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Analysis of organic compounds in coal gasification wastewater

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Abstract— A procedure for analysis of organic pollutants in coal gasification wastewater was developed, including a series extraction steps at different pH, followed by LC separation or resin adsorption, then analyzed by GC or GC/MS. More than 200 organic pollutants in 22 categories were determined. CH_2CL_2 extraction at $NaHCO_3$ presence was used to separate carboxylic acids with phenolic compounds in aqueous. Derivatization with acetic anhydride was used for analyses of mono-, di-, poly-hydroxyl phenolic compounds. 21 mono-hydroxyl phenols and 13 di-hydroxyl phenols were determined from the coal gasification wastewater samples. Derivatization with BF_3-CH_3OH was used for analysis of carboxylic acid, 17 mono-carboxyl, 4 di-carboxyl acids and 6 aromatic acids were determined from coal gasification wastewater samples.

Keywords: wastewater analysis; coal gasification pollutants; chromatography.

INTRODUCTION

The coal gasification wastewater contains complex pollutants, and the concentrations of different compounds are quite different, so sometimes it is difficult to get the qualitative and quantitative analytical results. A very important thing for wastewater analysis is to establish a good pretreatment procedure to collect the pollutants from aqueous before instrumental analysis. Liquid-liquid extraction, and resin adsorption are the most popular methods used for collecting organic compounds from aqueous. These methods are quite useful for collecting organic compounds in low polluted water or for collecting some individual compounds. But for high polluted wastewater with complex organic compounds and big variance in concentrations, a single stage of extraction or adsorption is not enough for fully collecting the total categories of compounds.

The method described in this article, which is used for analysis of complex organic pollutants in wastewater, includes a series extraction steps at different pH conditions to divide the pollutants into different categories, then followed by LC separation or resin adsorption to divide the extracted compounds into small groups, and finally by instrumental analysis in different conditions to get qualitative and quantitative results. Derivatization with different reagents was used for analysis of some special categories of compounds.

EXPERIMENTAL

Instruments and reagents

GC-9A Gas Chromatograph with FID, FPD detectors, and fused silica capillary column SE-52 50m × 0.2mm (i.d.) and DB-5 25m × 0.31 mm (i.d.) were used.

D-300 GC-MS Spectrometer was used in EI at 70 eV. The column used in GC/MS analysis

