

# Determination and Characterization of the Pyrolysis Products of Isoprocarb by GC–MS

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## Abstract

The pyrolysis behavior of isoprocarb (an insecticide with contact and stomach action) is investigated using pyrolysis-gas chromatography–mass spectrometry. The pyrolysis products are separated using an HP-5 column under temperature program with helium as the carrier gas. The total of 80 separated pyrolysis components at 600°C, 750°C, and 900°C under helium atmosphere are identified using a probability-based matching search procedure, combined with the correlation of boiling point (BP) and Lee retention index (RI). Some of the BP values of the tentative components are estimated using the group contributions method because experimental values are not available. The levels of the identified components are estimated by the peak area normalization method from the chromatogram. It is found that isoprocarb decomposes more with the increase of temperature, and a large number of mono aromatics and polycyclic aromatic hydrocarbons and their derivatives are produced when the pyrolysis temperature is higher than 750°C. The content of the decomposition products in the pyrolysate varies from 0.04% to 22.20%.

## Introduction

Isoprocarb is a carbamate pesticide with contact and stomach action. It has a rapid effect against pests and low toxicity to humans. Carbamate pesticides are now widely used throughout the world, and their use increased after the ban or restriction on various chlorinated hydrocarbon insecticides was lifted (1). Because of the massive use of carbamate pesticide, contamination by these pesticides has been extensively reported and has become an environmental concern (2–4). The residues of carbamate pesticides may persist in soil (5,6), atmosphere (7,8), water (9,10), fruits or vegetables (11,12), and plants or cereal crops (13,14).

Generally, carbamate pesticides are very polar and thermally unstable. Therefore, it is necessary to understand the changes in toxicity or biological activity of these compounds when they undergo thermal decomposition for the evaluation of their poten-

tial influence on roasted contaminated foods or on smoke generated by the smoldering of the tobaccos with these pesticide residues, etc. However, reports on the pyrolysis behavior of carbamate pesticides are few.

The identification of compounds in gas chromatography (GC)–mass spectrometry (MS) analysis is common by matching the measured mass spectrum against a reference spectrum (15–17). However, the pyrolysis products of an organic compound or chemicals are usually a complex mixture, which may include different homologous series (18–20), and this makes the identification of the pyrolysis components a difficult task. In the matching procedure, the hit list at one peak may consist of several tentative components. It is often difficult to determine which component should be selected only by the matching factors because the component with the higher matching factor may be unreasonable. For identification of unknown complex mixtures, additional effective criterion is frequently needed. It is known that the boiling point (BP) of a compound is highly correlated with its retention time or Lee retention index (RI) (21,22). The BP of a component should be located in the range of  $RI - 10$  to approximately  $RI + 50$  (°C) (22). Therefore, the correlation of BP and RI can provide very useful information for the identification of the components in the hit list. When the experimental BP of a compound in the hit list is unavailable, it can be estimated from group contributions (23,24).

In this study, isoprocarb was pyrolyzed under helium atmosphere at 600°C, 750°C, and 900°C for investigation of its pyrolysis behavior. The pyrolysis products were separated on a nonpolar column under temperature program with helium as the carrier gas. The separated pyrolysis components are identified using a probability-based matching (PBM) search in combination with the correlation of BP and RI. The contents of the determined components (80 in total) were estimated using the peak area normalization method.

## Experimental

### Reagents

Isoprocarb (97.6%) was purchased from ICAMA (Institute for

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Control of Agrochemicals, Ministry of Agriculture, Beijing, China). Toluene (98%), ethylbenzene (98%), 2-methyl-phenol (98%), fluorene (98%), phenanthrene (99%), and anthracene (99%) were purchased from Shanghai Chemical Reagent Corporation (China Medicine Group, Shanghai, China).

### Pyrolysis–GC–MS experiments

Isoproc carb was dissolved in methanol with ultrasonic assistance and prepared as a 36.2-mg/mL stock solution. An SGE micro-furnace pyrolyzer (SGE International Pty. Ltd., Victoria, Australia) was used for pyrolyzing the isoproc carb. A 1- $\mu$ L stock solution was transferred to the spiral of the solid injector coupled with the pyrolyzer. After the methanol solvent was vaporized in approximately 2 min, the deposited isoproc carb was injected into the furnace and pyrolyzed. Pyrolysis at 600°C, 750°C, and 900°C was investigated, respectively. The He pressure of the control unit of the pyrolyzer was set 5 psi above that of the GC column head.

