



Improvement and Conditions Optimization of a Carbon Dioxide Successive Determining Test Method

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(Received: 30 April 2012;

Accepted: 11 February 2013)

AJC-12977

A carbon dioxide successive determining method was improved and established for the determination of ultimate aerobic biodegradability of plastic materials under controlled composing conditions. The improvement and optimization of systematic operational conditions which include selection of desiccant, air flow velocity region and charges of absorbent *etc.*, were also studied. Measurement and optimization results confirmed that the system was fitted for designed purpose and more excellent than some reported ways. Those results can be a basement of automating the CO₂ and other gas production measurements.

Key Words: Carbon dioxide, Aerobic biodegradability.

INTRODUCTION

The method, determination of ultimate aerobic biodegradability of plastic materials under controlled composing conditions, is an international standards method¹ for determining the biodegradation rate of biodegradable polymers. The standard ISO14855 specifies a method for determining the biodegradation rate by gravimetric measurement of the amount of CO₂. It was already applied widely in degradation²⁻⁴ of polymers in laboratories and offered an important property parameter for a new polymer. Zhang *et al*⁵, had used the measurement method of alkali absorption to replace the gravimetric way for improving the precision. Infrared absorption method and chromatographic techniques were also used in the determination⁶⁻⁸.

The determination of ultimate aerobic biodegradability of plastic materials is a long time process. The period is always more than 2 months. As far as authors knew, those determination methods mentioned above except for chromatographic method couldn't meet the requirement of successive measurement in so long time. And the carrier gas of chromatographic method is waste seriously. Those disadvantages restrict the determination method of polymers being applied in large scale. In this paper, we report the results of the improvement and conditions optimization of a carbon dioxide successive determining method for solving those disadvantages mentioned above.

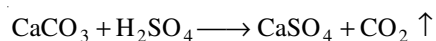
EXPERIMENTAL

Method establishment: A measurement system for simulating real one of determination of ultimate aerobic biodegradability of plastic materials was established. The system is made up of 4 subsystems *i.e.*, carrier gas supply and purge system, CO₂ generator system, absorption system and exhaust gas treatment system. Total 8 air valves used to control the flow velocity in system and for safety. The original patterns of the system is shown in figure A.1 of ISO14855-22¹.

Carrier gas supply and purge system: Carrier gas was supplied by a mechanical gas pump. The output power is 35 W and gas supply rate is 40 L min⁻¹ of the pump.

The gas supplied by pump was pumped through a gas purge system which had been made of 3 bottles with 2 mol L⁻¹ NaOH and a bottle with saturated Ca(OH)₂ solution for removing and determining the CO₂ of air.

CO₂ Generator system: CO₂ generator system was used to generate CO₂ quantitatively. Solid of Na₂CO₃ was dried in muffle furnace with 350 °C and 3.5 h and then was solved in deionized water quantitatively. The solution was dropped in excess H₂SO₄ of 0.5 mol L⁻¹ with the rate 2 droplets per second. The chemical reaction was described as the reaction equation below:



The CO₂ generator system was positioned on a thermostatic magnetic stirrer for keeping the temperature of CO₂ generated at 58 °C.

The CO₂ generated was accessed into absorption system by the carrier gas.

Absorption system: Absorption system was made of drier subsystem and absorption subsystem. The drier subsystem was made of a condensation bottle and 2-staged drier bottles. Four kinds of desiccant were chosen and measurement: 98 % H₂SO₄, silica gel, CaCl₂ and 3A molecular sieve.

The absorption subsystem was made of 4-staged absorption bottles. Three kinds of absorbent were chosen and measurement: soda lime granular, 2 mol L⁻¹ NaOH solution and 4A molecular sieve.

Exhaust gas treatment system: Exhaust gas treatment system was made of a bottle of saturated Ca(OH)₂ for determining the CO₂ absorption degree of absorption system and a foam flow meter for measuring the real gas flow velocity of whole system.

