

Component fractionation of wood-tar by column chromatography with the packing material of silica gel

WANG Ze, LIN WeiGang, SONG WenLi*, DU Lin, LI ZhengJie & YAO JianZhong

State Key Laboratory of Multi-Phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

Received October 31, 2009; accepted July 28, 2010

Bio-oil can be an important fuel resource for automobiles in the future, while its complex composition restricts the direct application of the bio-oil extremely. So it is necessary to separate the complex mixture to relatively simplified fractions for goal directed specific treatments to reach the fuel quality for automobiles, and meanwhile different functional chemical materials and fine chemicals can be obtained. So it is significant to investigate the bio-oil component separating methods. Herein the method of column chromatography by the packing material of silica gel with two series of eluants of cyclohexane-benzene-methanol and cyclohexane-dichloromethane-methanol were investigated for component fractionation of the raw wood tar (oil fraction of the liquid product by slow pyrolysis of wood). The analytical results show that the components in cyclohexane are rich in alkoxy-monophenols; the components of alkyl-monophenols and five ring oxygen-containing compounds are abundant in benzene and in dichloromethane similarly; in the methanol fraction, the components are diverse and diphenols are relatively in higher content, comparatively small polar molecules and five ring oxygen-containing compounds are more abundant in the methanol fraction after being eluted by dichloromethane, and the content of 1-(4-hydroxy-3-methoxyphenyl) -2-propanone is higher after being eluted by benzene.

biomass, wood-tar, column chromatography

Citation: Wang Z, Lin W G, Song W L, et al. Component fractionation of wood-tar by column chromatography with the packing material of silica gel. Chinese Sci Bull, 2011, 56: 1434–1441, doi: 10.1007/s11434-010-4144-x

With declining petroleum resource and more concerns on environment and climate, the development for renewable energy is getting more necessary. Biomass is an important renewable and environment-benign energy resource, but in low energy density, so it is advantageous to convert biomass to the pyrolytic liquid product of bio-oil [1,2]. Bio-oil can be directly used for burning in boilers, and also can be a potential resource for fuel of automobiles. While the components in bio-oil are very complex with high oxygen content, and therefore the method of component fractionation is considered for specific refinery for fuel and for chemicals. So it is significant to study the methods for component separation. Presently the main separating methods are solvent extraction, distillation, and column chromatography.

Through solvent extraction, neutral compounds, phenols,

acids etc. can be obtained, and some frequently used solvents are hexane, benzene, toluene, ether, ethyl acetate, chloroform, methanol, ethanol etc. [3–6]. As in petrochemical industry, distillation is also a common method in bio-oil fractionation [7–12], while the effect was not very satisfactory due to the conversion of much heat sensitive components in bio-oil by pyrolysis and polymerization reactions. To solve the problem, some modified distillation like flash distillation, vacuum distillation, and molecular distillation are also tested, combined with solvent extraction, and the effect can be improved.

Compared with solvent extraction and distillation, the reports on column chromatographic separation of bio-oil are much less. In Ba's work [13], an softwood bark bio-oil was eluted by solvents of pentane, benzene, dichloromethane, ethyl acetate, and methanol in sequence with the packing material of silica gel. The pentane fraction was found rich in

*Corresponding author (email: wlsong@home.ipe.ac.cn)

alkanes and alkenes, in the benzene fraction polycyclic aromatic hydrocarbons (PAHs) were abundant, many phenol derivatives and some oxygen containing compounds were detected in dichloromethane and ethyl acetate fractions, and in the methanol fraction some polar compounds like sugars were more concentrated. In Das's work [14], the bio-oil from pyrolysis of cashew nut shell was successively eluted by hexane/ethyl acetate mixtures and chloroform/methanol mixtures in different ratio with the packing material of silica gel, and five monocomponents in five fractions were obtained, and each component has the common unique head- and -tail like structure with the phenolic group being at the head and a long linear chain forming the tail. Rutkowski et al. [15] separated a dehydrated bio-oil into fractions by eluting solvents of hexane, benzene, ether and methanol, with the packing material of neutral Al_2O_3 . It was found that furan derivatives, phenol and its derivatives were the typical oxygen-containing compounds identified in ether and methanol fractions, and besides the methanol fraction was rich in C2-C10 carboxylic acids and glucose derivatives like levoglucosenone. In Xu's work [16], the neutral components in bio-oil obtained by solvent extraction was eluted by solvents of cyclohexane, benzene, and methanol in sequence with the column packing material of silica gel, and it was found that the main components in cyclohexane were paraffins, cycloparaffins, and PAHs; in benzene fraction, alkyl-aromatics, phenols, and a part of esters were abundant; the methanol fraction was rich in diisobutyl phthalate and di-n-butyl phthalate. Li et al. [17] fractionated the bio-oil free from water and asphaltene from pyrolysis of apricot pit and corncob by the same eluting solvents and the same column packing material as that in Xu's work, and the cyclohexane fraction was found rich in PAHs; the components in benzene is more complex including acids, phenols, and five ring oxygen-containing compounds. Zhang et al. [18] eluted the volatile fraction of the bio-oil from sawdust, by solvents of n-heptane, benzene, and methanol with the column packing material of Al_2O_3 , and it was found that the content of dimethyl-hydroxyphenol was the highest, and methyl furan, diethylphenol, phenethylol, phenyl acetic acid were also in high content.

