

## Thermal characteristics of lysine tri-isocyanate and its mixture with water

Xin-Rui Li\*, Hiroshi Koseki, Yusaku Iwata

National Research Institute of Fire and Disaster, 4-1 Nakahara 3-Chome,  
Mitaka-Shi, Tokyo 181-8633, Japan

Available online 28 June 2006

### Abstract

The thermal reactivity of lysine tri-isocyanate (LTI, 2-isocyanatoethyl-2,6-diisocyanato caproylate) and its mixture with 1% water was investigated after the occurrence of a runaway reaction at a plant. By using a sensitive thermal calorimeter, C80, and an adiabatic calorimeter, ARC, an onset reaction of LTI was observed at 70–100 °C and it became vigorous at 175–200 °C. The reaction is considered as co-polymerization at this stage, which causes a second decomposition reaction at 200 °C if the heat generation is accumulated in the vessel. On the other hand, the presence of water can catalyze LTI at much lower onset temperature and lead to a moderate reaction at 50 °C since carbamine is produced and in turn it induces decarbonization of the LTI molecule with significant release of CO<sub>2</sub> gas which was detected by a gas chromatography and an FT-IR gas analyzer.

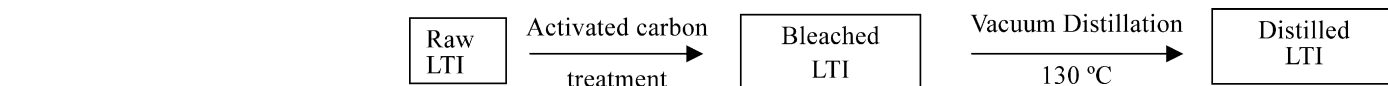
© 2006 Elsevier B.V. All rights reserved.

**Keywords:** LTI (lysine tri-isocyanate, 2-isocyanatoethyl-2,6-diisocyanato caproylate); Water contamination; Thermal calorimeter; Gas release

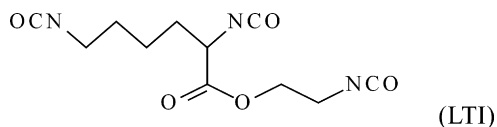
### 1. Introduction

A runaway reaction of lysine tri-isocyanate (LTI, 2-isocyanatoethyl-2,6-diisocyanatohexanoate, or 2,6-diisocyanato-hexanoic acid 2-isocyanatoethyl ester) in a 6901 vacuum

distillation vessel (0.03 Torr) led to a severe leakage through its sight-glass sealing joint at a fine chemical factory in Kyoto, Japan, November 2004 [1]. LTI, having the molecule of, is used as the crosslinking agent of polyurethane resin. It is classified as Class 4 hazardous material, flammable liquid, according to the Japanese Fire Service Law. Its flash point is 123 °C in the Cleveland flash point measurement and the boiling point is 156 °C.



distillation vessel (0.03 Torr) led to a severe leakage through its sight-glass sealing joint at a fine chemical factory in Kyoto, Japan, November 2004 [1]. LTI, having the molecule of, is used as the crosslinking agent of polyurethane resin. It is classified as Class 4 hazardous material, flammable liquid, according to the Japanese Fire Service Law. Its flash point is 123 °C in the Cleveland flash point measurement and the boiling point is 156 °C.



Although there were some uncertainties, it was suspected that water might contaminate the sample and deteriorate LTI during the process. It was a similar phenomenon to a runaway reaction of the mixture of methyl isocyanate (intermediate of insecticide) and water, which led to serious leakage of toxic gases in the Bhopal tragedy, India in 1984 [2,3]. Trace or certain amount of water sometimes is easily introduced into the system due to residue after water purging vessels or pipes, leakage of valves or corrosion of cooling water pipes.

In order to investigate the hazard potential of LTI and its water mixture, experiments were performed on the thermal behaviors of LTI and its mixture with 1% water, using a DSC, a highly sensitive thermal calorimeter, C80 and an adiabatic calorimeter, ARC. A gas chromatography (GC) and an FT-IR gas analyzer were used to analyze gaseous components from the reactions.

