Pyrolysis and Ignition of Branched-Chain Amino Acid Powders

Wookyung Kim[a*], Takuya Soga[a], Tomoyuki Johzaki[a], Takuma Endo[a], Tomonori Kato[b], Kwangseok Choi[c]
[a]Department of Mechanical Systems Engineering, Hiroshima University, Hiroshima, Japan

[b] Research Institute for Bioscience Products and Fine Chemicals, Ajinomoto CO., INC., Kanagawa, Japan

[c] Electrical Safety Research Group, National Institute of Occupational Safety and Health, Tokyo, Japan

1 Introduction

L-leucine, L-isoleucine and L-valine are among the essential branched-chain amino acid for the biosynthesis of proteins and hemoglobin formation. The branched-chain amino acid powders (BCAAs) with fine particles are widely used as nutritional supplements in a pharmaceutical industry. In the manufacturing process, the powders have a potential hazard to cause a dust explosion. In order to protect the catastrophic damages caused by the explosion, the properties of the combustible dust is required for performing a risk assessment. According to Pubchem provided by the National Center for Biotechnology Information, however, the characteristics of fire and explosion of amino acid powders are not available [1]. Previously, we experimentally investigated the Minimum Ignition Energy (MIE) and Minimum Explosible Concentration (MEC) of L-isoleucine and glycine powders [2, 3]. The results demonstrated that the values of MIE and MEC of L-isoleucine were lower than those of glycine, because of different pyrolysis. Although few combustible materials were formed during the pyrolysis of glycine due to the formation of polymerization, a number of flammable compounds for L-isoleucine were generated. In this study, we additionally investigated the characteristics of L-leucine and L-valine powders and compared with those of L-isoleucine and glycine powders. The objectives of this work are to understand the pyrolysis and pyrolyzates of amino acid powders, in particular, the BCAAs, and to evaluate the ignition characteristic such as MIE and MEC of the BCAAs powders.

2 Experimental specifications

Correspondence to: kimwk@hiroshima-u.ac.jp

In the present work, L-leucine, L-isoleucine and L-valine powders which have different distributions of particle size are used. The summary of particle size distributions of L-leucine, L-isoleucine and L-valine powders is shown in Table 1. D_{50} is considered as the mean particle diameter d in this manuscript. The images of a scanning electron micrograph (SEM) of the d = 21.83 μm for L-leucine, the d = 15.00 μm for L-isoleucine and the d = 20.31 μm for L-valine samples. The shapes of individual particles of L-leucine, L-isoleucine and L-valine are irregular and a few particles are agglomerated.

The pyrolysis of L-leucine, L-isoleucine and L-valine powders are investigated by Thermogravimetry (TG), Differential Thermal Analysis (DTA), and Gas Chromatography–Mass Spectrometry (GC-MS). TG, DTA curves of L-leucine, L-isoleucine and L-valine powders were obtained by TG/DTA6200 at heating rate of 5 °C/min under N_2 atmosphere and temperature range 25-1000 °C. In addition, the pyrolyzates were measured by JCI-22S under 670 °C and GC-MS. According to International Electrotechnical Commission (IEC) standard [4], the MIE tests were conducted by MIKE-3 by Kuhner. The MEC of BCAAs were determined using a 1.2 L specified Hartmann-type tube apparatus as per the Japanese Industrial Standard (JIS Z 8818: 2002). The MEC tests were performed with an ignition delay time after discharge of 0.1 s, and the pressure of compressed air of 70 kPa in accordance with JIS Z 8818: 2002. A detailed precise specification of test can be found in [5].

Table 1: Summary of particle size distributions.