The pyrolyzer was directly interfaced to an Agilent 6890 GC system (Agilent Technology, Palo Alto, CA) equipped with an Agilent 5973N mass selective detector (MSD) working in electron impact mode. The pyrolysis products were separated using an HP-5 capillary column (30-m  $\times$  0.30-mm i.d., 0.25- $\mu$ m film thickness, 5% phenyl–methylpolysiloxane) with helium as the carrier gas (a flow rate of 2.0 mL/min, constant flow mode.) The split ratio was 1:2. The temperature of the GC inlet and the MSD were both 250°C. The GC oven was set to 50°C for the first 5 min, then heated with a rate of 5°C/min up to 200°C, and held for 15 min. The electron impact ionization was tuned at 70 eV. The mass detection range was 12–450 amu. Figure 1 shows the total ion current chromatogram (TIC) of the pyrolysis products at different pyrolysis temperatures.

With the reference sample, it was found that the retention times of toluene, ethylbenzene, 2-methyl-phenol, naphthalene, isoproc carb, fluorene, and anthracene are 2.470, 4.174, 10.786, 14.604, 15.403, 25.041, and 29.476 min, respectively, under these GC–MS conditions. These retention times are used for the validation of the identification results or calculation of the RIs (or both).

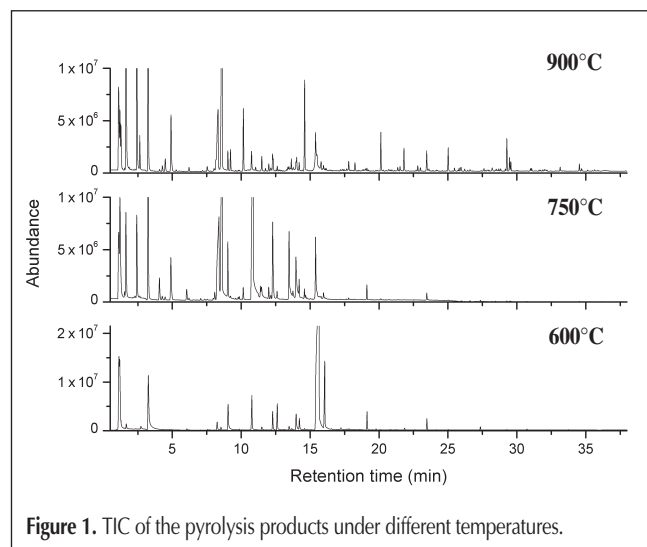


Figure 1. TIC of the pyrolysis products under different temperatures.

### Identification and quantitation of the pyrolysis products

The PBM algorithm (17) is commonly used for identification of electron ionization mass spectra. It uses a reverse search to verify whether the peaks in the reference spectrum are present in the unknown spectrum. The search identifies those spectra from the reference library that are most similar to the spectrum of the unknown compound. Spectral similarity is measured by reverse match factor. In a number of cases, the tentative components in the matching list (hit list) may need additional confirmation. This can be done using the estimated retention times of RI in the chromatogram.

In general, an unknown compound with a particular RI will have a BP ( $T_b$ ) in the range  $RI - 10$  to  $RI + 50$  (°C) (22). It can be estimated as:

$$T_b = RI + 20 \quad \text{Eq. 1}$$

with the maximum error of  $T_b$  being  $\pm 30^\circ\text{C}$ . The RI is calculated based on the polycyclic aromatic hydrocarbons (PAH) standard compounds with the following formula:

$$RI = 100 \left( z + \frac{t_{R_x} - t_{R_z}}{t_{R_{z+1}} - t_{R_z}} \right) \quad \text{Eq. 2}$$

where  $t_{R_x}$  represents the retention time of the substance of interest,  $t_{R_z}$  and  $t_{R_{z+1}}$  represent the retention times of the standards, and  $z$  represents the number of rings in the PAH standard. In general, if the BP of a tentative component is out of the range of  $T_b \pm 30$  (°C), it should be eliminated from the hit list.

The contents of the pyrolysis components can be estimated using the peak area normalization method.