\* Corresponding author. Tel.: +81 422 44 8392; fax: +81 422 44 8392.  
E-mail address: li@fri.go.jp (X.-R. Li).

## 2. Experimental

### 2.1. Samples

Samples of LTI were obtained at the accidental place. The following samples were used: bleached LTI (LTI before distilled, yellow, low purity), distilled LTI (colorless, purity >99%), and their mixtures with 1% water. Two methods were employed in the mixture measurements: (1) the mixture was measured in the calorimeter after stirring and (2) the LTI and water were put into the testing vessel together and was measured directly in the calorimetries (in situ addition).

### 2.2. Differential scanning calorimetry (DSC)

In the experiments, bleached LTI and its mixture were firstly tested in a DSC (Rigaku Co. Ltd.). The DSC can examine the thermal properties of the material in handiness and in a short time. The amount of the sample was about 2 mg in a sealing aluminum pan and the temperature rising rate was 10 K/min.

### 2.3. Heat flux calorimetry C80

All the samples were then measured by being loaded in a 12 ml high-pressure hermetic stainless steel cell of a C80, a heat flux calorimetry (Setaram Co. Ltd., France), which can measure a faint heat generation with its high sensitivity. The mass of the sample was about 0.5 g and an equivalent mass of alumina was loaded into the reference vessel. The programmed temperature was raised at a rate of 0.1 K/min in the range of the room temperature to 300 °C. Several isothermal measurements were also carried out at 40–50 °C to analyze the kinetic of the samples near the room temperatures.

### 2.4. Accelerating rate calorimetry (ARC)

An ARC (ADL Co. Ltd., USA) was used for determining self-heating and pressure change during the thermal reaction at HWS (heating-waiting-searching) mode with an adiabatic condition. About 0.5 g of the samples was placed in a spherical titanium vessel and the vessel was subsequently attached to the apparatus to form a closed, leak-tight assembly. The experiments were started at the room temperature. During the performance, the temperature of the vessel was raised from an initial temperature

by increments (the heat period) of 5 °C and the vessel was maintained adiabatic during both a wait period (which allowed the dissipation of thermal transients) and a search period. The system searched and recorded an exotherm during the search period, and whenever the sample's self-heating rate exceeded a chosen threshold value of 0.02 K/min, the surrounding temperature followed the sample temperature to minimize the temperature difference.

### 2.5. Measurement of gas production by gas chromatography (GC)

Gaseous products, mainly CO, CO<sub>2</sub>, CH<sub>4</sub> etc., from the reaction of LTI were analyzed by a gas chromatography (GC-14B, Shimadzu Corp.). The samples were stored in a constant temperature bath at 50 and 130 °C, respectively. After the storage over 4 h, the sample gases evolved from 5 g specimen in a 130 ml pyrex cell were collected by a syringe which was attached with the silicon tubes to form a closed, leak-tight system, and then injected into and analyzed by the GC. The sample gases were freeze-dried, digested with an alkaline solution, and then loaded into the gas chromatography capillary column, which was a thin tube with an inner column. The column, containing the solid stationary phase such as Shincarbon ST (activated carbon) as the packing agent, was placed in a thermostat-controlled oven. The carrier gas was helium. A reaction tube of methanizer (MTN-1) was installed between the column outlet and the detector to provide reduction of CO and CO<sub>2</sub> to CH<sub>4</sub> for detection by FID. The detector was the flame ionization detector (FID), which consisted of a flame fed by hydrogen and air, and a collector plate. Once passing through the GC column, the methanizer and the flame, the gas sample broke down the compounds and produced ions. An electrical signal generated by these ions was recorded as the amount of corresponding gases released from the sample.

