Development of carbon fibers from biomass tars

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Background

Biomass tar is a by-product in the carbonization, but the most is not utilized.

Effective utilization of the biomass tar is indispensable for sequestration of CO_2.

Charcoal from biomass is used as fuel, functional charcoal etc.

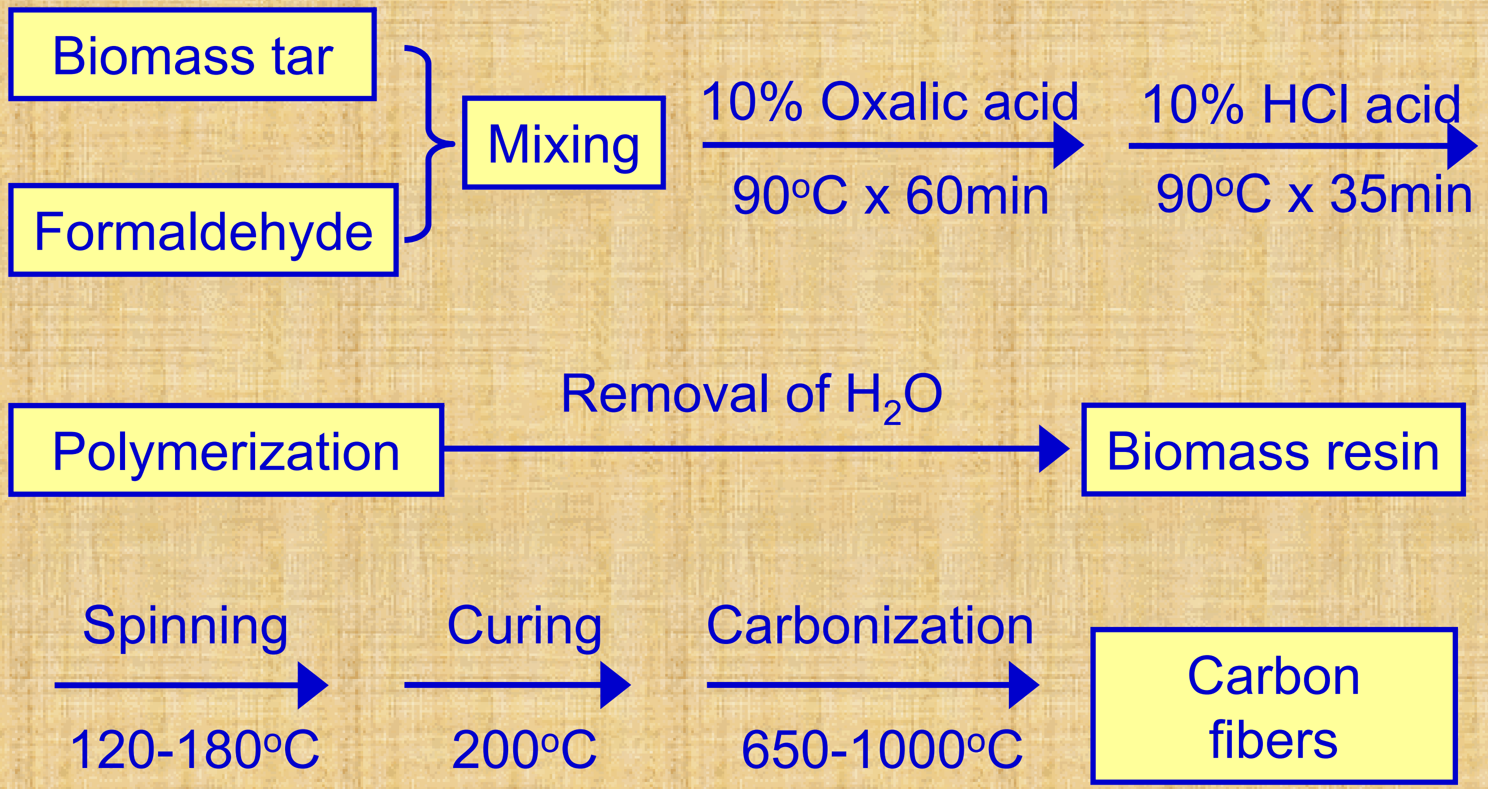
Tar from fossil fuel is the source for functional carbons.