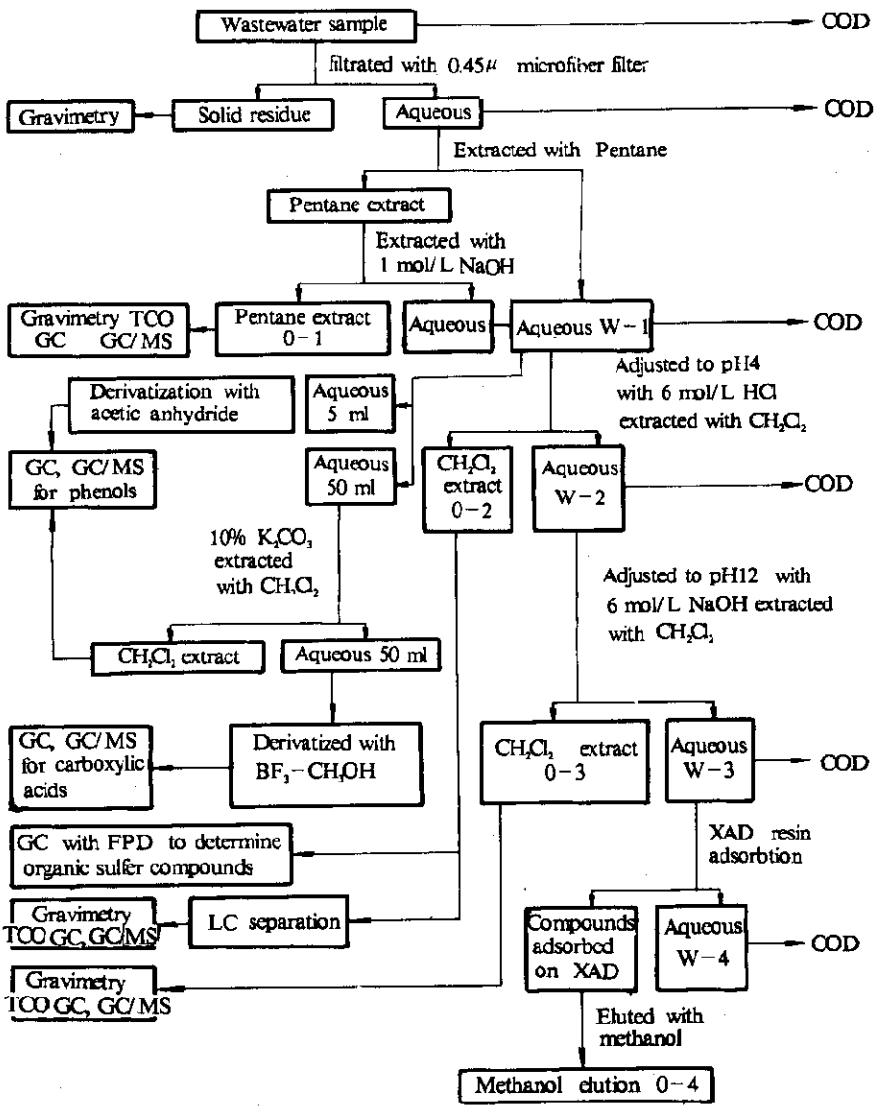

Fig. 1 The scheme of analysis of wastewater sample

was the same as those used in GC analysis.

Model HH-1 COD analyzer was used for COD determination.

The reagents: methylene chloride, ether, pentane were redistilled. XAD-7 resin was refluxed with pentane, methylene chloride and methanol sequentially for 6 hours before used for adsorption of organic compounds in water.

Procedure of analysis of wastewater sample

The procedure of analysis of wastewater sample is shown in Fig. 1. The conditions of pretreatment of sample are all explained in this scheme.

Derivatization was used for analyses of phenol, di-and poly-hydroxyl phenolic compounds. 5 ml of wastewater sample, 2 ml of 10% K_2CO_3 aqueous solution and 0.2 to 0.5 ml of acetic anhydride were added into a 10 ml of centrifuge tube. After 20 minutes of reaction at room temperature, followed by extraction with 5 ml of ether, then the aqueous phase and organic phase were separated by centrifugation. The organic phase was subjected to GC for GC/MS analysis.

Derivatization for carboxyl acids was carried out after the extraction of wastewater sample with CH_2Cl_2 in present of $NaHCO_3$, which was used for separation of carboxylic acids from phenolic compounds. In the extraction stage, the carboxylic acids remained in aqueous phase, meanwhile the phenolic compounds entered the organic phase. After the quantity of phenolic compounds were removed, the aqueous phase was evaporated gently to dry. The residue then was derivatized with BF_3-CH_3OH in flux for 20 minutes. The 10% NaCl aqueous solution was added and ether was used for extraction twice. The ether phase was dried with sodium sulfate anhydride and concentrated on 1.0 ml, then the concentrated ether phase was subjected to GC and GC/MS analyses.

RESULTS AND DISCUSSIONS

The efficiency of collecting organic compounds from water by series extraction and resin adsorption

The recovery extent of organic compounds in coal gasification wastewater by the series extraction and resin adsorption was measured by COD value in aqueous phase after treatment step for each. The pretreatment procedure of the wastewater sample before instrumental analysis can be expressed briefly as following scheme.

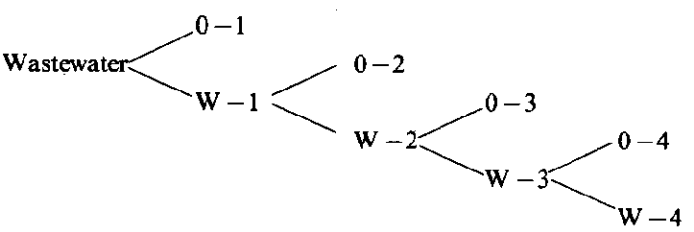

Table 1 The distributions of COD values of wastewater in extraction procedures

Item	Original wastewater	0－1	W－1	0－2	W－2	0－3	W－3	0－4	W－4
COD values, mg/L	18125		15645		4476		2126		623
Percentage in total COD of wastewater, %		13.7	86.3	61.6	24.7	12.3	12.4	8.97	3.43