### 2.6. Measurement of gas components and concentration by FT-IR gas analyzer

The GASMET Dx-4000 (Temet Instrument Oy, Finland) is a Fourier transform infrared, FT-IR spectrometer, designed for multicomponents gaseous analysis, as illustrated in Fig. 1 [4]. Similar to the way in the GC, gases from 5 g specimen in a 130 ml pyrex cell after the storage of 4 h at 50 and 130 °C, respectively, in a constant temperature bath, was introduced into a 3 l air bag

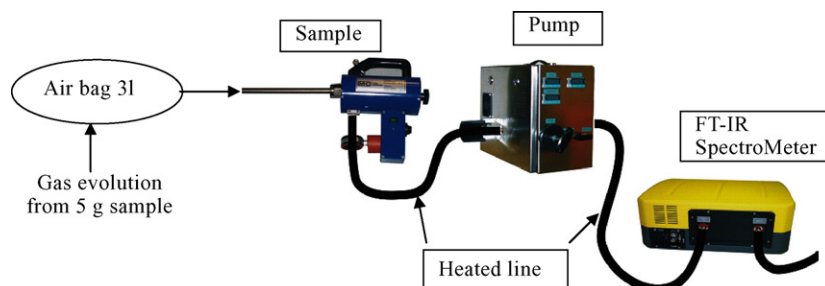


Fig. 1. FT-IR gas analyzer.

through silicon tubes, and then analyzed by the portable FT-IR gas analyzer. After the background calibration by  $N_2$ , test gases were conducted into the sampler and heated up to  $180^\circ\text{C}$  during the entire sampling procedure. In the FT-IR spectrometer, specific molecular components and structures were specified by the corresponding infrared absorption bands, which allowed computerized data searches to be performed against reference libraries. The concentrations of the gases were further confirmed by CLS (classical Least squares) algorithm.

### 3. Results and discussion

#### 3.1. Effect of water on heat generation of LTI

First of all, the experiment for the influence of water on heat generation of LTI before distilling (bleached LTI) was conducted with the DSC device, at a temperature rising rate of  $10\text{ K/min}$ . Fig. 2 shows the results. Heat generation of the bleached LTI happened at about  $100^\circ\text{C}$ , and the maximum appeared at about  $260^\circ\text{C}$ . On the other hand, heat generation of the one with water added (1%) began at a lower temperature of about  $70^\circ\text{C}$ . The reaction of LTI was accelerated at about  $100^\circ\text{C}$ , and it attained a maximum at about  $220^\circ\text{C}$ . This implies that the reaction is promoted by the addition of water and the runaway reaction is caused possibly at a lower temperature. LTI (re-test) in Fig. 2 was the same sample that, after measurement, was cooled down to the room temperature and was measured for the second time with the DSC. The heat generation was hardly seen in this case, indicating that all reaction finished during the first measurement.

The samples were then similarly examined by using the C80 and the heat flows versus temperature data from the C80 experiments are shown in Figs. 3–5. In the C80, the beginning of heat generation and the accelerated reaction greatly swerved to the lower temperatures compared to those in the DSC, thanks to its advantages of high sensitivity and large sample size measured. Meanwhile, a weak exothermic activity was possibly monitored at a working condition in which a slow scanning rate was used ( $0.1\text{ K/min}$ ), since it was much closer to the actual isothermally placed situation in industrial process.

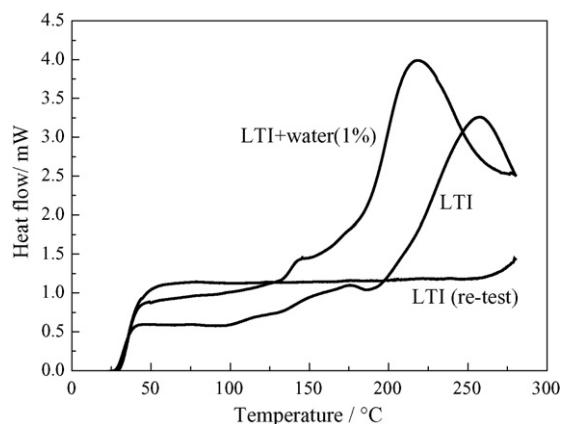


Fig. 2. Comparison of the heat generation of bleached LTI and LTI with water in the DSC.

