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Development and Validation of a Simplified Nordmann Titration Method for Monitoring Volatile Fatty Acids in Anaerobic Digestion Processes

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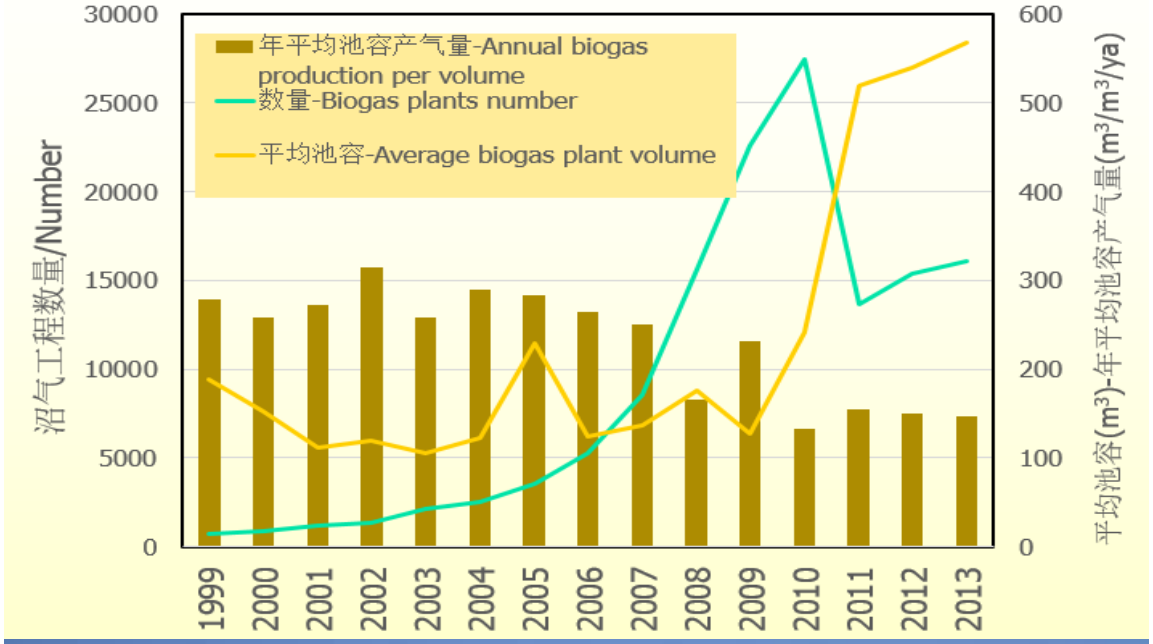
Rapid Development of Anaerobic Digestion Worldwide for Bio-waste Treatment



