperature increasing. This was mainly due to their poor thermal stability, causing these two types of compounds cleaved into smaller molecular, more stable phenols or aromatic compounds at higher temperature.

As about the phenolic products, it can be seen from Fig. 9 that, the guaiacols and syringols trends were similar to that of total phenols, while p-hydroxyphenols had a further increasing trend as the temperature increases. This may be because the branched-chains of the relatively larger molecules of phenols (such as some guaiacols and syringols) cause further cracking as the temperature increases, which resulting the increase of p-hydroxyphenols.

Fig. 10 shows the contents of guaiacols, syringols and p-hydroxyphenols of three types of lignin pyrolyzed at 600°C. As can be seen from the figure, compared with that of AHL, the guaiacols produced from EMAL and AL pyrolysis was much higher (29.21%, 32.92%), while the AHL produced the highest p-hydroxyphenols (19.16%). According to the structural analysis of the three types lignin (Tan, 2009), this product distribution depends qualitatively on the relative content of three basic structure units of lignin.

Compound class	Compounds	Yield, Area percent (%)			
		250°C	375°C	600°C	800°C
Benzenes	Benzene	-	-	-	1.69
	Toluene	-	-	-	2.08
	1,2,4-Trimethoxybenzene	-	-	5.63	-
	1,2,3-Trimethoxyl-5-toluene	-	-	1.30	-
p-Hydroxyphenols	Phenol	-	-	2.83	5.08
	p-Cresol	-	-	3.49	9.35
	4-Methoxyphenol	-	-	3.37	-
	2, 4-Dimethylphenol	-	-	-	1.37
	4 (or 3)-Ethylphenol	-	-	5.18	6.56
	2-Allylphenol	-	-	1.23	2.17
	4-(2-Propenyl)-phenol	-	-	-	4.29
	2,6-Ditert-butyl-4-methyl phenol	29.44	13.15	3.06	5.07
Guaiacols	2-Methoxy-4-methylphenol	-	-	3.64	-
	4-Ethyl-2-methoxyphenol	-	-	2.13	-
	2-Methoxyl-4-vinylphenol	6.91	9.19	7.48	3.71
	Vanillin	-	2.14	1.76	-
	2-Methoxyl-4-(1-propenyl)-phenol	-	0.95	2.48	-
Syringols	2,6-Dimethoxyphenol	-	-	8.19	-
	Syringaldehyde	-	1.23	-	-
	2,6-Dimethoxy-4-(2-allyl)-phenol	-	2.51	7.27	1.16
	4-Hydroxy-3,5-dimethoxyacetylbenzene	-	-	-	1.67
Heterocycles	2,3-Dihydrobenzofuran (DHBF)	55.04	66.28	34.70	26.84
	2, 3-Dihydro-2-methylbenzofuran	-	-	1.00	1.67
Esters	3-Butenevalerate	-	-	-	1.60
	Dibutyl phthalate (DBP)	8.61	4.56	1.50	-
Others	1,3-Butadiene	-	-	-	7.68
	Acetic acid	-	-	-	1.11
	Cyclopentanone	-	-	-	15.68
	3,5-Dimethoxy acetophenone	-	-	3.76	1.23

Table 5. Products identification from AHL Pyrolysis

Lignin pyrolysis producing high value-added phenolic chemicals is a new direction in the future research. The highest content of phenolic compounds occurred at 600°C, meanwhile the content of heterocyclics and esters were minimal, thus had the least effect on the desired phenols. If the temperature was controlled in a reasonable range in the industrial production process, fast pyrolysis of technical lignin could produce more phenols.