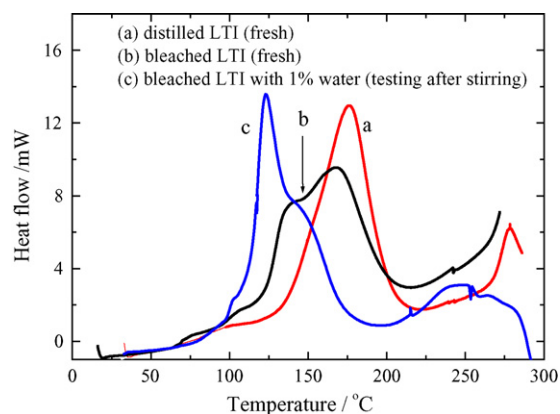


Fig. 3. Comparison of the heat generation of distilled LTI, bleached LTI and LTI with water in the C80.

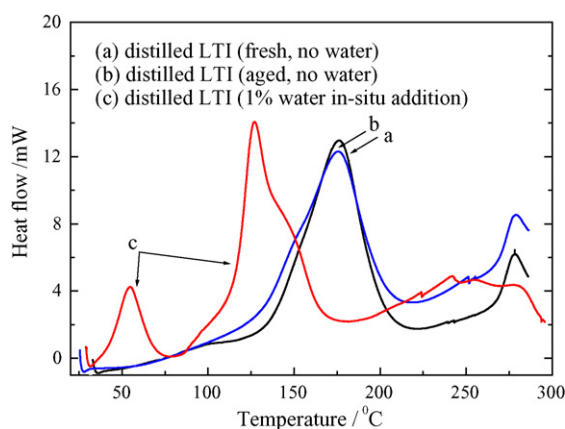


Fig. 4. The heat generation of fresh distilled LTI, aged sample for several months and the one with a direct addition of water in the C80.

As seen in Fig. 3, slight heat generation was initially observed from the distilled LTI (curve a) at about  $70^\circ\text{C}$ . The reaction became vigorous above  $130^\circ\text{C}$ , and the maximum heat flow was  $13\text{ mW}$  at  $175^\circ\text{C}$ . The purity of the bleached LTI (curve b), which includes oligomers such as dimer, trimer or other impurities, was lower. Compared to the distilled specimen, its initial reaction which started at about  $70^\circ\text{C}$  became accelerated

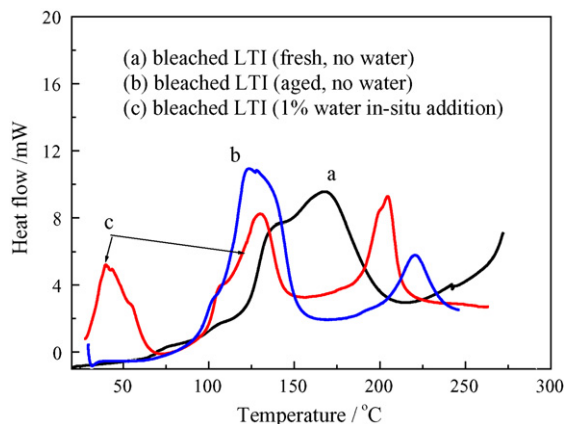


Fig. 5. The heat generation of fresh bleached LTI, aged sample for several months and the one with a direct addition of water in the C80.

at 100–150 °C and the width of heat generation expanded. At above 250 °C, another reaction started in both of these samples. It seems that the first reaction is a result of polymerization of the LTIs and the second reaction is the thermal decomposition of the samples. In contrast, in the case of presence of water (curve c), reaction of LTI became more vigorous at the first stage. The maximum heat flow was 14 mW at 120 °C. This specimen was measured in the calorimeter after the mixture was thoroughly stirred.

### 3.2. Aging of LTIs and their water mixtures

In order to characterize in more details the thermal activity of the two specimens of LTI and the effect of water and storage time on their thermal stability. Figs. 4 and 5 illustrate the heat generation versus temperature curves of the specimens, including the fresh (received after the accident) distilled and bleached ones, aged ones stored over several months in our laboratory and their mixtures with a direct addition (in situ) of water, respectively.