Complexity of Microbial Anaerobic Digestion Process

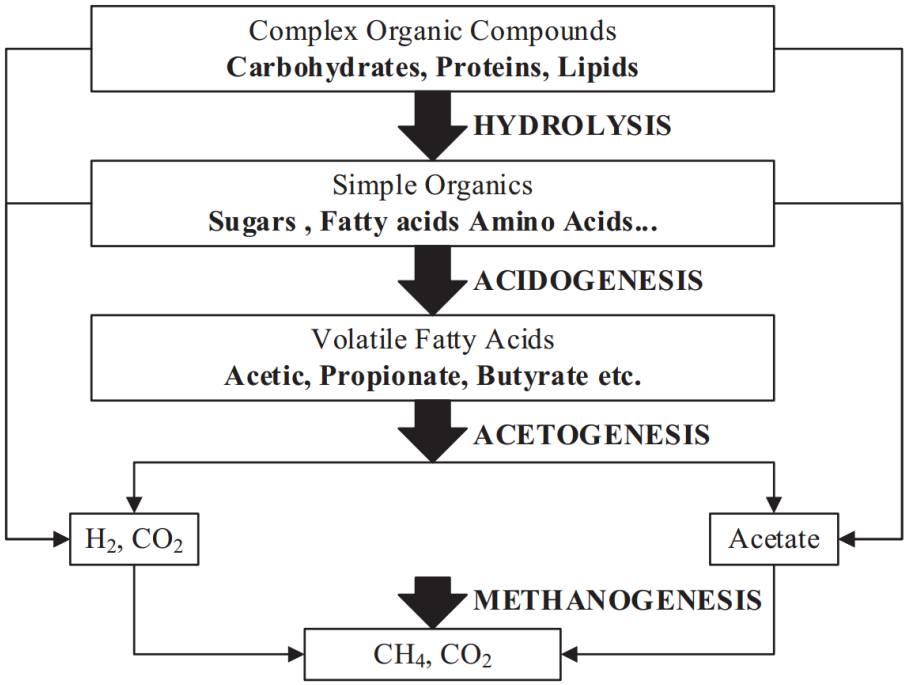
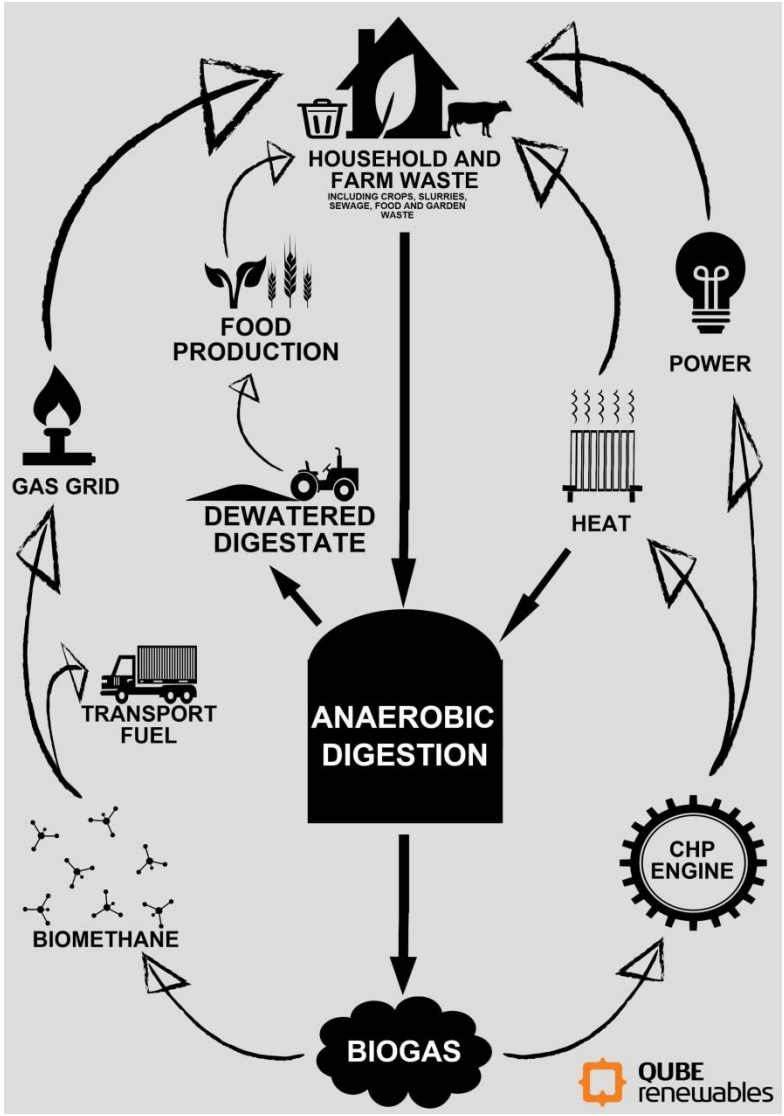
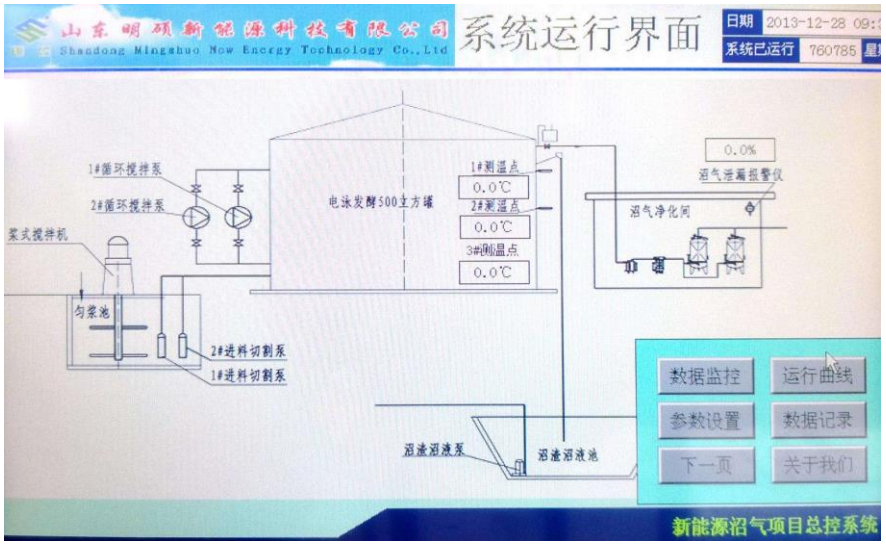