In this paper, the column chromatographic separation of the original wood-tar (oil-phase of bio-oil from slow pyrolysis of wood) with the packing material of silica gel was tested, the components of the raw wood-tar was analyzed, and the effects of different eluting solvents were compared.

1 Experimental method

Silica gel (200–300 mesh) of 60 g was packed in a glass tube (inner-diameter 2.8cm), and then 30 mL wood-tar was added to the top of the column. Three solvents of cyclohexane, benzene (dichloromethane), methanol were used for elution in sequence, and the process was promoted by increasing column

head pressure by balloon. The solvent in the eluting solution was firstly distilled away, and then the rest bottom solution was measured and analyzed by GC-MS. The corresponding conditions and measurements were listed in Table 1.

2 Analysis of the raw wood-tar

The composition analysis is the premise and guarantee for component separation. So herein the raw wood-tar was firstly analyzed by screened gas chromatogram column and optimized analytical conditions. The corresponding conditions are as follows: Varian 300 GC-MS; column of FFAP 25 mm×0.25 mm×0.2 μm ; injector temperature 240°C; EI temperature 250°C; oven temperature starts from 35°C (1 min), then increases to 50°C (1min) by 2°C/min, then increases to 80°C (1min) by 3°C/min, and then increases to 230°C (2 min) by 4°C/min, and finally increases to 240°C (10 min) by 4°C/min. The total ion chromatogram (TIC) of the raw wood-tar is illustrated in Figure 1.

It can be seen from Figure 1 that the components in wood-tar were complex, 191 peaks were found over 0.1(area)%, and 22 peaks were over 1(area)%. The components include almost all oxygen-containing compounds like phenols, alcohols, aldehydes, ketones, acids, ethers, esters, and some non-polar compounds like aromatics, paraffins, cycloalkanes, etc. Phenol derivatives were the most abundant components, occupying over 40(area)%, and five ring oxygen-containing compounds were also in high content. Small alcohols and ketones mainly distributed in the retention time of 2–15 min; in the range of 15–35 min small acids and five ring oxygen-containing compounds were abundant; monophenols were in high content in 35–55 min; in 55–60 min diphenols were abundant; and in the range of 60–70 min scattered some fatty hydrocarbons and fatty acids. The main components in raw wood-tar and the corresponding area percentages were listed in Table 2.

3 Results and discussion

3.1 Eluted by cyclohexane-benzene-methanol

Wood-tar was eluted by cyclohexane-benzene-methanol

Table 1 Amount of the solvents and the bottom solution after distillation

Exp.	Solvent	Volume of solvent (mL)	Mass of bottom solution (g)	Volume of bottom solution (mL)
Exp.1#	Cyclohexane	300	12.82	13.6
	Benzene	265	8.81	8.6
	Methanol	196.5	3.01	3.5
Exp.2#	Cyclohexane	304	12.48	13.1
	Dichloromethane	262.5	13.13	11.7
	Methanol	243	7.36	6.4