Objective

Biomass tar was modified through the polymerization of its phenol-containing components to develop biomass tar resin. Carbon materials such as carbon fibers were expected to be developed from the resin as unique precursor.

Experimental

Preparation procedure of biomass resin and its derived carbon fibers



Analysis and measurement

Biomass tar and its resin:

^{1}H-NMR for hydrogen distribution of tar

FT-IR for oxygen-containing components of tar

TG for thermal stability of tar and its resin

TOF-MS for molecular weight distribution of tar and its resin

GC-MS for determination of components of tar

Property measurement of carbon fibers:

XRD, Raman, SEM,

Mechanical properties (tensile strength and modulus)

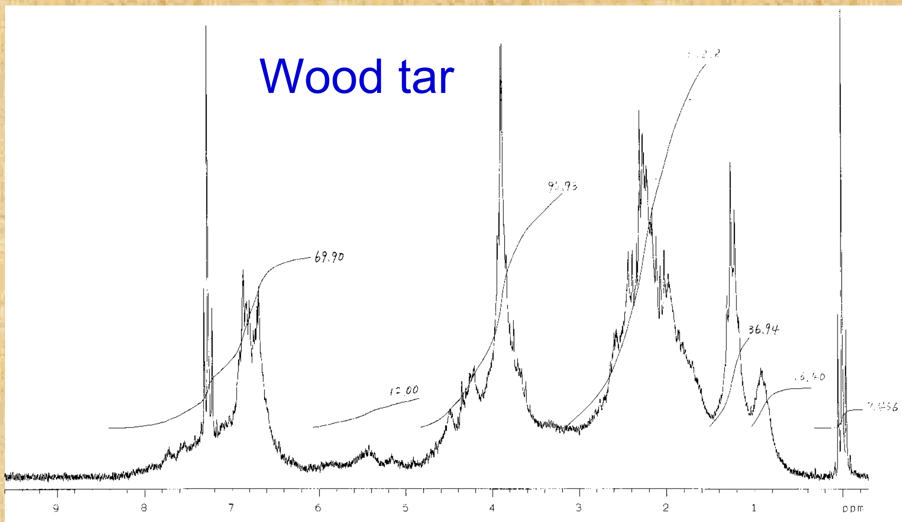
Results

Basic data of wood, bamboo tars and their resins after the polymerization

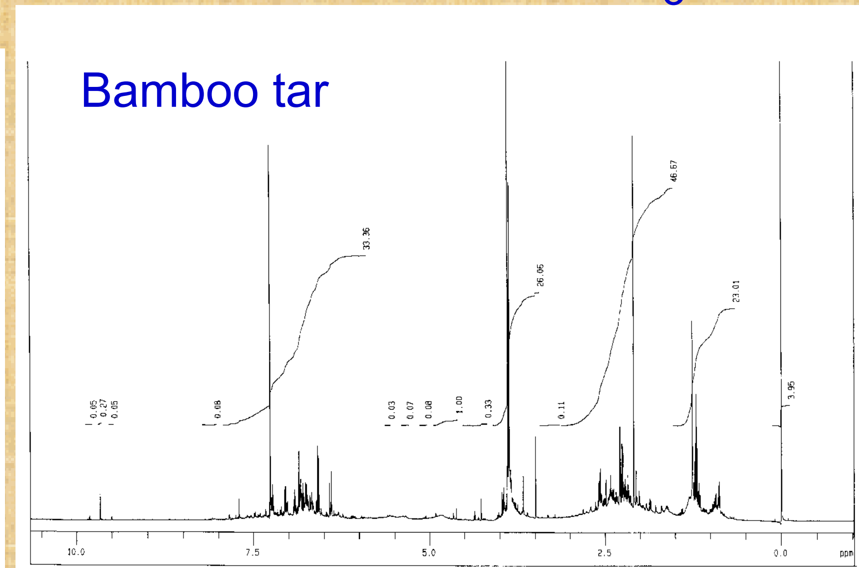
	Elemental analysis (wt%)				C/O	SP
	C	H	N	O (by diff)		(°C)
Wood tar	64.66	6.92	0.16	28.26	3.05	
Bamboo tar	61.98	7.33	0.42	30.27	2.73	
Wood tar resin	68.98	6.78	0.14	24.10	3.82	60
Bamboo tar resin	70.02	6.56	0.52	22.90	4.08	80