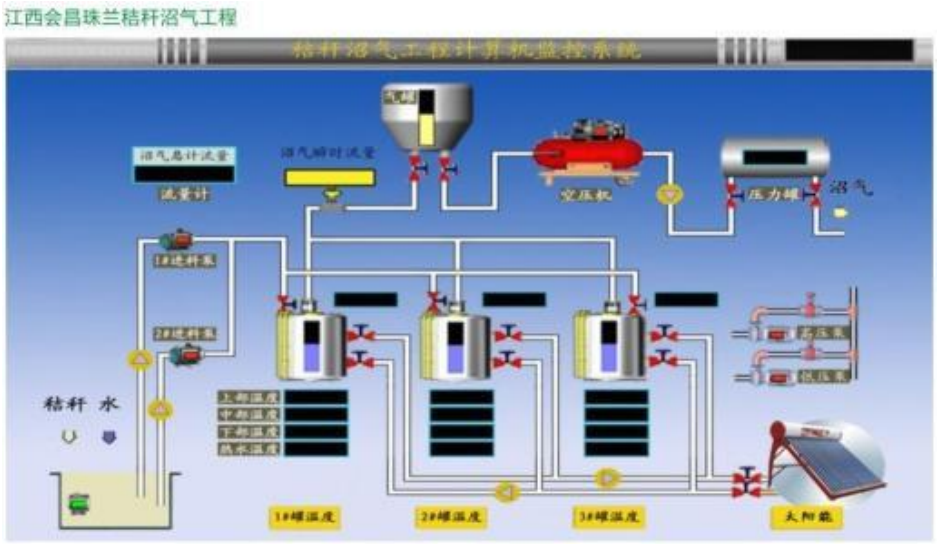
Figure 1. Simplified overview of the AD process; adapted from Drosg, 2013.

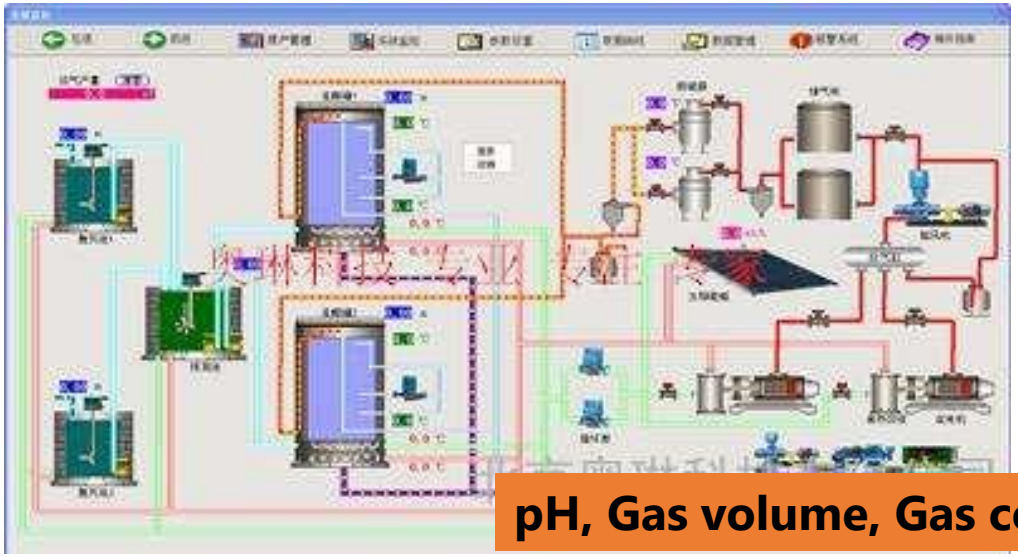
Although AD technology has been developing for two centuries, poor performance and system failure are still frequent in full-scale systems mainly due to inadequate operational management and lack of process monitoring and control.