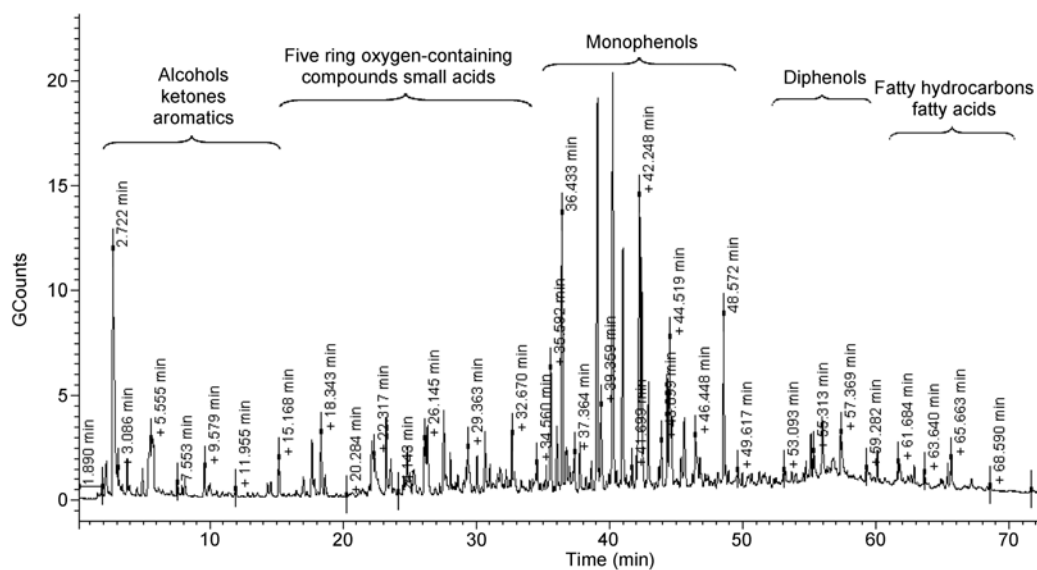


Figure 1 TIC of the raw wood-tar.

Table 2 Main components in the raw wood-tar and their area percentages

No.	RT (min)	Compound name	Area%	No.	RT (min)	Compound name	Area%
1	2.722	Methyl Alcohol	4.069	22	40.991	Phenol, 4-ethyl-2-methoxy-	2.795
2	5.555	Water	2.505	23	42.248	Mixture of 4-methyl-phenol and 2,4-dimethyl-phenol	4.206
3	17.657	2-Cyclopenten-1-one	0.602	24	42.398	Phenol, 3-methyl-	2.742
4	18.343	2-Cyclopenten-1-one, 2-methyl-	0.774	25	42.928	Phenol, 2-methoxy-4-propyl-	1.126
5	22.137	Acetic acid	1.843	26	43.899	Phenol, 2,3-dimethyl-	0.727
6	23.235	Furfural	0.796	27	44.325	Phenol, 2-ethyl-5-methyl-	1.155
7	24.831	Ethanone, 1-(2-furanyl)-	0.595	28	44.519	Phenol, 3,5-dimethyl-	1.672
8	25.299	2-Cyclopenten-1-one, 3-methyl-	0.543	29	44.657	Phenol, 3-ethyl-	0.768
9	26.145	Butanoic acid, 2-oxo-	1.045	30	45.612	Phenol, 3,4-dimethyl-	1.115
10	26.333	2-Cyclopenten-1-one, 2,3-dimethyl-	0.971	31	46.448	Phenol, 2-methoxy-4-(1-propenyl)- or Eugenol	1.179
11	27.556	2-Furancarboxaldehyde, 5-methyl-	0.934	32	46.788	Phenol, 2,6-dimethoxy-	0.58
12	29.363	Pentanoic acid	0.793	33	48.572	Phenol, 2-methoxy-4-(1-propenyl)- or Eugenol	1.836
13	30.651	2-Furanmethanol	0.556	34	49.617	1,4:3,6-Dianhydro-.alpha.-d-glucopyranos	0.824
14	32.67	Naphthalene	0.585	35	55.117	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.675
15	35.592	1,2-Cyclopentanedione, 3-methyl-	1.554	36	55.313	1,2-Benzenediol, 3-methyl-	1.04
16	36.048	Naphthalene, 2-methyl-	0.685	37	55.982	1,2-Benzenediol	1.42
17	36.433	Phenol, 2-methoxy-	2.962	38	56.817	2,5-Dimethylhydroquinone	1.022
18	37.772	Phenol, 2,6-dimethyl-	0.558	39	57.369	1,2-Benzenediol, 4-methyl-	1.523
19	39.1	Phenol, 2-methoxy-4-methyl-	4.642	40	59.282	3-Allyl-6-methoxyphenol	0.547
20	39.359	Unknown	1.148	41	65.663	Oleic acid	0.559
21	40.232	Phenol mixed with 2-methyl-phenol	5.22			Sum	60.891

with the packing material of silica gel. After the solvent in the eluting solution was distilled away, the bottom solution was analyzed. The total ion chromatograms of the bottom solutions were shown in Figures 2–4, and the area percentages of the main components were listed in Tables 3–5.

It can be seen from Figure 2 and Table 3 that monophenols were the most abundant components in the cyclohexane fraction; other types of compounds were rather little. Among the monophenols, alkoxy-monophenols were more distinct than alkyl-monophenols. For instance, the area per-

centages of 4-methyl-2-methoxy-phenol, 4-ethyl-2-methoxy-phenol, and 2-methoxy-phenol were all over 5(area)%. Alkyl-monophenols like 2-methyl-phenol and 2,4-dimethyl-phenol were also in higher content, but less than those of alkoxy-monophenols.