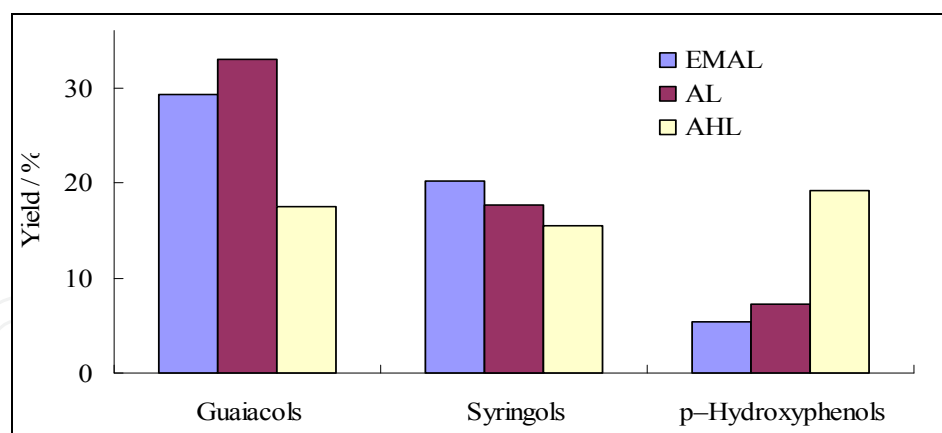


Fig. 10. Phenols contents of three types of lignin pyrolysis at 600°C

4.5 Effect of catalysts on technical lignin pyrolysis

The effects of metal ion catalysts, such as CaO, K₂CO₃, Na₂CO₃, NaCl and ZnCl₂, on the pyrolysis reactions of the two types of technical lignin were previously studied by using thermogravimetric analysis and their apparent activation energy were calculated by Coats-Redfern method (Coats & Redfern, 1964). It was found that the effects of these catalysts on both of two types of technical lignin are similar. The apparent activation energy could be reduced by the adding catalysts. In addition, the peak temperatures of lignin decomposition shifted to lower temperature region when adding catalysts, and thus accelerate the lignin pyrolysis reaction. The pyrolysis temperature of two types of technical lignin could be effectively reduced by the addition of K₂CO₃, while the yield of coke pyrolyzed from AL and AHL could be greatly reduced by the addition of NaCl and CaO, respectively.

In order to further study the effect of catalyst on the distribution of pyrolysis products, for each kind of technical lignin, two catalysts, whose effect had been proven to be more obvious by TG analysis, were selected for lignin Py-GC/MS test, i.e. K₂CO₃ and NaCl were selected for AL, while K₂CO₃ and CaO were selected for AHL. In experiment, K₂CO₃ and CaO were mixed with lignin as previously described, while NaCl was used by immersion and adsorption (Tan, 2009).

Products analysis of AL catalytic pyrolysis at 600°C is listed in Table 6, and the product distribution is shown in Fig. 11. It can be seen, the AL pyrolysis products changed dramatically after adding the K₂CO₃ catalyst. The 2, 3-Dihydrobenzofuran (DHBF) that possessed the highest content previously was not found in this condition, and the phenols content was reduced to 10.17%. Instead, there have emerged a large number of polycyclic aromatic compounds (are usually exceed two benzene rings of PAHs) and high molecular weight long-chain alkanes compounds. This indicates that K₂CO₃ can effectively promote the cleavage of heterocyclic compounds, but also facilitate further condensation of pyrolysis products, which generate large amounts of naphthalene-based compounds.

The effects of NaCl on lower DHBF and phenols content, increase polycyclic aromatic compounds yields are similar to that of K₂CO₃, but its effect is less dramatic. In addition, both two catalysts have led to the rupture of lignin alkyl side-chain, and produced some long-chain alkane compounds.

Compound class	Compounds	Yield, Area percent (%)		
		AL	+10%K ₂ CO ₃	+1%NaCl
Benzenes	1,2,4-Trimethoxybenzene	6.58	3.70	3.06
p-Hydroxyphenols	Phenol	1.42	-	-
	2-Methylphenol	1.79	-	-
	4 (or 3)-Ethylphenol	1.81	-	-
	4-(2-Allyl)-phenol	2.26	-	-
	4-Hydroxy-3-methoxyphenylacetyl	-	3.59	16.14
Guaiacols	2-Methoxyphenol	6.12	3.12	4.88
	2-Methoxy-4-methylphenol	-	-	4.27
	3-Methoxycatechol	3.74	-	-
	4-Ethyl-2-methoxyphenol	1.84	-	2.10
	2-Methoxyl-4-vinylphenol	13.60	-	3.92
	Vanillin	1.58	-	-
	2-Methoxy-3-(2-allyl)-phenol	6.04	-	-
Syringols	2,6-Dimethoxyphenol	7.43	3.46	6.71
	Syringaldehyde	0.95	-	-
	2,6-Dimethoxy-4-(2-allyl)-phenol	8.00	-	2.35
	4-Hydroxy-3,5-dimethoxyacetylbenzene	1.33	-	-
	2,3-Dihydrobenzofuran (DHBF)	25.09	-	21.55
Heterocycles PAH	Phenanthrene	-	7.40	-
	2-Naphthalene acid methyl ester	-	11.98	7.74
	2-Naphthalene-1-butanone	-	7.11	2.98
	1-Phenyl naphthalene	-	11.73	2.88
	2-Acetonaphthone	-	3.99	2.60
	4,5,9,10-Tetrahydropyrene	-	6.17	-
	1,4-2-(2-Dinaphthyl)-butanone	-	7.04	3.39
	4-(2-Naphthyl)-4-ketobutyric acid	-	6.79	-
	Phenyl glyoxylate-2 'acetyl benzene ester	1.76	-	-
Esters	Benzoic acid, phenylmethyl ester	2.18	1.44	-
	4-Methyl-benzoic acid cyclobutyl eater	-	2.99	-
	2,3-dimethyl-2-hexadecylenic acid methyl ester	-	-	1.09
	9-Octadecenoic acid methyl ester	-	-	1.59
	Alkanes	n-Nicosane	-	1.61
Hexatriacontane		-	2.42	-
Triacontane		-	3.90	3.80
Others	Methanol	-	2.08	-
	Docosa-13-en-1-ol	-	2.14	2.48
	1-Triacontanol	-	7.34	6.48
	3,5-Dimethoxy acetophenone	6.77	-	-