### Estimation of BP from group contributions

Group contribution methods for estimation of chemical properties have the advantage of simplicity and generality, with which a chemical property can be simply estimated from the substitute groups in the chemical structure of a compound. BP can be estimated by summing up the group increment values according to the relation:

$$T_b \text{ (K)} = 198.2 + \sum_i n_i g_i \quad \text{Eq. 3}$$

where

$$g_i = (\Delta T_b)_i \quad \text{Eq. 4}$$

represents the increment value of a group, and  $n_i$  is the number of times that the group occurs in the structure of a compound. The estimation of BP of the polar compounds and those involving hydrogen bonding were improved by increasing group sizes and considering interactions between groups. Joback and Reid (23) used a set of 41 groups for estimation of the BP of a compound. Stein and Brown (24) developed a new set of 85 groups.

In this work, the unavailable experimental BPs of the tentative components in the hit list were calculated using equation 3 with the set of groups developed by Joback and Stein et al. (23,24).

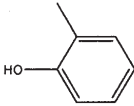
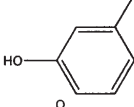
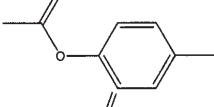
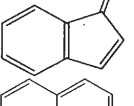
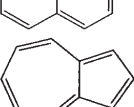
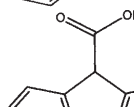
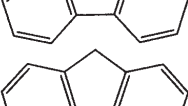
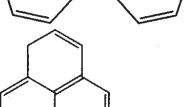
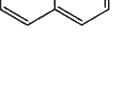
## Results and Discussion

### Identification of pyrolysate components using PBM and BP-RI correlation

Table I shows the PBM search result obtained with the National Institute of Standards and Technology (NIST) MS search program for the three peaks at 10.752, 14.604, and 25.018 min, respectively, in the TIC of the pyrolysis products at 900°C (Figure 1). Three tentative components of every peak were obtained by a library search and are given in Table I. For the components in the hit list of compound number 1, the estimated BP of acetic acid *p*-tolyl ester was out of the range of the BP-RI correlation. Thus it should be eliminated from the hit list. The reverse match factors of 2-methyl-phenol and 3-methyl-phenol were very good (the perfect match factor is 999), but the difference between the BP of 2-methyl-phenol and its  $T_b$  calculated by equation 1 is less than that of 3-methyl-phenol. Therefore, the component at 10.752 min

should be identified as 2-methyl-phenol. For the components in the hit list of compound number 2, the BP of naphthalene was closer to the  $T_b$  calculated by equation 1. Therefore, the component at 14.604 min should be identified as naphthalene. For the components in the hit list of compound number 3, the BP of 9-fluorene-carboxylic acid was out of the BP-RI range, and it should be eliminated from the hit list. The BPs of fluorene and perinaphthene were both close to the  $T_b$  calculated by equation 1. However, if the fact that the reverse match factor of fluorene is higher than that of perinaphthene and the estimated BP of perinaphthene is less than that of the experimentally measured BP of fluorene is taken into account, the component at 25.018 min should be identified as fluorene. The identification of 2-methyl-phenol, naphthalene, and fluorene was also validated by the retention times of the reference materials. It shows that, by comprehensively using the PBM search results and the correlation of BP and RI, the tentative components in the hit list of the PBM

**Table I. Demonstration of the Identification of the Pyrolysis Products**

Compound no.	$t_R^*$ /min	RI <sup>†</sup>	Compound name	Structure	R. match <sup>‡</sup>	$T_{b,exp}^{\S}$ /C	$T_{b,est}^{**}$ /C
1	10.752	170.3	2-Methyl-phenol		947	191.0	191.0
			3-Methyl-phenol		930	202.2	191.0
			Acetic acid <i>p</i> -tolyl ester		838	– <sup>††</sup>	223.4
2	14.604	200.0	1-Methylene-1H-indene		965	–	196.8
			Naphthalene		964	218.0	201.1
			Azulene		938–	–	201.1
3	25.018	271.0	9-Fluorene-carboxylic acid		935	–	364.7
			Fluorene		912	295.0	290.2
			Perinaphthene		875	–	290.2

\*  $t_R$  = retention time.  
<sup>†</sup> Lee retention index.  
<sup>‡</sup> R. match = reverse match factor.  
<sup>§</sup>  $T_{b,exp}$  = boiling point obtained from <http://chemfinder.cambridgesoft.com>.  
<sup>\*\*</sup>  $T_{b,est}$  = boiling point estimated by group contributions method (23,24).  
<sup>††</sup> Not available.