	L-leucine		L-isoleucine		L-valine		Glycine	
d (μm)	21.83	122.9	15.00	198.14	20.31	172.0	19.59	203.36
D_{10} (μm)	2.41	41.55	2.34	22.16	3.03	64.96	4.35	99.17
D_{50} (μm)	21.83	122.9	15.00	198.14	20.31	172.0	19.59	203.36
D_{90} (μm)	72.48	220.4	53.64	416.51	87.96	321.4	49.52	302.54

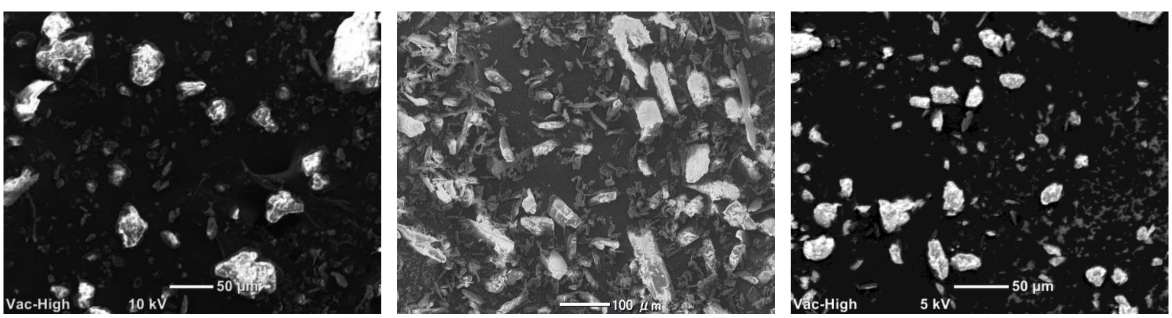
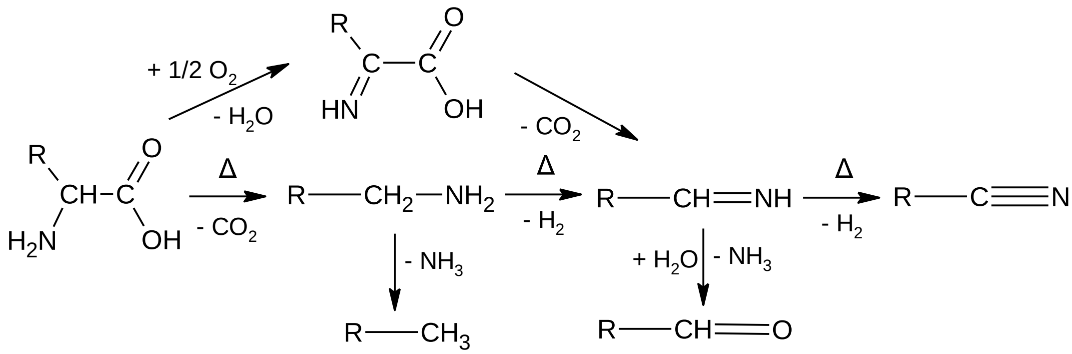


Figure 1. Scanning electron micrograph: L-leucine, L-isoleucine and L-valine.

3 Pyrolysis and pyrolyzates

The pyrolysis and pyrolyzates of L-leucine, L-isoleucine and L-valine powders was investigated using TG, DTA, and GC-MS. Figure 2 show that TG, DTA curves of L-leucine, L-isoleucine and L-valine powders at heating rate of 5 °C/min under N_2 atmosphere. Same tendency of TG curves with a rapid mass loss are observed in the temperature range of 200-300°C. The endothermic peak of L-leucine, L-isoleucine and L-valine powders are similar, and the weight of the powders reached nearly 0% at 280-300 °C. The polymerization in pyrolysis of the BCAAs was not observed, although the glycine is polymerized due to the least steric hindrance. The primary decomposition reactions of the BCAAs might be the deamination, dehydration, and decarboxylation, and many types of pyrolyzates are generated [6]. The several flammable compounds from BCAAs are formed by the deamination, dehydration, and decarboxylation reactions, as shown below:



In the privous work, a number of flammable and combustible materials are observed in the pyrolyzates of L-isoleucine, although few flammable compounds were generated from glycine [2]. In the present study, the pyrolyzates of L-leucine and L-valine powders are additionally measured by GC-MS. L-leucine powders formed the many flammable products: $C_2H_6N_2$, C_3H_6O, C_4H_8O, $C_6H_{13}N$, $C_3H_2O_2$, C_4H_8O, C_5H_9N, $C_3H_7NO_2$, $C_6H_{12}O$, $C_{10}H_{21}N$. A number of flammable materials such as are also C_4H_8, C_4H_7N, C_4H_8O, C_5H_9N, $C_4H_9NO_2$, C_4H_5N, $C_3H_2O_2$, $C_3H_7NO_2$,$C_7H_{15}N$ formed from L-valine. In particular, $C_2H_6N_2$, C_4H_8, C_4H_7N, in the flammable products are extremely flammable. This result demonstrated that a number of flammable materials are formed from the BCAAs compared with other amino acids such as glycine.