Biomass tar contains a lot of oxygen-containing groups

^{1}H-NMR analysis of wood and bamboo tars in $CDCl_3$



Chemical shift, ppm



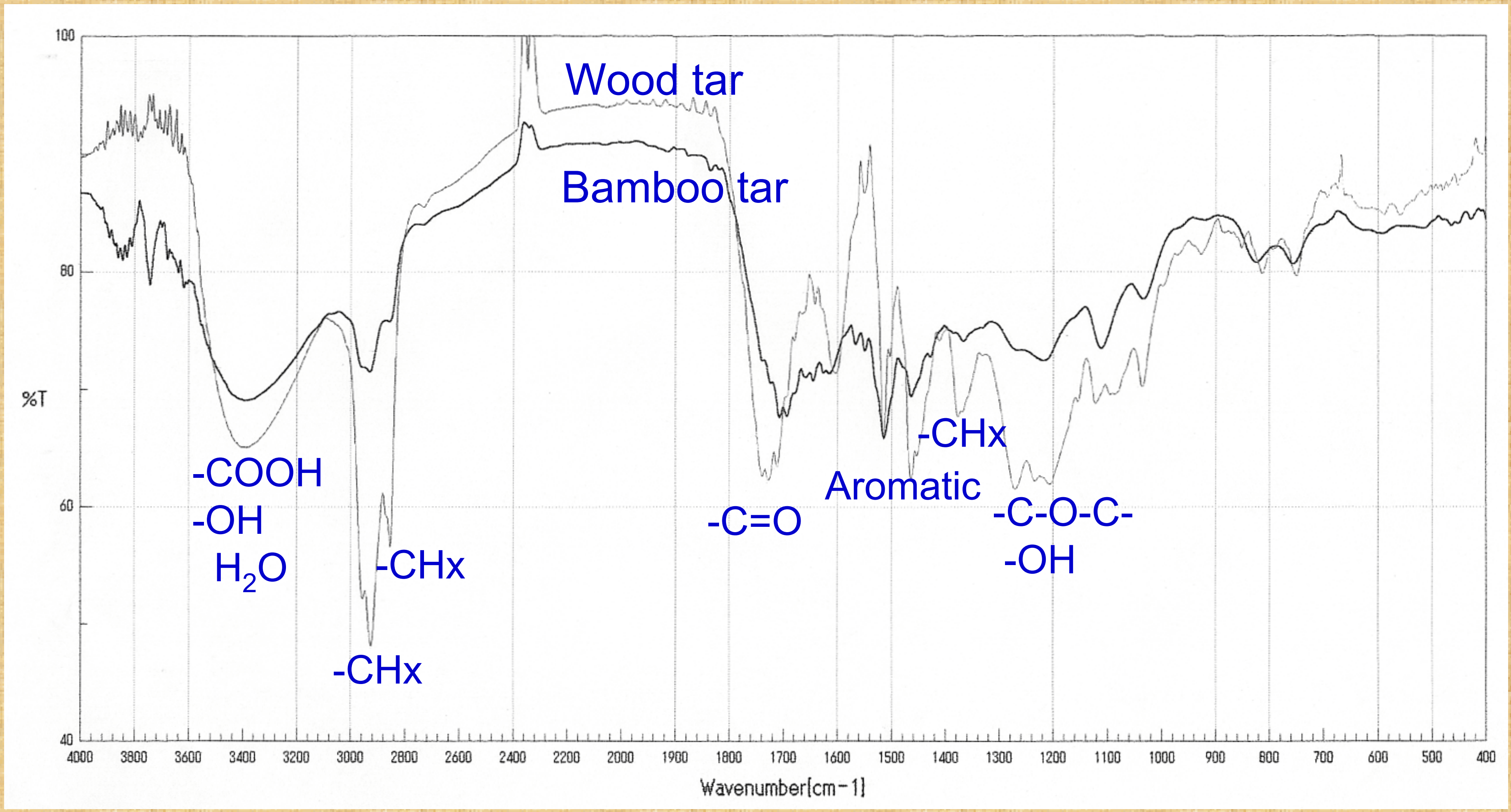
Chemical shift, ppm

	Hydrogen distribution, %			f_a
	H_a	H_α	$H_\beta + H_\gamma$	
Wood tar	19.0	66.5	14.5	0.48
Bamboo tar	25.8	56.3	17.8	0.47

H_a:aromatic hydrogen $\delta(^1H)$=6~9ppm; H_α: α-hydrogen $\delta(^1H)$=1.7~4;
H_β: β-hydrogen $\delta(^1H)$=1~1.7; H_γ: γ-hydrogen $\delta(^1H)$=0.5~1.