Table II. Identification and Quantitation of the Pyrolysis Products

Compound no.	$t_R^*$ / min	RI <sup>†</sup>	Compound name	CAS no. <sup>‡</sup>	$T_b^{\S}$ / °C	Content/%		
						600°C	750°C	900°C
1	1.203	96.7	Methyl isocyanate	624-83-9	39	11.83	8.58	7.00
2	1.276	97.2	Cyclopentadiene	542-92-7	42	—**	—	2.80
3	1.636	100.0	Benzene	71-43-2	80	—	5.25	14.66
4	2.427	106.1	Toluene	108-88-3	110.8	—	4.53	9.49
5	2.727	108.4	Methyl <i>N</i> -methylcarbamate	6642-30-4	103.6	0.81	—	—
6	4.078	118.3	Ethylbenzene	100-41-4	136.3	—	1.25	0.13
7	4.284	120.4	<i>p</i> -Xylene	106-42-3	141.3	—	0.25	0.37
8	4.490	122.1	Phenyl acetylene	536-74-3	123.4	—	0.20	0.85
9	4.909	125.2	Styrene	100-42-5	133	—	2.97	4.30
10	6.047	134.0	2-Phenylpropane	98-82-8	151	0.18	0.62	—
11	7.059	141.8	Propylbenzene	103-65-1	159	—	0.10	—
12	7.977	148.9	4-Ethyltoluene	622-96-8	164.2	—	0.08	—
13	8.083	149.7	1-Propynyl-benzene	673-32-5	185	—	0.42	—
14	8.177	150.4	Benzonitrile	100-47-0	191	—	—	0.69
15	8.323	151.6	Phenol	108-95-2	166.2	1.08	11.06	7.62
16	8.609	153.8	Benzofuran	271-89-6	178.8	0.30	19.38	17.45
17	10.159	165.7	4-Ethynyltoluene	766-97-2	197	—	0.58	3.35
18	10.752	170.3	2-Methyl-phenol	95-48-7	191	4.43	22.20	1.41
19	11.051	172.6	2-Methyl-benzonitrile	529-19-1	205	—	—	1.41
20	11.397	175.3	2,3-Dihydrobenzofuran	496-16-2	189	—	0.63	—
21	11.497	176.0	3-Methyl-phenol	108-39-4	202	0.64	1.76	0.45
22	11.763	178.1	4-Methyl-benzonitrile	104-85-8	218	—	—	0.23
23	12.003	180.0	2-Methyl-benzofuran	4265-25-2	206.7	—	0.62	0.42
24	12.149	181.1	3-Methyl-benzofuran	/	206.7	—	0.30	0.30
25	12.282	182.1	7-Methyl-benzofuran	1504-78-1	206.7	2.11	4.76	0.91
26	12.542	184.1	3-Methyl-indene	767-20-2	198.6	—	—	0.06
27	12.608	184.6	2,3-Dihydro-2-methylbenzofuran	1746-11-8	197.9	2.96	0.50	—
28	12.621	184.7	2-Methylindene	2177-47-1	202.6	—	—	0.24
29	13.307	190.0	2-Ethyl-phenol	90-00-6	194.1	—	—	0.13
30	13.387	190.6	3-Ethyl-phenol	620-17-7	216.9	—	—	0.23
31	13.466	191.2	4-Ethyl-phenol	123-07-9	218	0.46	4.56	0.33
32	13.673	192.8	2-(2-Propenyl)-phenol,	1745-81-9	220	0.25	—	—
33	13.753	193.4	3,5-Dimethyl-phenol	108-68-9	222	—	0.74	—
34	13.992	195.3	2-Phenylethanol	60-12-8	228.5	2.55	3.82	—
35	14.604	200.0	Naphthalene	91-20-3	218	0.14	0.44	5.05
36	14.678	200.5	4-Methylcinnamaldehyde	71277-10-6	239.9	—	0.14	—
37	15.403	205.4	Isoprocab	2631-40-5	273.6	63.24	3.95	3.84
38	15.503	206.1	4-(1-Methylethyl)-phenol	99-89-8	213	—	—	2.03
39	15.975	209.3	2-Propylphenol	644-35-9	225	8.84	0.13	—
40	17.805	221.8	1-Methylnaphthalene	90-12-0	240	—	0.08	—
41	18.257	224.9	2-Methylnaphthalene	91-57-6	241	—	—	0.48
42	19.788	235.3	2,6-Diisopropylphenol	2078-54-8	312.6	0.11	—	—
43	20.134	237.7	Biphenyl	92-52-4	255	—	0.07	2.04
44	20.706	241.6	Diphenylmethane	101-81-5	264	—	—	0.17
45	20.932	243.1	Naphthyleneethylene	83-32-9	279.2	—	—	0.09
46	21.358	246.0	1-Vinylnaphthalene	827-54-3	247.4	—	—	0.21
47	21.811	249.1	Biphenylene	259-79-0	263.1	—	—	1.28
48	22.695	255.1	1,8-Dihydro-as-indacene	18837-46-2	263.9	—	—	0.08
49	22.815	256.0	$\alpha$ -Phenyltoluene	643-58-3	259	—	—	0.31
50	23.008	257.3	<i>p</i> -Methylbiphenyl	644-08-6	268	—	—	0.23
51	23.461	260.4	Dibenzofuran	132-64-9	285	—	—	1.23