Figure 3 and Table 4 showed that monophenols were still the most abundant component in benzene, while the composition of the monophenols was different to that in cyclohexane. The content of alkyl-monophenols increased obviously, higher than that of alkoxy-monophenols. For instance, the content of phenol, 4-methyl-phenol, and 3-me-

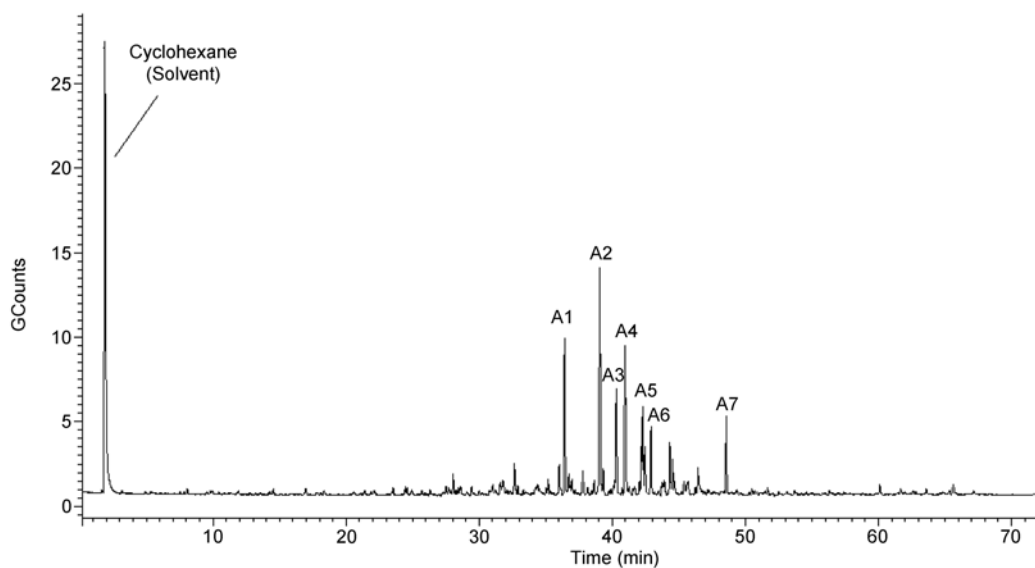


Figure 2 TIC of the distilled cyclohexane solution.

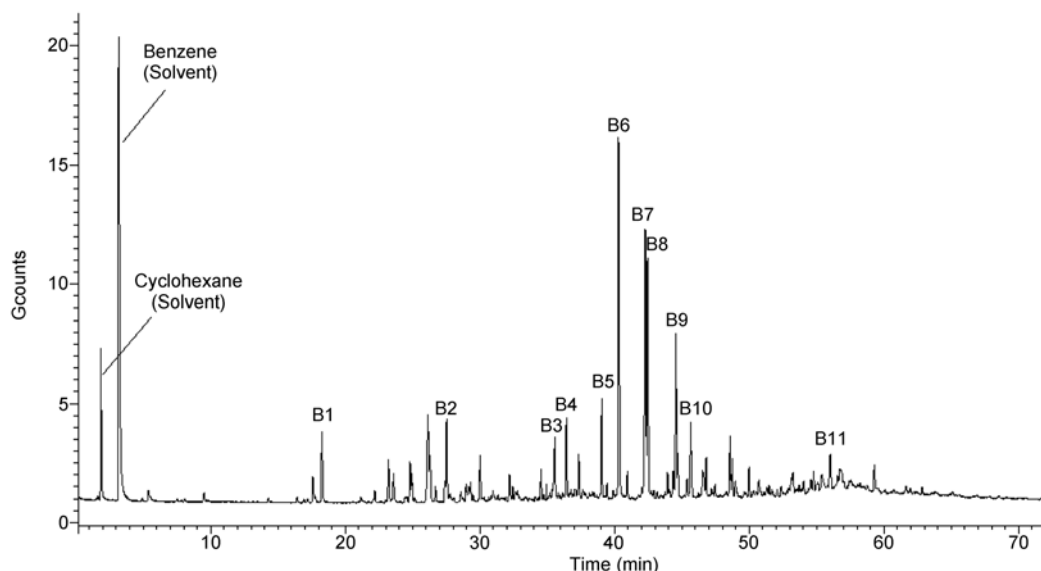


Figure 3 TIC of the distilled benzene solution.

thyl-phenol was higher than that of the top abundant alkoxy-monophenol of 2-methoxy-4-methyl-phenol. The content of five ring oxygen-containing compounds also increased a lot, and the main representative components were 5-methyl-2-furancarboxaldehyde, 2-hydroxy-3-methyl-2-cyclopenten-1-one, and 2-methyl-2-cyclopenten-1-one.

It can be seen from Figure 4 and Table 5 that the types of the components were diverse and the diphenols were relatively more abundant. For instance, the compound of 4-methyl-1,2-benzenediol was the richest component. The five ring oxygen-containing compounds like 3-methyl-1,2-cyclopentanedione and 3-methyl-2-cyclopenten-1-one were also in a relatively higher content. The content of monophenols including both alkyl- and alkoxy- monophenols

decreased generally, while it was interesting that the monophenol compound of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone was in a rather high content.