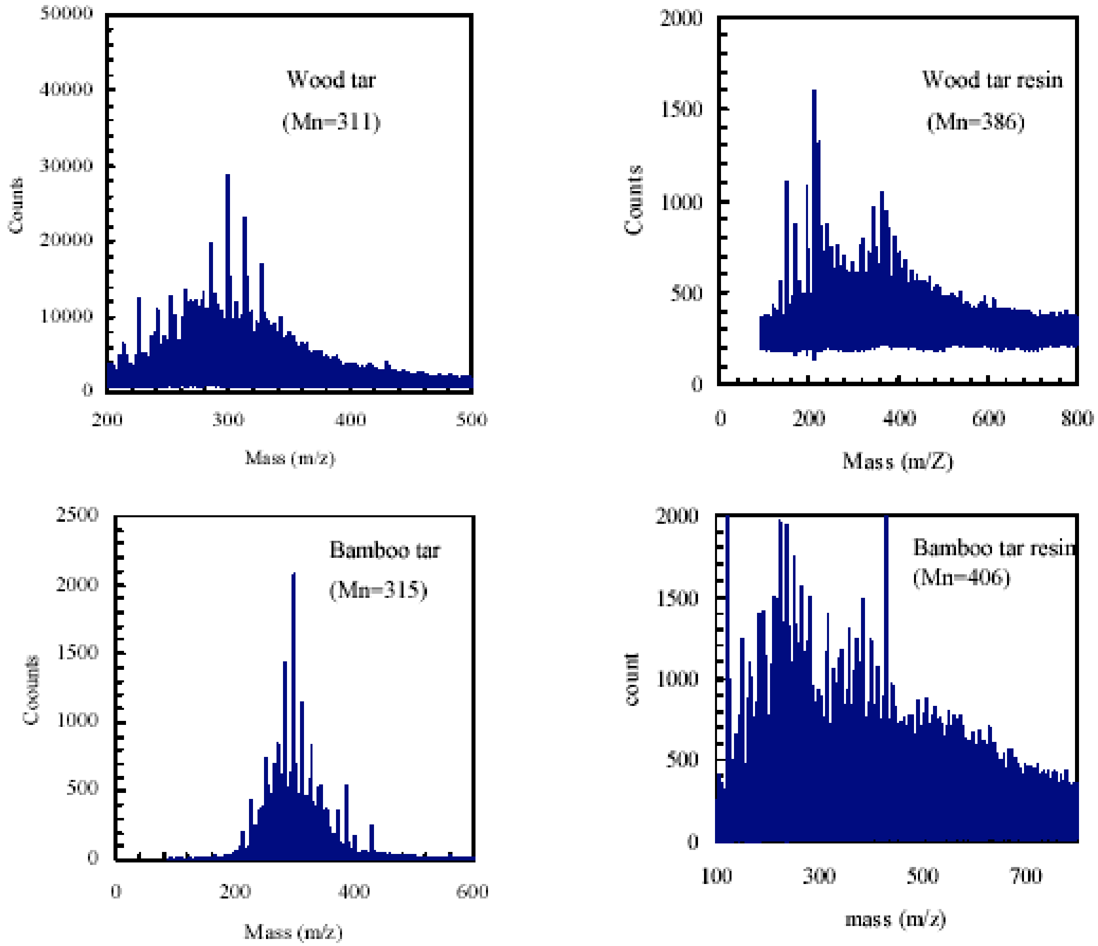
Biomass tar shows low aromatic fraction

FT-IR spectra of wood and bamboo tars



Bamboo tar contains more oxygen groups, namely phenol-group fraction.

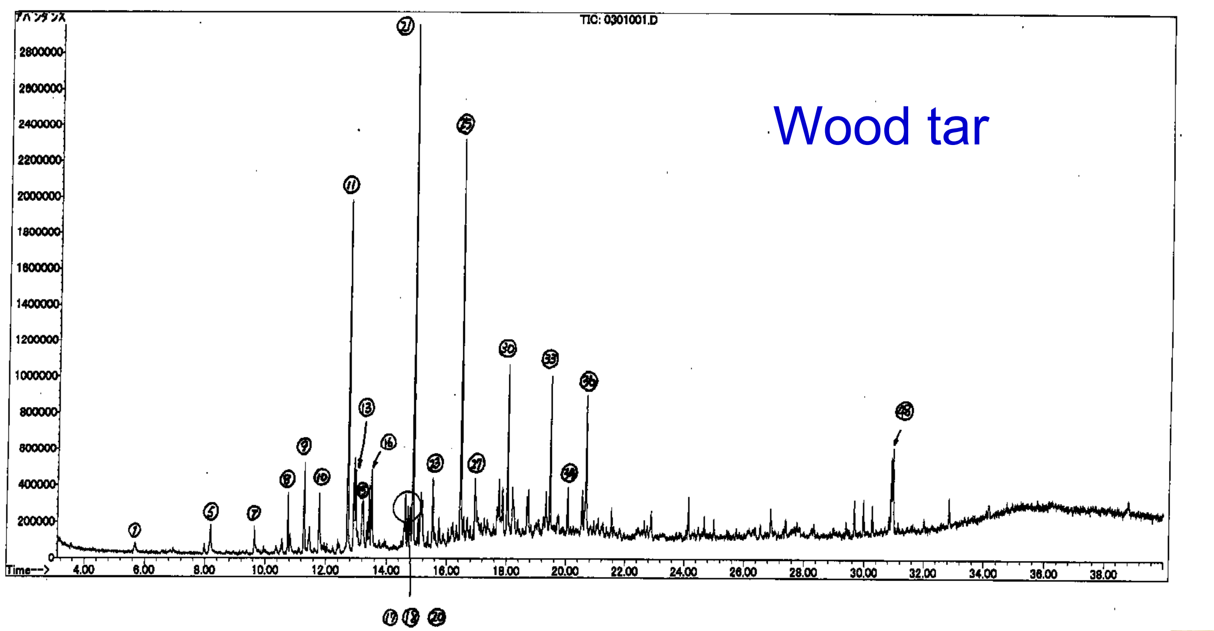
Molecular weight distribution of tars and their resins