Table 6. Products identification from AL pyrolysis with catalysts at 600°C

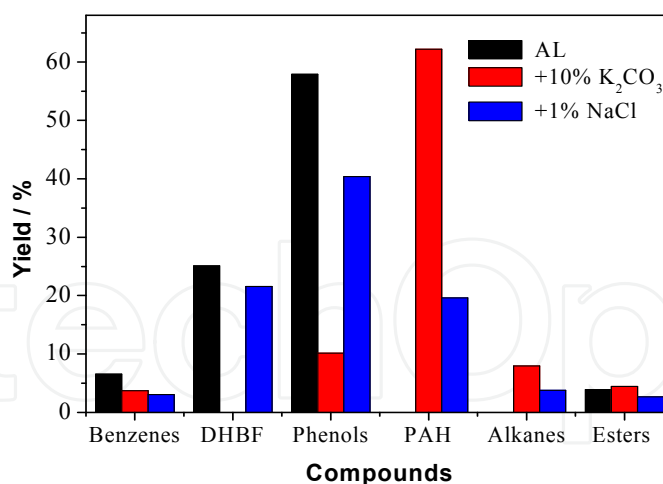


Fig. 11. Effect of catalysts on AL pyrolysis

Table 7 lists the products of AHL pyrolysis with or without catalyst. And Fig. 12 shows the product distribution plotted accordingly. From the figure it can be clearly seen that, the catalytic performance of CaO and K₂CO₃ to AHL pyrolysis was mainly lies in emerging lots of small molecule compounds, particularly for CaO. This is because the catalyst CaO can effectively improve the volatile yield of AHL, and reduce the coke production. In addition, adding CaO also increased the production of heterocyclic compounds, while reducing the phenols content.

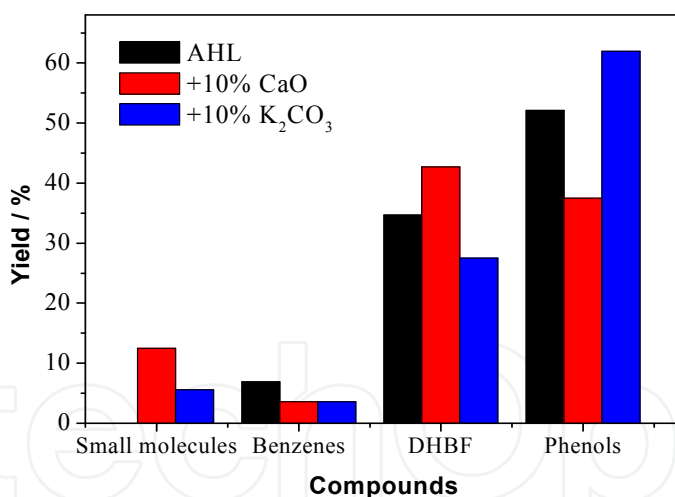


Fig. 12. Effect of catalysts on AHL pyrolysis

In this regard, the effect of K₂CO₃ on AHL pyrolysis is just the opposite. Same as that to AL, K₂CO₃ reduced heterocyclics content of AHL pyrolysis products. The difference is that, for AHL, it did not make further condensation of pyrolysis products to form PAHs, but facilitate the fracture of aromatic compounds side chains, leading to produced more phenolic compounds.

From this it can be seen, as the different structure of lignin, the catalytic effect of a catalyst on different lignins also may be different. The effect of K₂CO₃ on phenolic compounds yield from two technical lignins pyrolysis is a good proof.