It can be seen from the above results that the wood-tar eluted by cyclohexane-benzene-methanol with the packing material of silica gel can be separated into three feature distinct fractions. In general, the alkoxy- monophenols were most abundant in cyclohexane; the alkyl-monophenols and five ring oxygen-containing compounds were rich in benzene; in methanol, the components were diverse and the content of diphenols was relatively higher. In the viewpoint of application or post processing of the three fractions, the process for obtaining the cyclohexane fraction may be referential to the concentration of alkoxy-monophenols, or to

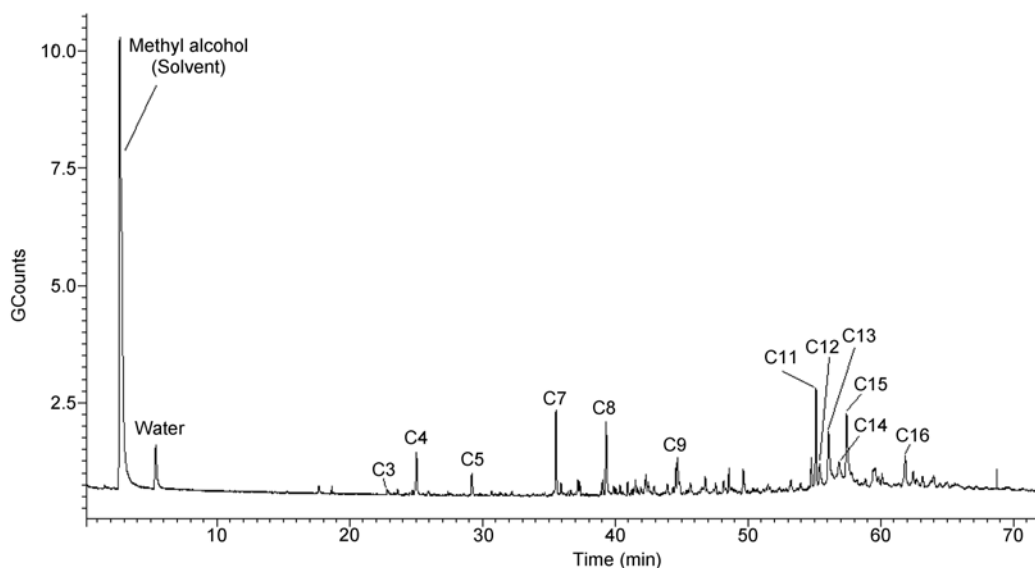


Figure 4 TIC of the distilled methanol solution after being eluted by benzene.

Table 3 Main components in distilled cyclohexane system

No.	RT (min)	Compound name	Area%
A1	36.423	Phenol, 2-methoxy-	5.39
A2	39.068	Phenol, 2-methoxy-4-methyl-	9.023
A3	40.311	Phenol, 2-methyl-	3.903
A4	40.966	Phenol, 4-ethyl-2-methoxy-	5.766
A5	42.289	Phenol, 2,4-dimethyl-	3.043
A6	42.917	Phenol, 2-methoxy-4-propyl-	2.42
A7	48.568	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	2.48

Table 4 Main components in distilled benzene and dichloromethane systems

No.	RT (min)	Compound name	Exp.1#		Exp.2#	
			Area%	Sum	Area%	Sum
B1	18.278	2-Cyclopenten-1-one, 2-methyl-	1.702		1.557	
B2	27.543	2-Furancarboxaldehyde, 5-methyl-	1.872	5.355	1.615	5.529
B3	35.549	1,2-Cyclopentanedione, 3-methyl- or 2-hydroxy-3-methyl-2-cyclopenten-1-one	1.781		2.357	
B4	36.42	Phenol, 2-methoxy-	1.62		1.795	
B5	39.039	Phenol, 2-methoxy-4-methyl-	1.891	3.511	1.987	3.782
B6	40.29	Phenol mixed with 2-methyl-phenol	8.914		8.684	
B7	42.272	Phenol, 4-methyl-	7.249		7.069	
B8	42.438	Phenol, 3-methyl-	5.777	27.423	5.418	26.312
B9	44.537	Phenol, 3,5-dimethyl-	3.514		3.359	
B10	45.64	Phenol, 3,4-dimethyl-	1.969		1.782	
B11	55.12	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.233 ^{a)}		1.473	
		Summary	36.522		37.096	

a) Non-major component, just for comparison.

separation between alkoxy- and alkyl- monophenols; the abundant alkyl-monophenols and five ring oxygen-containing compounds in benzene can be further separated by solvent extraction due to their different acidities; the methanol fraction can be a source for more concentrated diphenols, and the other components can be more conveniently concentrated by post treatments like distillation

and/or solvent extraction, since the diverse components were more different in properties. It is worth mentioning that the structure unique compound of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone in high content in methanol, makes the further concentration of this component more easily, bringing an opportunity for its fine extraction.