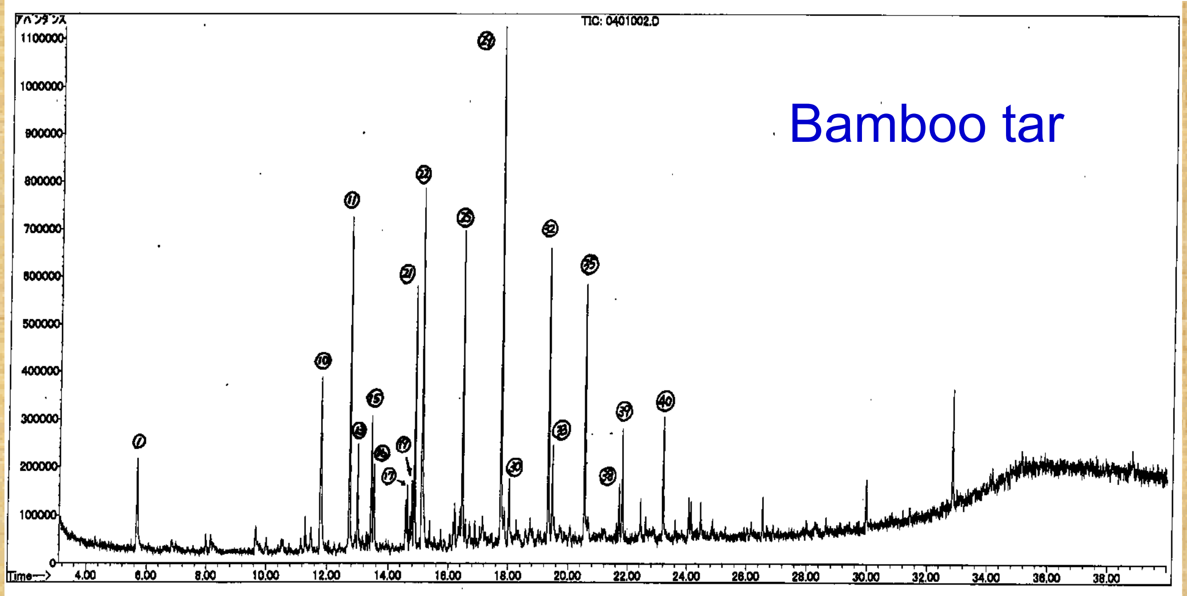


Modification of biomass tar improves its molecular weight

Phenol-containing