Compound class	Compounds	Yield, Area percent (%)		
		AHL	+10%CaO	+10%K ₂ CO ₃
Small molecules	Methanol	-	6.66	-
	Vinyl methyl ether	-	-	1.31
	Methyl acetate	-	-	2.13
	2-Butanone	-	2.78	-
	Glycollic aldehyde	-	1.15	-
	Acetic acid	-	1.91	2.13
Benzenes	Metoxybenzene	-	-	0.74
	1-Vinyl-4-methoxybenzene	-	0.95	-
	1-Ethyl-4- methoxybenzene	-	-	0.49
	1,2-Dimethoxylbenzene	-	-	0.56
	1,2-Dimethoxyl-3-toluene	-	-	1.19
	1,2,4-Trimethoxylbenzene	5.63	2.63	0.63
	1,2,3-Trimethoxyl-5-toluene	1.30	-	-
p-Hydroxyphenols	Phenol	2.83	2.87	9.73
	2-Methyl phenol	-	0.75	1.71
	p-Cresol	3.49	1.86	1.53
	4-Methoxyphenol	3.37	-	-
	4-Vinylphenol	-	-	1.33
	4 (or 3)-Ethylphenol	5.18	2.89	3.44
	2-Allylphenol	1.23	-	-
	4-Hydroxy-3-methylphenylacetyl	-	9.65	9.40
	2,6-Ditert-butyl-4-methyl phenol	3.06	-	-
Guaiacols	2-Methoxyphenol	-	4.06	10.52
	2-Methoxy-4-methylphenol	3.64	4.42	3.20
	4-Ethyl-2-methoxyphenol	2.13	1.66	2.32
	2-Methoxyl-4-vinylphenol	7.48	3.29	0.78
	Vanillin	1.76	-	-
	2-Methoxyl-4-(1-propenyl)-phenol	2.48	-	1.71
Syringols	2,6-Dimethoxyphenol	8.19	4.39	16.31
	2,6-Dimethoxy-4-(2-allyl)-phenol	7.27	1.64	-
Heterocycles	2,3-Dihydrobenzofuran (DHBF)	34.70	42.71	27.52
	2, 3-Dihydro-2-methylbenzofuran	1.00	-	-
Esters	Dibutyl phthalate (DBP)	1.50	-	-
Others	1,4-Dioxane	-	2.52	-
	p-Isopropyl benzaldehyde	-	1.20	1.33
	3,5-Dimethoxy acetophenone	3.76	-	-

Table 7. Products identification from AHL pyrolysis with catalysts at 600°C

5. Conclusion

Pyrolysis of several types of lignins was investigated by using Py-GC/MS, with the focus mainly on the effects of temperatures and catalysts. Significant differences in terms of yields of pyrolysis products and phenolic compounds were observed.

For lignin pyrolysis, temperature is an important parameter, and has a significant impact on both the type and the content of pyrolysis products. High temperature (above 600°C) undoubtedly favored the thermal chemical conversion of lignin. And as the temperature increases, pyrolysis products tend to be more diversified. The 2, 3-Dihydrobenzofuran usually emerged at low pyrolysis temperature and reached its highest yield at about 320°C-400°C. As the temperature increased further, the yield of 2, 3-Dihydrobenzofuran decreased, while the phenolic compounds increased dramatically. At 600°C, the maximum content of phenolic compounds from lignin pyrolysis can reach up to 58%.

The impact of catalysts and its dosage on EMAL pyrolysis mainly reflected in the product distribution, while for technical lignin the impact of catalysts are more evident in the increase of new pyrolysis products. Both NaCl and permutite can promote the generation of small molecule compounds during EMAL pyrolysis, such as acetic acid, benzene series, furfural, and phenols etc., and the yields of those products increase with an increase of catalyst dosage. However, the impact of the two catalysts on the selectivity of 2, 3-Dihydrobenzofuran is opposite. The addition of K₂CO₃ resulted in the dramatically decrease of heterocycles and yielded large amounts of naphthalene-based compounds for the alkali lignin. While the same effect was not happened for the acid hydrolysis lignin, but relatively increase the phenols and small molecules yields.

6. Acknowledgment

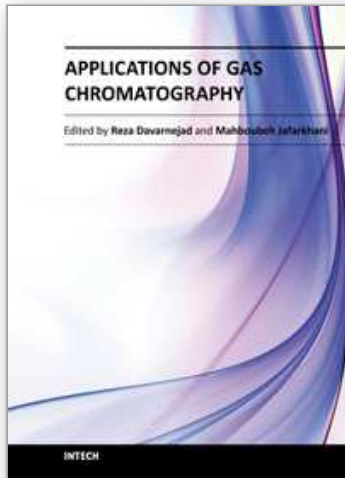
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This valuable book aims to provide a connection between various chromatography techniques and different processes. Authors applied these techniques in supercritical technology, medical, environmental, physique and chemical processes. Most of them prepared mathematical support (such as correlation) for their original results obtained from the chromatography techniques. Since chromatography techniques (such as GC, HPLC & etc) are separating and analyzing methods, this chapters will help other researchers and young scientists to choose a suitable chromatography technique. Furthermore, this book illustrates the newest challenges in this area.

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