Table 2 The categories of organic compounds found in coal gasification wastewater and their contributions to COD

No.	Percentage of COD, %	Conc. in wastewater, mg/L	TCO, mg/L	Compound categories and numbers	
				Category	Number
0－1	13.7		171.5	Aliphatic hydrocarbons	24
				Aldehydes, Ketones	20
				Ethers, Esters	5
				Furance	3
0－2	61.6	11000	10230	Phenols	44
				Mono-hydroxy phenols	31
				Di-hydroxy phenols	13
				Arometic hydrocarbons	14
				Alcohols	19
				Aldehydes	2
				Organic sulfer compounds	7
0－3	12.3	90.0		Amines	3
				Other organic nitrogen compounds	31
				Phenols	7
				Organic oxygen, nitrogen Containing compounds	5
Total extractable compounds		11348			

The COD values in each W phase and their contribution in percentage of total wastewater are showing in Table 1. It was observed the COD values in aqueous phase decreased step by step. Finally, only 3.43% of total COD value of the wastewater was left in aqueous phase, that means more than 96% of organic compounds was collected by this treatment procedure.

The quantitative analysis of pollutants in wastewater

The organic pollutants in coal gasification wastewater were selected as categories into different organic phases. Table 2 shows the categories of organic compounds and their distributions in each extract. Most of the aliphatic hydrocarbons are in the pentane extract, the phenolic compounds are in the CH_2Cl_2 extract which was got under pH 4 condition. The most of nitrogen organic compounds are in the CH_2Cl_2 extract which was got in pH 12.

Because the content of phenolic compounds is much higher than any of the other categories of compounds in coal gasification wastewater, and it interferes the determination of other compounds, so the further separation was carried out before GC analysis. Column separation with sillica gel for 0−2 extract was performed. The gravimetry results of column separation for 0−2 are shown in Table 3. The elution solvent used in this column separation is also listed in Table 3. The results mean that the most of phenolic compounds were separated with other compounds after the column elution. So some compounds in 0−2 which could not be determined when the phase was analyzed by GC directly, but can be determined distinctly after the column separation. The numbers of determined compounds after 0−2 column separation are much more than those without column separation.

Table 3 The LC separation for organic extracts of coal gasification wastewater

LC fraction	Elution solvent	Collected volume of elution, ml	Collected weight, mg	Percentage in total, %
LC-1	100% n-Hexane	25	0.002	0.009
LC-2	80% Hexane+20% CH_2Cl_2	10	0.003	0.036
LC-3	50% Hexane+50% CH_2Cl_2	10	1.963	8.910
LC-4	100% CH_2Cl_2	25	9.890	44.910
LC-5	95% CH_2Cl_2+5% CH_3OH	10	1.900	8.630
LC-6	80% CH_2Cl_2+20% CH_3OH	10	6.084	27.630
LC-7	50% CH_2Cl_2+50% CH_3OH	10	1.938	8.800
LC-8	100% CH_3OH	10	0.064	0.290
LC-9	100% CH_3OH	10	0.002	0.009
Sum			21.850	99.220
Total sample recovery			22.022	99.220

The derivatization analysis of phenolic compounds

The phenolics are polar compounds which can soluble in water. The more hydoxyl groups are in the molecule of the compound, the higher polarity the compound has. Usually, the GC analysis can only determine the mono-hydroxyl phenolics. The di-and poly-hydroxyl phenolic compounds can not be determined by GC analysis directly, even can not be extracted from aqueous because of their high polar property. Derivatization of phenolic compounds with acetic anhydride gave the good results for mono-, di- and poly- hydroxyl phenolic compounds. The analysis procedure for phenolic compounds (Fig. 2, 3 and 4) shows the chromatograms of phenolic compounds, which were collected by CH_2Cl_2 extraction directly and derivatization followed by the ether extraction respectively. Comparing the two chromatograms, which were got from a same sample, it can be seen that the peaks in Fig. 4 are more abrupt than those in Fig. 3. The group of peaks having retention time longer than 34 minutes in Fig. 4, which did not appear in Fig. 3, were identified by GC/MS, mostly as acetate derivatives of dihydroxyl phenols, methyl, dimethyl, and trimethyl-dihydroxyl phenols as well as the other substituted dihydroxyphenols. Table 4 lists the analytical results of phenolic compounds in coal gasification wastewater by the methods of CH_2Cl_2 extraction and derivatization. Only 15 phenolic compounds have been determined by CH_2Cl_2 extraction method, those are all mono-hydroxyl phenols, but, 43 phenolic compounds have been determined by derivatization method. 16 di-hydroxyl phenols were found by derivatization treatment, which could not be determined by CH_2Cl_2 extraction method. The data in Table 5 show that the quantitative results of mono-hydroxyl phenols are almost the same by direct extraction and derivatization. The deviation of the two methods is only 1.9%. But for the di-hydroxyl phenol, the results are very different, they can be determined only by derivatization method.