Silica gel has a stronger polarity due to the rich hydroxyl

Table 5 Main components in distilled methanol systems

No.	RT (min)	Compound Name	Exp.1#		Exp.2#	
			Area%	Sum	Area%	Sum
C1	15.213	2-Propanone, 1-hydroxy-	0.028 ^{a)}		1.829	
C2	18.651	1-Hydroxy-2-butanone	0.034 ^{a)}	0.264	0.991	7.278
C3	22.161	Acetic acid	0.202 ^{a)}		4.458	
C4	25.058	2-Cyclopenten-1-one, 3-methyl-	1.249		1.847	
C5	29.193	2-Cyclopenten-1-one, 3-ethyl- or Butyrolactone	0.888		0.228 ^{a)}	
C6	30.663	2-Furanmethanol	0.126 ^{a)}	4.48	1.325	7.936
C7	35.588	1,2-Cyclopentanedione, 3-methyl-	2.217		4.536	
C8	39.401	Maltol	2.572		4.973	
C9	44.571	Butanoic acid, 2-propenyl ester or 2-Furanmethanol, tetrahydro-	1.772		3.561	
C10	48.134	Pentanoic acid, 4-oxo-	0.531		1.018	
C11	55.121	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	2.93		0.234 ^{a)}	
C12	55.296	1,2-Benzenediol, 3-methyl-	1.951		2.101	
C13	55.915	1,2-Benzenediol	4.268		6.529	
C14	56.81	1,4-Benzenediol, 2,6-dimethyl-	2.706	13.391	2.12	16.942
C15	57.32	1,2-Benzenediol, 4-methyl-	4.466		6.192	
C16	61.852	Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	2.546		1.424	
		Summary	28.486		43.366	

a) Non-major component, just for comparison.

group on the surface. When the wood-tar was eluted by non-polar solvent of cyclohexane, the component with stronger polar bond has a more intense force with silica gel and harder to be eluted off the column compared to that with weaker polar bond. The different eluting effect by cyclohexane between alkoxy- and alkyl-monophenols is related to the difference between their molecular structures. Alkoxy and alkyl group are both electron-donating groups. The repulsive effect of the electron-donating group makes the electron density on the benzene ring increase, and makes the polarity of the phenolic hydroxyl bond δ_{O-H} on the ortho-position and para-position decrease through the alternative polarization on the benzene ring by conjugative effect[19]. Alkoxy group has a stronger electron-donating effect than alkyl group, so the force between silica gel and the phenolic hydroxyl bond of alkoxy-monophenol is weaker than that of alkyl-monophenol, and therefore the alkoxy-monophenols are easier to be eluted by cyclohexane than alkyl-monophenols. When the solvent of benzene with higher solubility and higher polarity than cyclohexane is applied, besides the remaining alkoxy- and alkyl-monophenols, some stronger polar five ring oxygen-containing compounds were also eluted away by benzene. When the solvent of methanol with even higher polarity was applied, more components in even higher polarities including dihydric compounds like diphenols, multi oxygen containing compound like 1-(4-hydroxy-3-methoxyphenyl)-2-propanone and Maltol, and some remaining five ring oxygen-containing compounds were eluted by methanol. So the wood-tar can be separated to three feature-distinct fractions when eluted by the solvents of cyclohexane-benzene-methanol with the

packing material of silica gel.

3.2 Eluted by cyclohexane-dichloromethane-methanol

In the above case (Exp.1), the solvent of benzene is a toxic agent with a relatively higher boiling point (80°C), which is disadvantageous for the operating security and the stability of those heat sensitive components, so herein the solvent of dichloromethane with slight toxicity and low boiling point (40°C) in displacement of benzene was tested with the same packing material of silica gel. The total ion chromatograms of the distilled dichloromethane and methanol solutions were shown in Figures 5 and 6, and the compositions of the two systems were listed in Tables 4 and 5 respectively, together with the former results obtained from Exp.1 for convenient comparisons.

It can be seen from Figure 5 and Table 4 that the compositions of the dichloromethane and benzene systems were very similar. In dichloromethane fraction, the alkoxy-monophenols and five ring oxygen-containing compounds were still in high content and still less than the most abundant components of alkyl-monophenols as that in benzene, and phenol and 4-methyl-phenol were still the top two abundant compounds. While the content of alkyl-monophenols in dichloromethane was reduced a little bit, and the compound of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone increased obviously compared with that in benzene. It may be because the polarity of dichloromethane is higher than that of benzene, and easier to elute away more polar components.