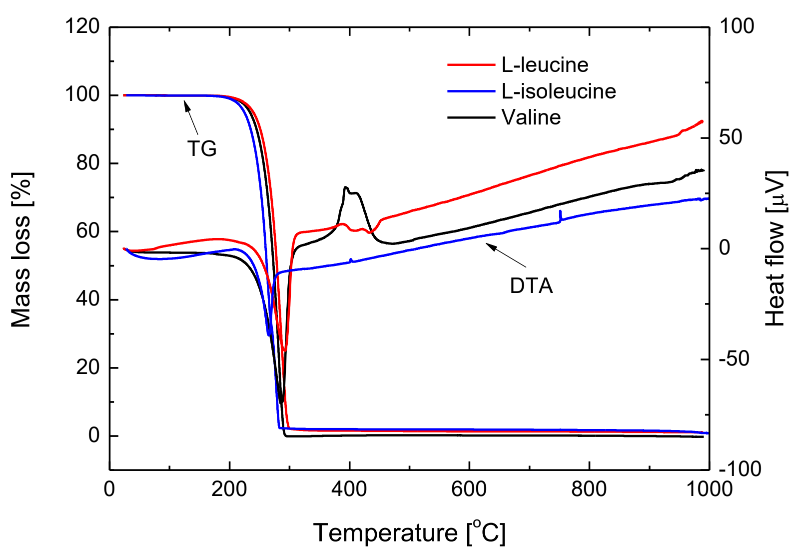


Figure 2. TG/DTA curves of L-leucine, L-isoleucine and L-valine in N_2 atmosphere.

4 MIE and MEC

Ignition characteristics, in particular, MIE and MEC of L-leucine and L-valine powders are measured and compared with those of L-isoleucine and glycine. In this manuscript, MIE is the statistic minimum ignition energy between non-ignition and ignition. The measured values of MIE and MEC are summarized in Table 2. The evaluated values of MIE of L-leucine and L-valine powders are very low and are similar to that of L-isoleucine powder. These values of MIE of the BCAAs are much lower than that of glycine powder. These results agree well with the data from GC-MS which a number of flammable materials in the pyrolysates of the BCAAs were formed.

The MEC test was repeated five times until the value of MEC was found. The value of MEC could be determined as the concentration at which flame propagated across 100 mm distance from the ignition source. The MEC values of L-leucine and L-valine powders irrespective of particle size are much lower than that of glycine powder. It is indicated that the BCAAs are very sensitive to ignite and has a higher reactivity and dust explosion hazard compared to glycine powder.

Table 2: Summary of MIE and MEC.

	L-leucine		L-isoleucine		L-valine		Glycine	
d (μm)	18.37	122.9	15.00	198.14	20.31	172.0	19.59	203.36
MIE (mJ)		22	4	8	4	26	540	> 1000
MEC (g/m^3)	50	55	40	45	50	45	180	> 2000

5 Summary

The pyrolysis and ignition of the BCAAs such as L-leucine, L-isoleucine and L-valine were experimentally investigated. For the BCAAs, the same tendency of TG was observed, and a number of flammable products were formed in the pyrolyzates. MIE and MEC of the BCAAs with two different particle size distributions were experimentally evaluated. The values of MIE and MEC of the BCAAs were much lower than that of glycine powder. These results demonstrated that the BCAAs powders has a high risk of dust explosion with lower MIE and MEC as compared to glycine powder, and the risk assessment is necessary in the field of powder handling.

References

[1] NIH: U.S. National Library of Medicine, National Center for Biotechnology Information, PubChem

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