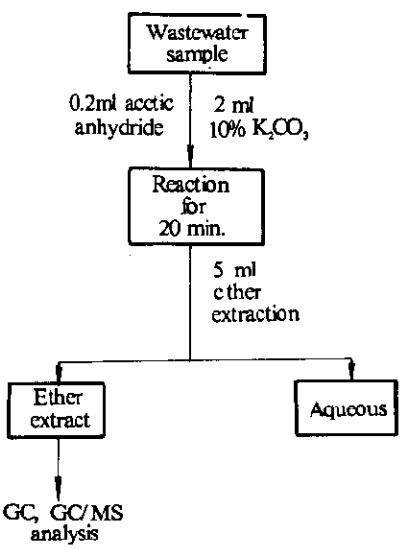

Fig. 2 The derivatization procedure for polyhydroxyl-phenolic compounds in coal gasification wastewater

Analysis of carboxylic acids in wastewater containing high concentration of phenolic compounds

Carboxylic acids and phenols are high polar compounds, it is difficult to collect them from water and analyze by GC, especially when there are very high concentration of phenolic compounds presented. The suitable pretreatment procedure is very important for analyses of carboxyl acids. The difference in acidity between carboxylic acids and phenolic compounds is used to separate the two catagories of compounds. Only phenols can enter the CH_2Cl_2 extract when the extraction was carried out at presence of sodium bicarbonate

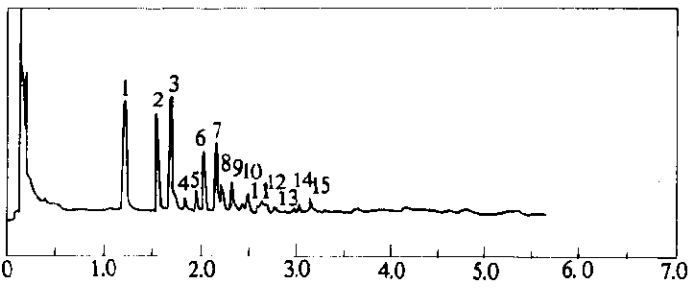

Fig. 3 The chromatogram of CH_2Cl_2 extract of coal gasification wastewater at pH 4

Table 4 The analytical results for phenolic compounds in coal gasification wastewater by direct extraction and derivatization method followed by GC and GC/MS analysis

CH_2Cl_2 extraction at pH 4		Derivatization with acetic anhydride, ether extraction			
No.	Compounds	No.	Compounds	No.	Compounds
1	Phenol	1	Phenol	18	3, 4, 5-Trimethyl phenol
2	o-methyl cresol	2	o-methyl phenol	19	o-dihydroxyl phenol
3	m-and p- cresol	3	m-methyl phenol	20	m-, p-dihydroxyl phenol
4	2, 6-dimethyl phenol	4	p-methyl phenol	21	Methyl dihydroxyl phenol
5	2, 4-, 2.5-dimethyl phenol	5	Othyl phenol	22	Tert methyl phenol
6	3, 5-methyl phenol	6	2, 6-dimethyl phenol	23	Butyl phenol
7	2, 3-methyl phenol	7	2, 5-dimethyl phenol	24	Methyl dihydroxyl phenol
8	3, 4- methyl phenol	8	2, 4-dimethyl phenol	25	Methyl dihydroxyl phenol
9	3-ethyl-5-methyl phenol	9	3, 5-dimethyl phenol	26	Methyl dihydroxyl phenol
10	2, 4, 6- trimethyl phenol	10	2, 3-dimethyl phenol	27	Dimethyl dihydroxyl phenol
11	2, 3, 5-trimethyl phenol	11	3, 4-dimethyl phenol	28	Ethyl dihydroxyl phenol
12	2, 3, 4-trimethyl phenol	12	Vinyl-phenol	29	Methyl, ethyl, dihydroxyl-
13	3, 4, 5-trimethyl phenol	13	Propyl phenol	30	Methyl, ethyl phenol
14	Tertmethyl phenol	14	2, 4, 6-trimethyl phenol	31	Dimethyl dihydroxyl phenol
15	Butyl phenol	15	2, 3, 5-trimethyl phenol	32	Dimethyl dihydroxyl phenol
		16	2, 3, 4-trimethyl phenol	33	Trimethyl dihydroxyl phenol
		17	Allyl phenol	34	Propyl dihydroxyl phenol