Operation of system: The system was run a definable period of time in each experiment. The gross weights of absorption subsystem were weighed at the beginning and the end of each experiment. The value of theoretical yield of CO₂ was *via* dripping the volume amount of Na₂CO₃. Deionized water was dripped into system for letting the gross liquid addition amount be up to 70 mL each experiment.

Conditions optimization experiment

Desiccant: The 4 kinds of desiccant were filled in the bottles of drier subsystem and then ran the system 3 times for 10 h each time in turn. 70 mL deionized water was dripped into system every time and the soda lime granular was used to be the absorbent. Flow velocity region was controlled in 10-13 mL/min.

Average weight increment $\Delta\bar{m}$ was used to be the assessment index of effect quality of desiccant. The less the value of $\Delta\bar{m}$ is relatively, the better the drying performance of desiccant.

Responsibility and absorption volume of absorbent: Three kinds of absorbent were filled in the bottles of absorption subsystem respectively and then ran the system 3 times for 3 h each time in turn. A series of different weights of CO₂ were generated for per series of testing of using one same absorbent and CaCl₂ was used to be the desiccant. Flow velocity region was controlled in 10-13 mL/min.

Responsibility was defined as the real weight increment corresponding to theoretical value. Theoretical value region was 0.0934-0.934 g.

Absorption volume was defined as the real weight increment corresponding to big theoretical value. Theoretical values were set as 0.25, 0.5, 1, 2, 3 times as the CO₂ yield of 10 g microcrystalline cellulose been degraded completely.

Flow velocity region: Real weight increments of different theoretical yields of CO₂ were measured in different flow velocity regions for 3 h each time. The soda lime granular was used to be the absorbent and CaCl₂ was used to be the desiccant.

RESULTS AND DISCUSSION

Desiccant: Although result of using 3A molecular sieve had the minimum value (Table-1), it is a broad-spectrum gas,

Desiccant	Amount (× 2)	$\Delta\bar{m}$ (g)	Desiccant	Amount (× 2)	$\Delta\bar{m}$ (g)
98 % H ₂ SO ₄	500 mL	0.17	CaCl ₂	500 g	0.04
Silica gel	500 g	0.24	Molecular sieve	500 g	0.02

including CO₂, descant and may absorb the measured gas. CaCl₂ is the best choice of the 4 desiccants.

Absorbent: The responsibility curve of soda lime granular has the best liner correlation (highest value of related coefficient) and the volume curve of soda lime granular has the minimum MSE. Soda lime granular is the best choice of the 3 absorbents (Fig. 1, Table-2).