It can be seen in Fig. 4 that the reactivity of the distilled LTI (curve b) did not change so much over the holding time compared to the fresh one (curve a), implying that it is stable to be stored in the air. However, when the sample was directly contaminated by 1% water, a moderate reaction (curve c) initiated from 30 °C and reached the maximum at 60 °C. This reaction is completely different from that in neat LTIs.

Comparably, Fig. 5 shows that the fresh bleached LTI (curve a) was more reactive than the distilled LTI. Similar to the results of the DSC in Fig. 3, this seems that lower purity of the bleached LTI makes the sample more unstable. It became further unstable when exposed in the air for longer time. The reactivity in the neat bleached LTI after aging for several months (curve b in Fig. 5) was similar to that added by 1% water, as the specimen (curve c) of mixture in Fig. 3. It is considered that the moisture in the air deteriorates the bleached LTI easily compared to the distilled LTI. Whereas the direct addition of water, resembling what happened in the distilled LTI, caused an obvious reaction (curve c) starting from 30 °C and attaining the maximum at 60 °C, implying that the sample contacting water directly will lead to a new reaction near the room temperature, regardless of the types of LTI.

### 3.3. ARC test results

Fig. 6 shows the results using the ARC, which were performed on the same 0.5 g specimens. Consistent in the C80 results, the ARC-detected onset temperature of the distilled LTI was 120 °C and the temperature by the self-heating of this exothermic reaction went up to about 150 °C. At this stage pressure hardly increased since the polymerization did not produce much gas. The lack of reaction appeared thereafter and the temperature went up stepwisely under the outer heating by the apparatus. A further temperature rise by the self-heating was observed as an occurrence of decomposition at about 270 °C. This second reaction was accompanied by zooming of the pressure, resulting from a large amount of gas generation from the pyrolysis. The profile of the temperature of the bleached LTI

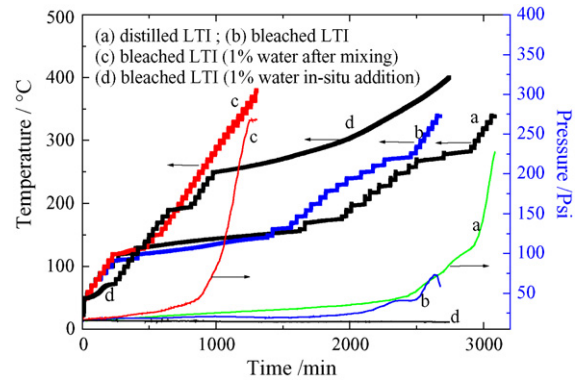


Fig. 6. Results of the ARC tests. (Pressure increases in measurements (a) and (c) were only observed. Cases of no pressure increase in (b) and (d) were observed due to chokes of the tubes connected between the bomb and the pressure sensor by the eruption of particle products from LTI.)

(curve b) was alike to that of the distilled one (curve a), though the onset temperature was a little bit lower due to its instability as mentioned before. On the other hand, the specimen in the presence of water (curve c) had the major reaction at about 130 °C and the pressure at this stage increased markedly. And the one (curve d) by an in situ adding of water started the reaction at 50 °C (self-heating was observed at this temperature, however pressure signal which was expected to increase significantly as sample (curve c) was not obtained due to the readily choking of the tubes connected between the bomb and the sensor by the eruption of particle products from LTI), which is in good agreement with what has been observed in the C80. It is clear that in the water mixture, a new reaction takes place with moderate exothermic effect and gas is evidently released near the room temperature.