in the aqueous phase, the caboxylic acids was remained in aqueous because of sodium acetate was formed. The phenols can be removed from aqueous by this way. Then the aqueous was adjusted to pH 2 with HCl and extracted with ether. This procedure is shown in Fig. 5. The vola-

Table 5 The quatitative analysis results of phenolic compounds in coal gasification wastewater by different analytical methods

Compounds		GC analysis derivatization, mg/L	Direct extraction, mg/L	Colorimetric analysis with 4-Aminoantipyrine, mg/L
Mono-phenols	Phenol	1590	1412	Volative phenols
	O-cresol	265	264	
	m, p-cresol	1193	1179	
	Dimethylphenol	392	667	
	Trimethylphenol	140	201	
	Other phenols	14	38	
	Sum	3594	3661	4378
Dihydroxyl phenols	O-dihydroxylphenol	1125	can not be determined	Nonvolative phenols
	m, p-dihydroxyl-phenol	492		
	Methyl-dihydroxyl phenols	1543		
	Dimethyl dihydroxyl phenols	379		
	Trimethyl dihydroxyl phenols	118		
	Other dihydroxyl phenols	172		
	Sum	3829		1921

tile carboxylic acids can be analyzed by GC with fused sillica capillary column. Fig. 6 shows the chromatograms of carboxylic acids, which was extracted from coal gasification wastewater. For analysis of unvolatile organic acids by GC, such as di-and poly-carboxylic acids and aromatic acids, derivatization is necessary before instrumental analysis. Fig. 7 shows the chromatograms of the methyl ester derivatives of carboxylic acids, which were collected from the same wastewater sample that was analyzed by ether extraction directly. Comparing these two chromatograms, the

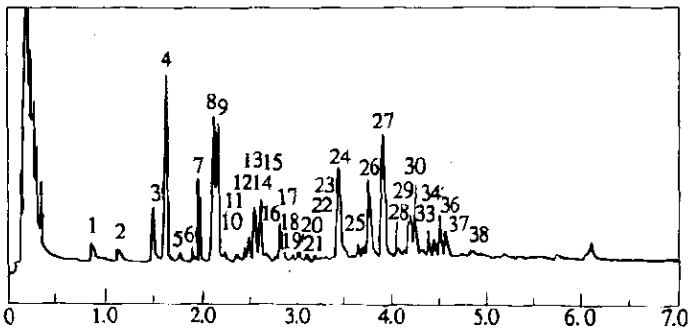

Fig. 4 The chromatogram of ether extract of coal gasification wastewater after derivatization with acetic anhydride

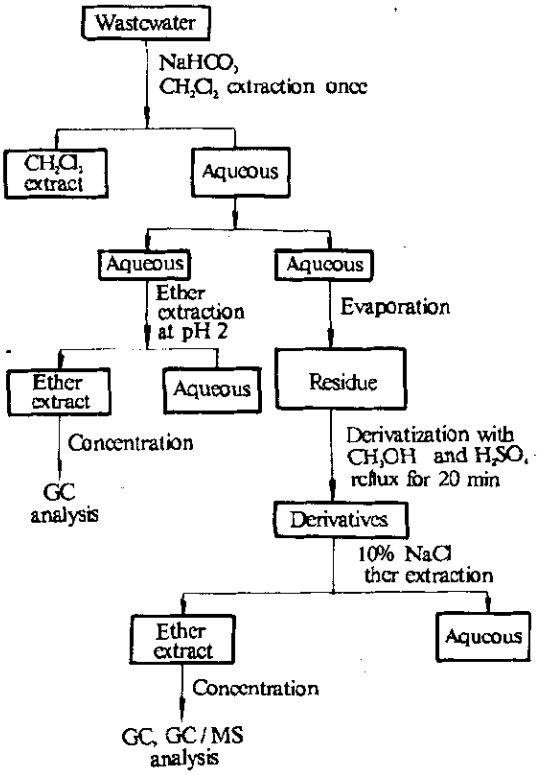

Fig. 5 The scheme for analysis of carboxylic compounds in the wastewater containing high concentration of phenolic compounds