\*  $t_R$  = retention time.

† RI = Lee retention index.

‡ CAS no. = Chemical Abstract Service Registry number.

§  $T_b$  boiling point obtained from <http://chemfinder.cambridgesoft.com> (indicated as integer value) or estimated by group contributions method (23,24).

\*\* Not available.

Table II. (continued) Identification and Quantitation of the Pyrolysis Products

Compound no.	$t_R^*$ / min	RI <sup>†</sup>	Compound name	CAS no. <sup>‡</sup>	$T_b^{\S}$ / °C	Content/%		
						600°C	750°C	900°C
52	23.620	261.5	2-Naphthalenecarbonitrile	613-46-7	298.7	–	–	0.21
53	24.585	268.0	Perinaphthene	203-80-5	290.2	–	–	0.04
54	25.018	271.0	Fluorene	86-73-7	295	–	–	1.28
55	25.477	274.1	Dihydrofurano[4,3,2-jk]fluorene	–	309.3	–	–	0.14
56	25.736	275.9	4-Vinylbiphenyl	2350-89-2	301.9	–	–	0.06
57	25.816	276.4	9-(1-Methylethyl)-9H-fluorene	3299-99-8	305.9	–	–	0.18
58	25.949	277.3	Fluorene-9-methanol	24324-17-2	325.4	–	–	0.12
59	26.215	279.1	4-Methyldibenzofuran	7320-53-8	322.2	–	–	0.15
60	26.601	281.8	9-H-Xathene	92-83-1	321.5	–	–	0.12
61	27.619	288.7	2-Methylfluorene	1430-97-3	318.1	–	–	0.15
62	27.906	290.7	1-Methylfluorene	1730-37-6	318.1	–	–	0.06
63	28.212	292.7	2-Fluorene-carboxaldehyde	30084-90-3	363.8	–	–	0.27
64	28.438	294.3	Fluorenone	486-25-9	342	–	–	0.10
65	28.538	295.0	2-Phenyl-benzofuran	10014-74-4	347.8	–	–	0.13
66	28.697	296.1	3-Phenyl-benzofuran	–	347.8	–	–	0.13
67	28.830	297.0	Anthrone	90-44-8	375.2	–	–	0.18
68	29.163	299.2	1-Phenyl-1H-indene	1961-96-2	337.0	–	–	0.13
69	29.276	300.0	Phenanthrene	85-01-8	340	0.05	0.04	1.84
70	29.476	301.4	Anthracene	120-12-7	340	–	–	0.74
71	29.569	302.0	2-Phenylbenzofuran	–	347.8	–	–	0.51
72	30.993	311.7	9-Vinylanthracene	2444-68-0	364.0	–	–	0.17
73	31.080	312.3	2-Methylphenanthrene	2531-84-2	344.4	–	–	0.17
74	31.618	316.0	1-Methylanthracene	610-48-0	344.4	–	–	0.08
75	31.885	317.8	2-Methylanthracene	613-12-7	344.4	–	–	0.06
76	32.004	318.6	4,5-Methylenephenanthrene	203-64-5	353	–	–	0.05
77	33.149	326.4	1-Phenylnaphthalene	612-94-2	370.0	–	–	0.22
78	34.699	337.0	Fluoranthene	206-44-0	375	–	–	0.18
79	35.138	340.0	Pyrene	129-00-0	378.6	–	–	0.08
80	35.651	343.5	Acephenanthrene	201-06-9	379.4	–	–	0.09

\*  $t_R$  = retention time.  
<sup>†</sup> RI = Lee retention index.  
<sup>‡</sup> CAS no. = Chemical Abstract Service Registry number.  
<sup>§</sup>  $T_b$  boiling point obtained from <http://chemfinder.cambridgesoft.com> (indicated as integer value) or estimated by group contributions method (23,24).  
\*\* Not available.

search can be determined, and it is not always true that the component with the highest match factor in the hit list should be selected.