### 3.4. Isothermal measurements in the C80

To quantify the kinetic of the water mixture at the low temperature, the heat flow versus time data of C80 experiments at 40–50 °C for the LTI and water mixtures are shown in Fig. 7. No reaction occurred for LTI at 50 °C at all. In contrast, exothermic peaks for water mixtures were observed after 5 h at 50 °C, 6 h at 45 °C and 16 h at 40 °C. The heat of reaction and kinetic of the

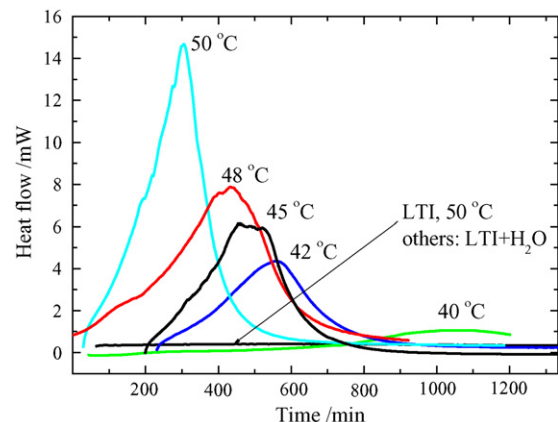


Fig. 7. Results of the isothermal measurements in the C80.



water mixture can be estimated at this temperature range, based on the following equation [5,6]:

$$\ln\left(\frac{dH}{dt}\right)_{\max} = \ln A - \frac{E}{RT} \quad (1)$$

where  $dH/dt$  is the instant heat flow of a reaction at a certain time, and its maximum value is used in the catalytic reaction.  $A$  and  $E$  are the pre-exponential factor and the activation energy,  $T$  the absolute temperature, and  $R$  the gas constant. The slope of  $\ln(dH/dt)_{\max}$  against  $1/T$  yields the activation energy of the LTI–water mixture, which is 22.1 kJ/mol.

### 3.5. Gaseous components measurement by gas chromatography and FT-IR gas analyzer

The evolved gases from the storage of LTI and its mixture with water at 50 and 130 °C after 4 h are shown in Table 1, which were detected by the GC. At 50 °C, a large amount of CO<sub>2</sub> was identified in the specimen of mixture, whose volume was 1.78 ml/g LTI and it was 26 times of that in neat LTI. At 130 °C, the amount of CO<sub>2</sub> produced from the specimen of mixture was 4.47 ml/g LTI, which was 3.6 times of that in the neat LTI.

More gas species were determined by the FT-IR gas analyzer, as in Table 2. However, the results show similar tendency to the GC results for CO and CO<sub>2</sub>: other gas species, including some toxic gases like HCN, were not found in LTI or its water mixture. Only the concentration of CO<sub>2</sub> which was produced from the LTI–water mixture was significantly noticeable, being 9.36% and 28 times of that in neat LTI at 50 °C. At 130 °C, the concentration of CO<sub>2</sub> did not change largely. Meanwhile, CO evolved from LTI–water was not different from LTI at 50 °C and was slightly increased at 130 °C.

According to Refs. [1,7], it is considered that the presence of water can accelerate the reaction of LTI during its onset stage at near the room temperature since carbamine is produced and in turn it induces decarbonization of LTI molecule with gas release. CO<sub>2</sub> is evolved considerably. The scheme of water effect on the reaction is supposed as below:

- (1) At near the room temperature, the following reaction occurs in LTI mixture with water, accompanied by the formation of CO<sub>2</sub>:

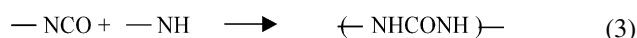
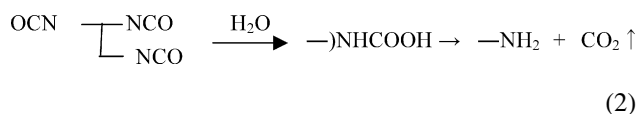


Table 1  
Gases released from the LTI and mixture with water by the GC

Released gas	50 °C (ml/g LTI)		130 °C (ml/g LTI)	
	LTI	LTI–water	LTI	LTI–water
Carbon dioxide (CO <sub>2</sub> )	4E–4	0	0.03	0.02
Carbon monoxide (CO)	0.06	1.78	1.26	4.48

Table 2

Concentration of gases released from the LTI and mixture with water by the FT-IR gas analyzer