components are polymerized in biomass tar

GC-MS spectra





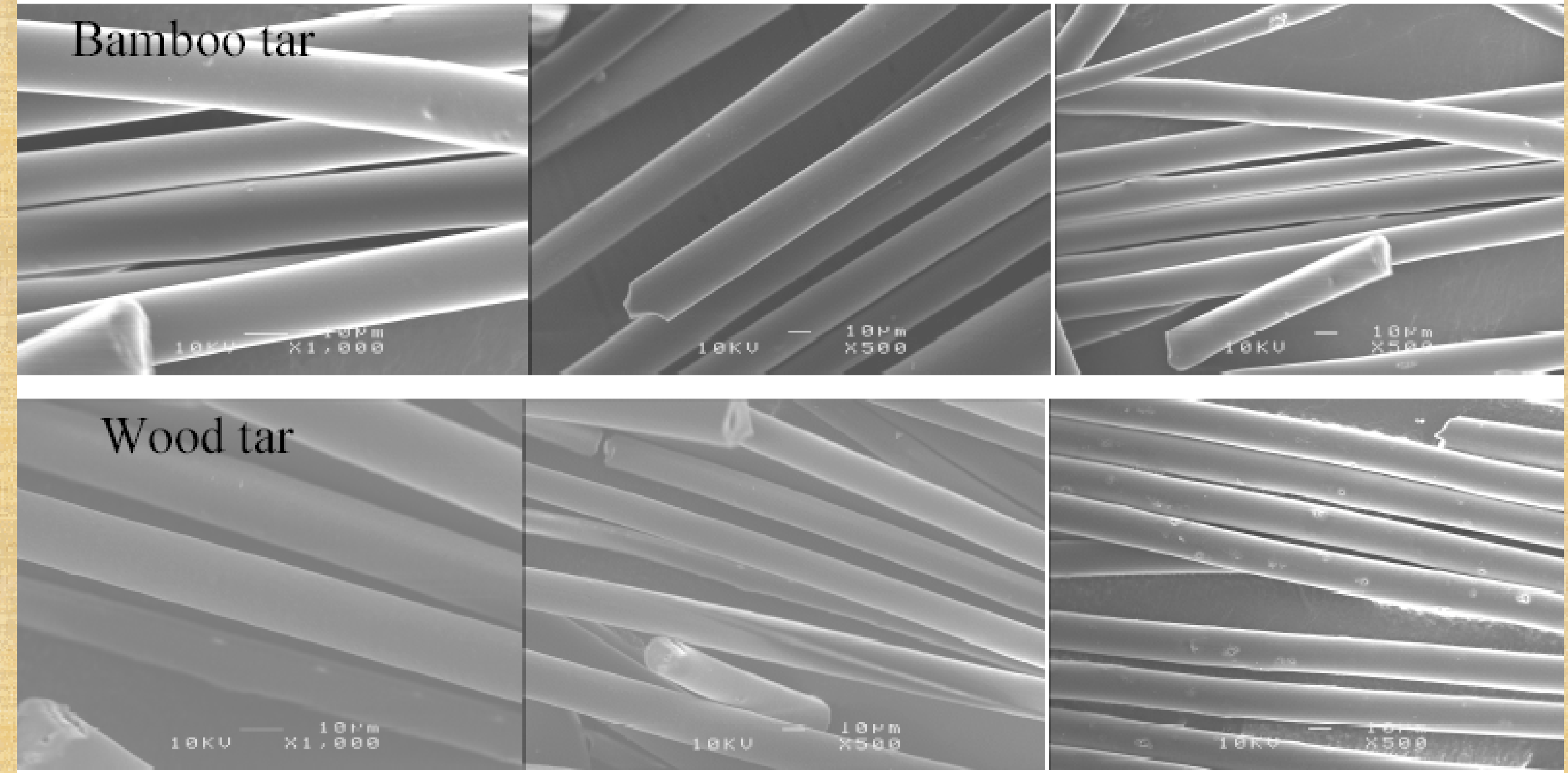
Retention time (min)