It can be seen from Figure 6 and Table 5 that similar to

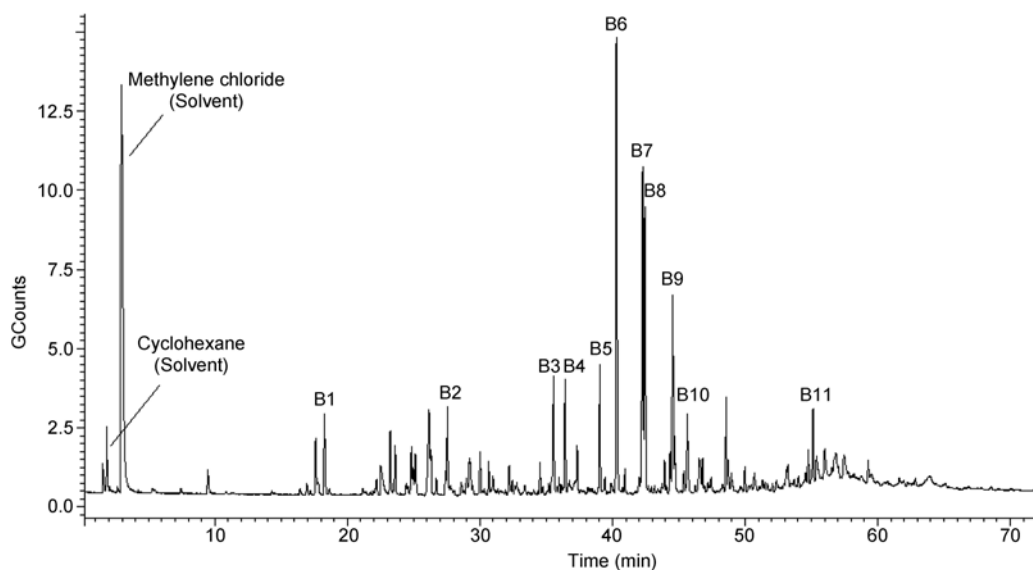


Figure 5 TIC of the distilled dichloromethane solution.

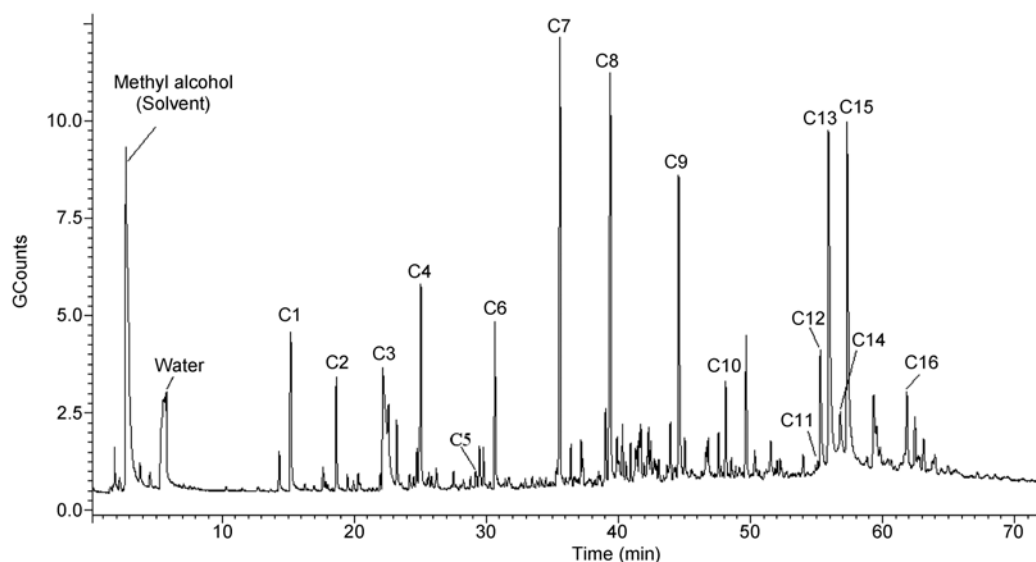


Figure 6 TIC of the distilled methanol solution after being eluted by dichloromethane.

the case after benzene elution, the components in methanol after being eluted by dichloromethane were also very diverse, diphenols were relatively higher too, and the most abundant diphenols were still 1,2-benzenediol and 4-methyl-1,2-benzenediol. But the five ring oxygen-containing compounds and some small polar molecules like 3-methyl-1,2-cyclopentanedione, acetic acid, and 1-hydroxy-2-propanone were more concentrated, and on the contrary the content of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone was distinctly reduced, compared with that after being eluted by benzene.

The increase of the small polar molecules and five ring oxygen-containing compounds in methanol after being eluted by dichloromethane should be related to the difference of the polarity between dichloromethane and benzene.

The polarity of dichloromethane is a little bit higher than that of benzene but still in low level generally. Most of the of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone can be eluted off the column by dichloromethane, while the more polar compounds like acids are still hard to be completely eluted away, but to the near end district of the column, and it makes these components more easily to be eluted by methanol, and therefore makes their content higher in the methanol fraction.