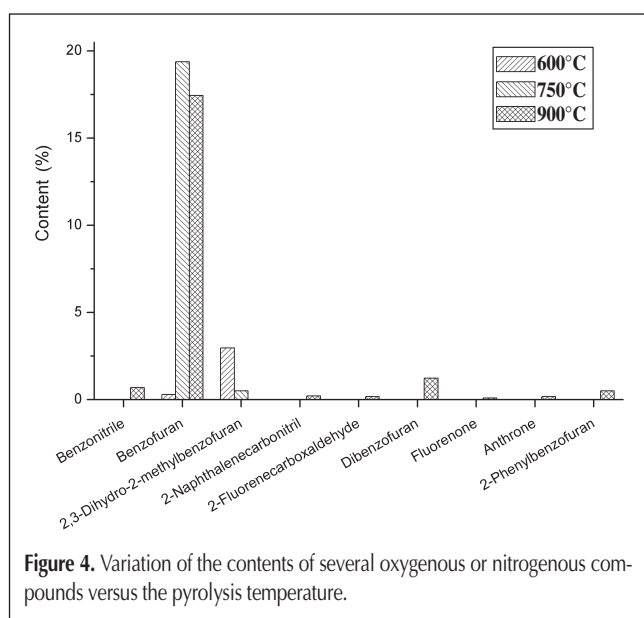
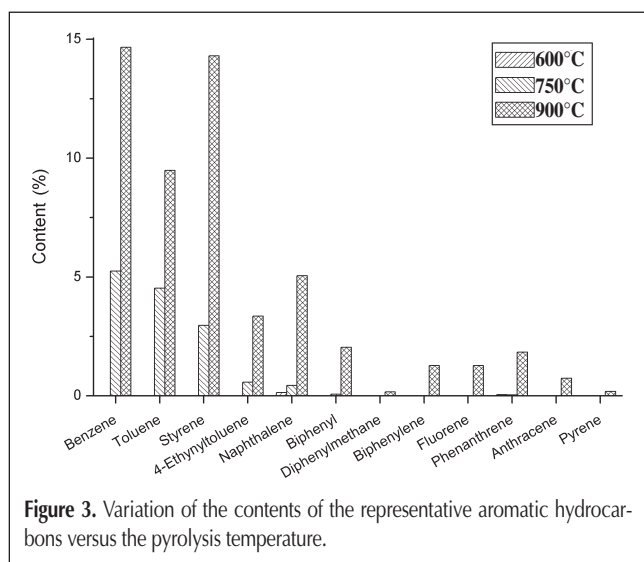
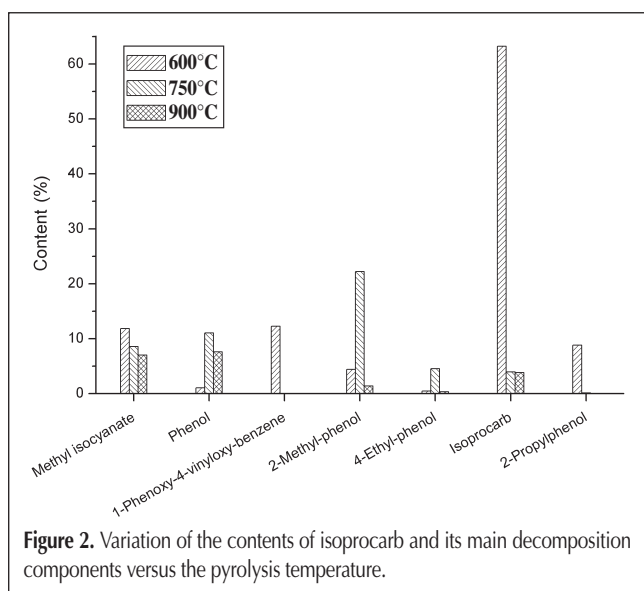
The unavailable experimental BP of a compound in the hit list was estimated by group contributions method (23,24). For validation of the method, the four components with the experimentally measured BP in Table I were investigated. It was found that the maximum absolute error of the estimated BP using the group contributions method is  $-16.9^\circ\text{C}$  (for naphthalene). This shows that the estimated BP of the tentative components is accurate and can be used for identification.