Compound formulas in wood and bamboo tars

No	RT min	Compound	MW	Formula	GC peak area, % Wood tar	GC peak area, % Bamboo tar
1	5.68	2-furancarboxalfehyde	96	$C_5H_4O_2$		2.697
2	6.80	2-furanmethanol	98	$C_5H_6O_2$		
3	7.96	2-methyl-2-cyclopenten-1-one	96	C_6H_8O		
4	8.13	1-(2-franyl)-ethanone	110	$C_6H_6O_2$		
5	8.18	Butyrolactone	86	$C_4H_6O_2$	0.822	
6	8.77	3-methyl cyclopentanone	98	$C_6H_{10}O$		
7	9.64	5-methyl-2-furancarboxalfehyde	110	$C_6H_6O_2$	0.461	
8	10.74	Tetrahydro-2-furanmethanol	102	$C_5H_{10}O_2$	1.260	
9	11.29	3-methyl-1,2-cyclopentanedione	112	$C_6H_8O_2$	2.358	
10	11.77	Phenol	94	C_6H_6O	1.195	5.420
11	12.72	Methoxy phenol	124	$C_7H_8O_2$	8.315	7.080
12	12.93	No known				
13	12.99	Methyl phenol	108	C_7H_8O	2.106	2.403
14	13.20	Maltol	126	$C_6H_8O_6$		
15	13.43	Methyl phenol	108	C_7H_8O	1.355	2.926
16	13.52	Methyl phenol	108	C_7H_8O	2.544	2.417
17	14.63	Dimethyl phenol	122	$C_8H_{10}O$	1.185	
18	14.70	Dimethyl phenol	122	$C_8H_{10}O$	0.870	
19	14.77	Naphthalene	128	$C_{10}H_8$		
20	14.78	2-methoxy-4-methyl phenol	138	$C_8H_{10}O_2$	1.081	
21	14.86	2-methoxy-4-methyl phenol	138	$C_8H_{10}O_2$	11.606	5.407
22	15.09	2-ethyl phenol	122	$C_8H_{10}O$		9.025
23	15.52	Dimethyl phenol	122	$C_8H_{10}O$	1.869	
24	15.53	1,4:3,6-dianhydro-α-d-glucopyranose	144			
25	16.47	4-ethyl-4-methoxy phenol	152	$C_9H_{12}O_2$	0.768	7.222