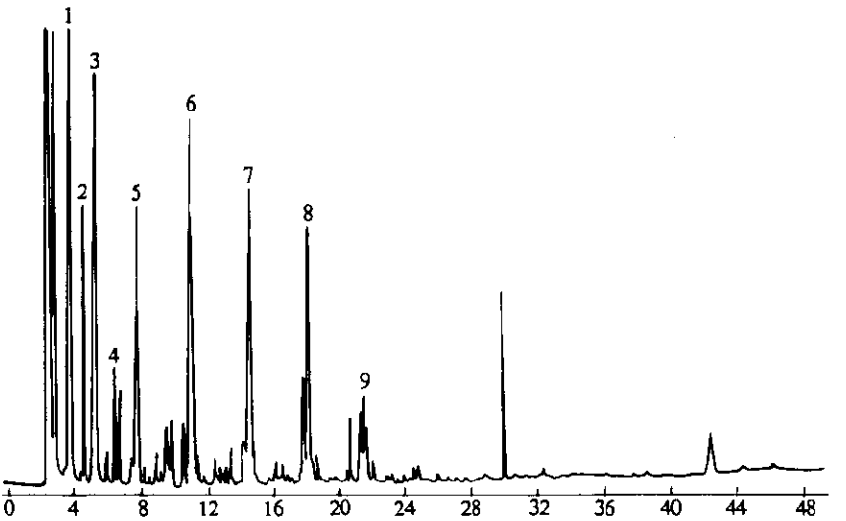

Fig. 6 The chromatogram of carboxyl compounds in coal gasification wastewater analysis by ether extraction directly
Analytical condition: DB-5 fused silico capillary column 25m × 0.31mm (i.d.), temperature programed 65 −230℃ (4℃ / min)

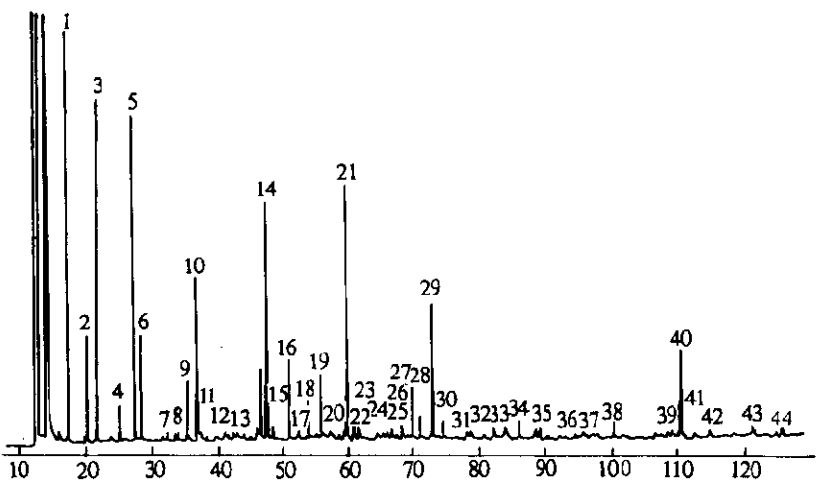

Fig. 7 The chromatogram of derivatives of carboxyl compounds in coal gasification wastewater
The analytical condition is the same as in Fig. 6

peaks in Fig. 7 are very sharp and separated well, and many small peaks appeared clearly. These peaks were identified by GC/MS. Many dicarboxylic acids and other unvolatile acids such as oxalic acid, malonic acid, succinic acid, toluic acid, methyl-toluic acid and so on were determined very successfully by derivatization method. Table 6 lists the analytical results by these two methods and Table 7 gives the qualitative and quantitative analytical results of carboxylic acids in coal gasification wastewater.