### Characterization of the pyrolysis products

The total of 80 pyrolysis components were identified using the procedure discussed in the Identification of pyrolysate components using PBM and BP–RI correlation section. Specially, the identification of isoprocarb was validated by the PBM search and the retention time of the reference material. The relative levels of the pyrolysis components for each of the three temperatures were estimated by the peak-area-normalization method from the chro-

matograms. The results are listed in Table II. It was found that the pyrolysis products of isoprocarb was a complex mixture, including a large number of mono aromatics and PAHs and their derivatives. Except for the content of the isoprocarb (63.24%), the content of the identified decomposition components varied from 0.04% to 22.20% under the studied pyrolysis conditions.

Figure 2 shows the variation of the contents of isoprocarb and its main decomposition components versus the pyrolysis temperature. It can be seen that isoprocarb (the estimated BP was  $273.6^\circ\text{C}$ ) was thermally unstable, and it was obviously decomposed at  $600^\circ\text{C}$ . From the content in Figure 2, it can be calculated that 36.76% of the isoprocarb was decomposed at the temperature. It was obvious that the higher the pyrolysis temperature, the more the isoprocarb was decomposed. At  $900^\circ\text{C}$ , the percentage of the decomposed isoprocarb was up to 96.16%. However, the decomposed amount at  $750^\circ\text{C}$  and  $900^\circ\text{C}$  was almost identical. This indicates that when the pyrolysis temperature was higher than  $750^\circ\text{C}$ , most of the isoprocarb was decomposed. On the other hand, by comparison of the content of the main decomposition compounds (e.g., methyl isocyanate, 2-propylphenol, and



2-methylphenol) at different temperature, it was found that some of them were further pyrolyzed at temperatures higher than 750°C. This result showed that the pyrolysis behavior of isoprocarb was a complex process with the decomposition of isoprocarb and the secondary pyrolysis of its decomposition compounds.

Figure 3 shows the variation of the contents of the representative aromatic hydrocarbons versus the pyrolysis temperature. It was seen that when the pyrolysis temperature was higher than 750°C, a large number of aromatic hydrocarbons were produced, and with the increase in temperature, the contents of these compounds increase significantly. Under a lower temperature (< 600°C), little aromatic hydrocarbons were produced. The aromatic hydrocarbons produced under high temperature were mainly benzene, styrene, 4-ethynyltoluene, and other PAHs such as naphthalene, biphenyl, biphenylene, fluorene, phenanthrene, anthracene, pyrene, etc. It was likely that these aromatic hydrocarbons were produced by the secondary pyrolysis of the decomposition compounds of isoprocarb.

Besides the decomposition components of isoprocarb and the aromatic hydrocarbons formed during the pyrolysis process, it was also found that there were a number of oxygenous or nitrogenous compounds formed in the pyrolysate, as shown in Table II. Figure 4 displays the variation of the contents of these representative compounds versus the pyrolysis temperature. Figure 4 also shows that a large amount of benzofuran was produced at the temperature higher than 750°C (up to 19.38% and 17.45% at 750°C and 900°C, respectively). The comparison of Figures 3 and 4 shows that the content of oxygenous and nitrogenous compounds, except for benzofuran, was much lower than that of the aromatic hydrocarbons (e.g., the maximum content of 2,3-dihydro-2-methylbenzofuran was only 2.96%). It can be deduced that these oxygenous or nitrogenous compounds were also produced by the secondary pyrolysis of the decomposition compounds of isoprocarb.

## Conclusion

The pyrolysis behavior of isoprocarb was studied using the pyrolysis-GC-MS. The pyrolysis products, including decomposition compounds of isoprocarb, the aromatic hydrocarbons, and oxygenous or nitrogenous compounds formed during the pyrolysis process, were identified using the PBM search in combination with the correlation of BP and RI. The unavailable experimental BPs of the tentative components in the hit list of the PBM search were estimated by a group contributions method. From the analyzed results, especially the variation of the contents of isoprocarb and its pyrolysis products versus the temperature, it was found that the pyrolysis process of isoprocarb includes thermal decomposition and secondary pyrolysis of the decomposed compounds, and mono aromatics or PAHs and their derivatives are formed in the secondary pyrolysis.

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