4 Conclusions

The column chromatographic fractionation of wood-tar was

investigated, by two series of eluants of cyclohexane-benzene-methanol and cyclohexane-dichloromethane-methanol, with the packing material of silica gel. It was found that the content of alkoxy-monophenols was the highest in cyclohexane; the components of alkyl-monophenols and five ring oxygen-containing compounds were abundant in benzene and in dichloromethane fractions similarly, while the content of alkyl-monophenols in dichloromethane reduced a little bit compared with that in benzene system; in methanol the components were diverse and diphenols were in higher content relatively, and comparatively some small polar molecules and five ring oxygen-containing compounds were more abundant in the methanol fraction after being eluted by dichloromethane, and the content of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone was higher in the methanol solution after being eluted by benzene.

The higher content of alkoxy-monophenols in cyclohexane indicates a referable approach for the separation of alkoxy-monophenols and alkyl-monophenols. The methanol fraction can be a source for more concentrated diphenols, and the other components inside can be more conveniently concentrated by post treatments like distillation and/or solvent extraction too. The compound of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone in high content in methanol after being eluted by benzene makes the concentrating of this component more easily, bringing an opportunity for its fine extraction.

This work was supported by the National Basic Research Program of China (2004CB719704), and the National Natural Science Foundation of China (0202017127).

- 1 Mohan D, Pittman C U, Steele P H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energ Fuel*, 2006, 20: 848–889
- 2 Bridgwater A V. Renewable fuels and chemicals by thermal processing of biomass. *Chem Eng J*, 2003, 91: 87–102
- 3 Karagöz S, Bhaskar T, Muto A, et al. Low-temperature catalytic hydrothermal treatment of wood biomass: Analysis of liquid products. *Chem Eng J*, 2005, 108: 127–137
- 4 Karagöz S, Bhaskar T, Muto A, et al. Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose

- by hydrothermal treatment. *Fuel*, 2005, 84: 875–884
- 5 American Can Company. Fractionation of oil obtained by pyrolysis of lignocellulosic materials to recover a phenolic fraction for use in making phenol-formaldehyde resins. US Patent, US4209647, 1980-06-24
- 6 Midwest Research Institute. Process for fractionating fast-pyrolysis oils, and products derived therefrom. US Patent, US4942269, 1990-07-17
- 7 Xu B J, Lu N, Li J S, et al. Experimental research on the bio-oil derived from biomass pyrolysis liquefaction (in Chinese). *Trans Chin Soc Agric Engin*, 1999, 15: 177–181
- 8 Pütün A E, Özcan A, Pütün E. Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: Yields and structural analysis of bio-oil. *J Anal Appl Pyroly*, 1999, 52: 33–49
- 9 Boucher M E, Chaala A, Roy C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenerg*, 2000, 19: 337–350
- 10 Adjaye J D, Sharma R K, Bakhshi N N. Characterisation and stability analysis of wood-derived bio-oil. *Fuel Process Technol*, 1992, 31: 241–256
- 11 Murwanashyaka J N, Pakdel H, Roy C. Separation of syringol from birch wood-derived vacuum pyrolysis oil. *Sep Purif Technol*, 2001, 24: 155–165
- 12 Guo Z G, Wang S R, Zhu Y Y, et al. Separation of acid compounds for refining biomass pyrolysis oil (in Chinese). *J Fuel Chem Technol*, 2009, 37: 49–52
- 13 Ba T, Chaala A, Garcia-Perez M, et al. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark storage stability. *Energ Fuel*, 2004, 18: 188–201
- 14 Das P, Sreelatha T, Ganesh A. Bio oil from pyrolysis of cashew nut shell-characterisation and related properties. *Biomass Bioenerg*, 2004, 27: 265–275
- 15 Rutkowski P. Influence of zinc chloride addition on the chemical structure of bio-oil obtained during co-pyrolysis of wood/synthetic polymer blends. *Waste Manage*, 2009, 29: 2983–2993
- 16 Xu S P, Liu J, Li S G, et al. Solvent extraction-column chromatographic separation of bio-oil from fast pyrolysis of apricot stone and manufacture technology (in Chinese). *J Dalian Univer Technol*, 2005, 45: 505–510
- 17 Li S G, Xu S P, Lu Q H, et al. Column chromatographic separation of bio-oil from fast pyrolysis of biomass (in Chinese). *Acta Energ Sol Sin*, 2005, 26: 549–555
- 18 Zhang S P, Yan Y J, Ren Z W, et al. Analysis of liquid product obtained by the fast pyrolysis of biomass (in Chinese). *J East China Univer Sci Tech*, 2001, 27: 666–668
- 19 Guo H M. Explanation on the effect of position and type of substituent group on the chemical properties of aromatic compound by electronic effect regulations (in Chinese). *Univer Chem*, 2008, 23: 54–57

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.