Table 6 Carboxylic acids in coal gasification wastewater determined by ether extraction and derivatization method

Ether extraction		Derivatization method			
No.	Compounds	No.	Compounds	No.	Compounds
1	Propanoic acid	1	Methyl propionate	23	4,7-diene-nonanoate
2	Iso-butanoic acid	2	Methyl iso-butanoate	24	1,5-diene-methyl nonanoate
3	n-butanoic acid	3	Methyl butanoate	25	Methyl 3-oxo-octanoate
4	Iso-petanoic acid	4	Methyl isopentanoate	26	Methyl 0-toluate
5	n-petanoic acid	5	Methyl pentanoate	27	Methyl m-toluate
6	n-hexanoic acid	6	Dimethyl oxalate	28	Methyl p-toluate
7	n-heptanoic acid	7	2-Methyl thiocyclobutane	29	Methyl n-nonanoate
8	n-octanoic acid	8	Methyl isohexanoate	30	Methyl 2,6-dimethyl octanoate
9	n-nonanoic acid	9	Dimethyl malonate	31	Methyl 3-ethyl-4-ene-octanoate
		10	Methyl caproate	32	Methyl 2-formyl benzoate
		11	Dimethyl succinate	33	Methyl 4-formyl benzoate
		12	Methyl 4-methyl valerianate	34	Methyl iso-decanoate
		13	Methyl 4-ethyl valerianate	35	Methyl n-decanoate
		14	Methyl heptanoate	36	Methyl-alpha-cyanocinamate
		15	Methyl 5-ketohexanoate	37	Methyl 2,4,5-trimethyl benzoate
		16	Dimethyl 2-methyl succinate	38	Methyl n-undecoate
		17	Methyl iso-caprylate	39	Methyl hippurate
		18	Methyl benzoate	40	Carnegine
		19	8-ene-decanol-1	41	Methyl dodecanoate
		20	Methyl 5-ene-caprylate	42	4-hydroxyl, 3-methoxyl benzoate
		21	Methyl caprylate	43	-hydroxyl dimethyl octanoate
		22	4-ethylamine methyl pentanoate	44	Methyl 3-hydroxyl benzoate

Table 7 Comparison of the analytical results of carboxylic acids in coal gasification wastewater by ether extraction and derivatization method

Ether extraction directly			Derivatization with CH_3OH		
	Compounds	Conc., mg/L		Compounds	Conc., mg/L
Mono-carboxyl acids	Propanoic acid	45.37	Mono-carboxyl acids	Propanoic acid	126.60
	Iso-butanoic	9.46		Iso-butanoic	12.80
	n-butanoic	26.37		n-butanoic	47.10
	Iso-pentanoic	2.05		Iso-pentanoic	4.10
	n-pentanoic	14.70		n-pentanoic	41.60
	n-hexanoic	16.84		Iso-hexanoic	1.70
	n-heptanoic	16.87		n-heptanoic	30.30
	n-octanoic	9.15		Iso-octanoic	1.70
	n-nonanoic	2.04		n-octanoic	33.70
				n-nonanoic	17.60
				Iso-decanoic	2.70
				n-decanoic	1.80
				n-undecanoic	2.20
				n-dodecanoic	0.50
				Other mono-carboxylic	9.63
	Sum	142.88		Sum	349.03
			Di-carboxyl acids	Oxalic acid	11.30
				Malonic acid	6.50
				2-methyl-succinic acid	9.90
			Aromatic acids	Benzoic acid	4.8
				o-methyl-benzoic acid	2.2
				m-methyl-benzoic acid	7.0
				p-methyl-benzoic acid	2.6
				Methyl-2-formyl benzoic acid	1.3
				Methyl-4-formyl benzoic acid	1.7
	Total	142.88		Total	395.83

CONCLUSSION

The procedure introduced in this paper can be used for analysis of wastewater which has complex organic pollutants with high concentration. This method has been used for analysis of all organic pollutants in coal gasification wastewater. Nearly 200 organic compounds were determined and identified.

Acetate derivatization method for various phenolic compounds analysed by GC is successful both in qualitative and quantitative.

By using CH_2Cl_2 extraction in presence of sodium bicarbonate, the carboxylic acids can be separated well with phenols. The method of methyl ester derivatization of carboxylic acids gave better results in GC analysis.

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