Released gas	50 °C (ppm)		130 °C (ppm)	
	LTI	LTI–water	LTI	LTI–water
Water vapor (H <sub>2</sub> O)	1.88E+4	2.08E+4	1.18E+4	1.68E+4
Carbon dioxide (CO <sub>2</sub> )	3.32E+3	9.36E+4	2.56E+3	8.58E+4
Carbon monoxide (CO)	4.64	6.66	9.72	56.8
Nitrous oxide (N <sub>2</sub> O)	0.71	1.30	0.35	1.82
Nitrogen monoxide (NO)	0	0	0	0
Nitrogen dioxide (NO <sub>2</sub> )	1.17	0.90	1.59	1.32
Ammonia (NH <sub>3</sub> )	0.98	1.02	0.84	0.47
Methane (CH <sub>4</sub> )	0	0	0	0
Ethane (C <sub>2</sub> H <sub>6</sub> )	0.28	0.19	0.28	2.49
Propane (C <sub>3</sub> H <sub>8</sub> )	0.01	0.24	0.21	1.57
Benzene (C <sub>6</sub> H <sub>6</sub> )	0	0	0	0.11
Toluene (C <sub>7</sub> H <sub>8</sub> )	0	0.49	0.23	0
Methanol (CH <sub>4</sub> O)	0	0	0	0
Hydrogen cyanide (HCN)	0.08	0	0	0
Phenol (C <sub>6</sub> H <sub>8</sub> O)	0.81	0.24	0.37	0.87
Acrolein (C <sub>3</sub> H <sub>4</sub> O)	0	0	0.52	0
Acetone (C <sub>3</sub> H <sub>6</sub> O)	0	0	0	0
Hexane (C <sub>6</sub> H <sub>14</sub> )	1.08	0.05	0.40	1.63
Heptane (C <sub>7</sub> H <sub>16</sub> )	1.63	1.04	0.56	0.54
Octane (C <sub>8</sub> H <sub>18</sub> )	0.53	0.33	0.59	0
Ethanol (C <sub>2</sub> H <sub>6</sub> O)	3.36	2.15	1.67	2.39

\*The table lists possible gaseous components from the studied samples based on reference libraries. There might be other species that the libraries do not include. The concentrations of the compounds were confirmed by CLS (classical Least squares) algorithm.

- (2) At 130 °C, copolymerization reaction of LTI occurs, and little gas is produced.  
 (3) Above 270 °C, thermal decomposition reaction (pyrolysis) of LTI occurs, with the production of CO, NO<sub>x</sub>, and HCN [1].

## 4. Conclusions

The reactivity of LTI presumably consists of two stages in reactions: polymerization at 70–130 °C and pyrolysis at above 250 °C. However, the onset temperature and the scheme of the reaction vary from the samples, such as the bleached and the distilled, as well as the bleached one aged in the air. It is suggested that water affects the reaction of the LTI in two ways. The moisture in the air deteriorates the bleached LTI when exposed and makes it unstable at a lower temperature of 70 °C. In particular, when the samples, no matter what types of the LTI are, contact with water directly, though only 1% contamination, a moderate reaction in the LTI in several hours at the room temperature arises, and CO<sub>2</sub> is the main production in the water mixture.

## References

- [1] Kyoto Fire Department, Report of an accident at a fine chemical factory, 2005.
- [2] I. Eckerman, The Bhopal Saga, Universities Press, Hyderabad, India, 2005.
- [3] J.P. Gupta, Bhopal gas tragedy and its effects on process safety, J. Loss Prev. Process Ind. 18 (4–6) (2005) 195–199 (July–November, special issue of Selected Papers Presented at the International Conference on Bhopal Gas Tragedy and its Effects on Process Safety).

- [4] Temet Instruments Oy, Manual of GASMET Dx-4000, 2005.
- [5] L.D. Hansen, E.A. Lewis, D.J. Eatough, R.G. Bergstrom, D.D. Johnson, Kinetics of drug decomposition by heat conduction calorimetry, *Pharm. Res.* 6 (1989) 20–27.
- [6] W.L. Ng, Thermal decomposition in the solid state, *Aust. J. Chem.* 28 (1975) 1169–1178.
- [7] L. Bretherick, *Handbook of Reactive Chemical Hazards*, 3rd ed., London, 1987.