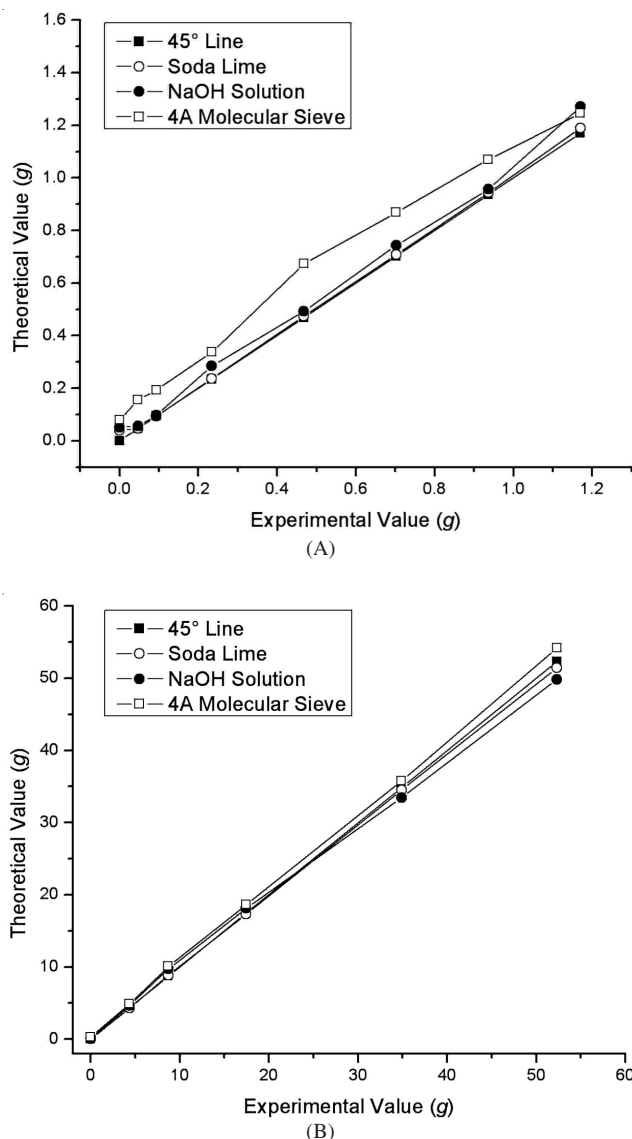


Fig. 1. Plot-plot images of theoretical and experimental values of absorption (A) and volume (B)

Flow velocity region: There is a mutation between the results and MSE of flow velocity 22.1-30.5 mL min⁻¹ observed from Fig. 2 and Table-3, respectively. These experimental evidences can support the conclusion that the best flow velocity for the method operation should be in the range of 5.2-22.1 mL min⁻¹.

Absorbent	Amount (× 4)	Responsibility related coefficient	Volume MSE
Soda lime granular	117-132 g	0.9991	0.1661
NaOH solution	150 mL	0.9968	1.1937
4A molecular sieve	140-152 g	0.9901	0.2148

Flow velocity (mL min ⁻¹)	MSE (10 ⁻⁶)	Flow velocity (mL min ⁻¹)	MSE (10 ⁻⁶)
5.2-6.7	8.9536	21.1-22.1	28.8
9.8-11.1	10.1	29.5-31.2	921
15.3-17.1	60.2	41.0-44.3	1321

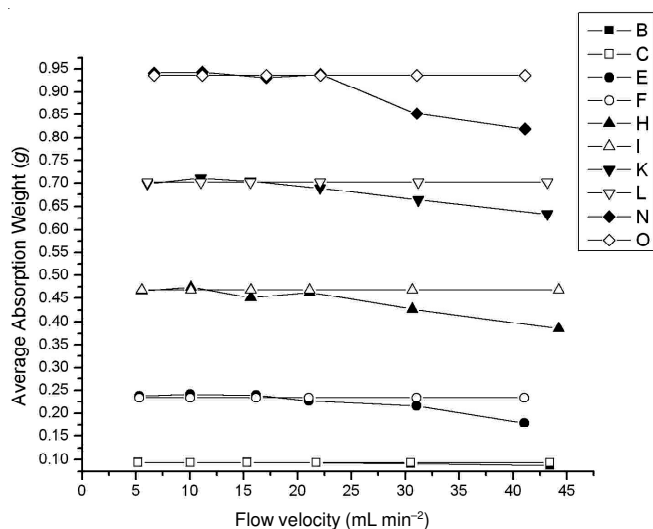


Fig. 2. Plot-plot images of theoretical and experimental values of flow velocity

Conclusion

The results obtained in these works that the improvement and conditions optimization show that it is possible to perform the successive determining of CO₂ for the determination of ultimate aerobic biodegradability of plastic materials under controlled composing conditions. And the cost of agents and labor is lower than other methods known significantly. Therefore, the system could be applied in large scale. The kind of desiccant, CaCO₃, is neutral and can be used very widely to dry gas except for the substance with activate hydroxyl groups. Its gas resistance is low and water absorption efficiency is enough for common industrial use. The system can be not only used in the degradation but also other conditions which need gas successive determination in long period *via* changing the absorbent. Those results can be a basement of automating the CO₂ and other gas production measurements.

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