26	16.89	Benzenediol	110	$C_6H_6O_2$		
27	16.95	Benzenediol	110	$C_6H_6O_2$	2.747	
28	17.66	Methyl-1,2-benzenediol	124	$C_7H_8O_2$		
29	17.75	2,6-dimethoxy phenol	154	$C_8H_{10}O_3$		11.339
30	18.03	2-methoxy-4-propyl phenol	166	$C_{10}H_{14}O_2$	4.210	1.993
31	18.19	Methyl-1,2-benzenediol	124	$C_7H_8O_2$		
32	19.36	4-hydroxy-3-methoxy benzoic acid	168	$C_8H_8O_4$		6.491
33	19.46	2-methoxy-4-(1-propenyl)-phenol	164	$C_{10}H_{12}O_2$	3.846	
34	20.06	1-(4-hydroxy-4-methoxyphenyl)-ethanone	166	$C_9H_{10}O_3$	1.328	
35	20.54	1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone	182	$C_9H_{10}O_4$		5.508
36	20.67	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	180	$C_{10}H_{12}O_3$	4.572	
37	21.54	2,4-dihydroxy-3-methyl propiophenone	180	$C_{10}H_{12}O_3$		
38	21.71	2,6-dimethoxy-4-(2-propeny)-phenol	194	$C_{11}H_{14}O_3$		1.200
39	21.81	No known				2.745
40	23.20	2,6-dimethoxy-4-(2-propeny)-phenol	194	$C_{11}H_{14}O_3$		2.672
41	24.14	No known				
42	24.69	No known				
43	25.01	No known				
44	26.90	(5α,9α,10β)-kaur-15-ene	272	$C_{20}H_{32}$		
45	29.67	2-(1,1-dimethylethyl)-anthrancene	234	$C_{18}H_{18}$		
46	30.27	No known				
47	30.90		286	$C_{20}H_{30}O$		
48	30.96		314	$C_{21}H_{30}O_2$	2.404	
Other peak area, %					43.10	23.45
Peak area of phenol-containing group, %					49.60	71.10

Morphology of spun, cured and carbonized fibers from derived from bamboo and wood tar resins



Spun fibers | Cured fibers | Carbonized fibers

Carbon fibers with smooth surface, diameter: 15~20 μm

Properties of carbon fibers derived from tar resins

Fiber	Curing conditions	Curing yield*	Carbonization conditions	Carbonization yield**	d_{002}	R
	^oC-h-^oC/h	%	^oC-h-^oC/min	%	nm	(I_{1350}/I_{1580})
Bamboo tar resin	200-1-10	90	650-1-1	47	0.417	0.722
	200-1-10	90	1000-1-1	49	0.388	0.914
	200-1-20	87	1000-1-1	47	0.385	0.967
Wood tar resin	200-1-10	87	1000-1-1	40	0.386	1.097
	200-1-10	87	1000-1-2	40	0.385	1.093

Yield base:*resin; **cured resin

Mechanical properties of carbon fibers derived from bamboo and wood tar resins

Precursor	Carbonization	Diameter of fiber	Tensile modulus	Tensile strength
	^{o}C	μm	GPa	MPa
Bamboo tar resin	650	19.3	27	342
	800	17.0	44	632
	1000	13.4	43	616
Wood tar resin	1000	20.9	37	247
Phenol resin*	800	11-12	20-30	500-700
	2000	11-12	15-20	300-400

*Kynol carbon fiber derived from phenol resin

Conclusions

1. Biomass tar contains a lot of phenol-group compounds. The components can be polymerized into a thermol-setting resin, which is confirmed a useful precursor to develop high performance carbon materials.
2. Carbon fibers (10~20 μm in diameter) have been successfully prepared through spinning, curing and carbonization from biomass tar resins. Their properties (tensile strength of 250~630 MPa and tensile modulus of 27~44 GPa) are comparable to those of commercial isotropic carbon fibers.
3. Activated carbon fibers can be derived.