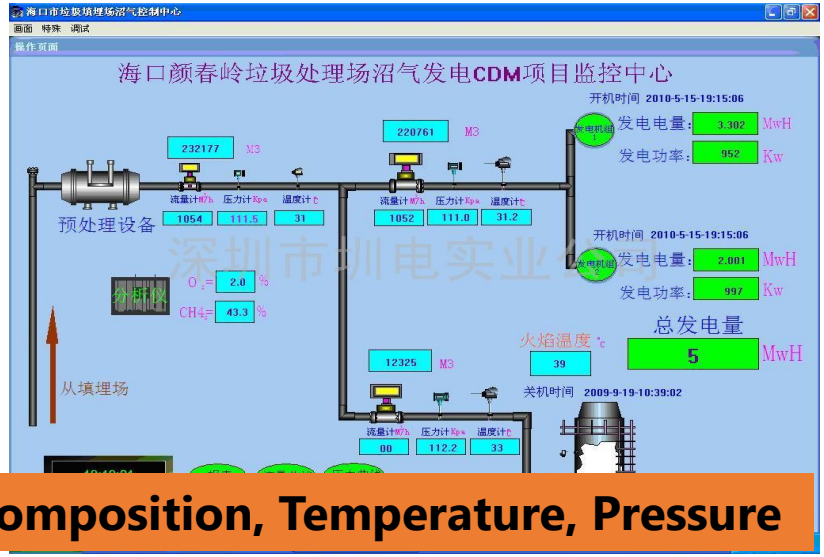


Current Monitoring Status of Anaerobic Digestion Plants in China



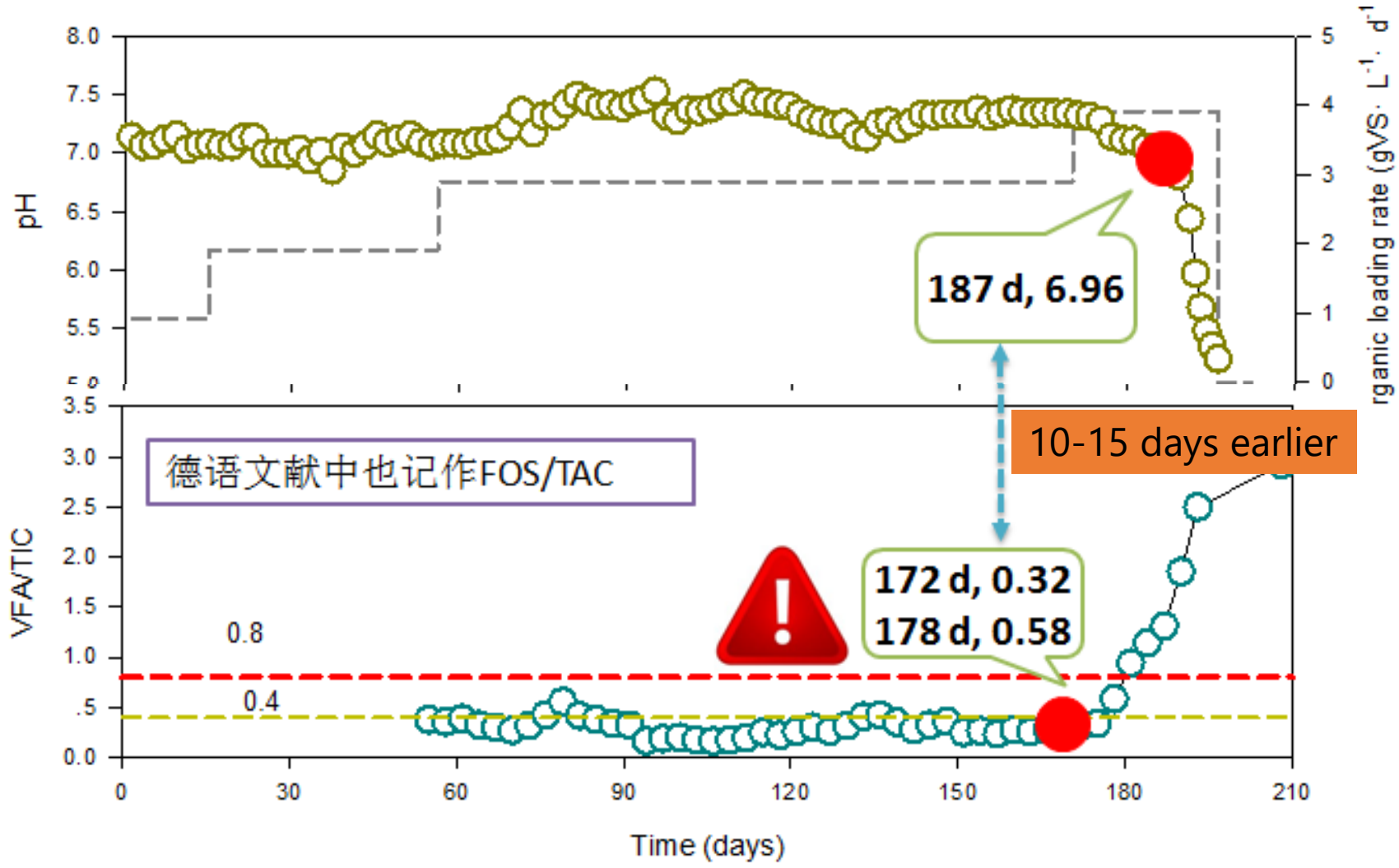






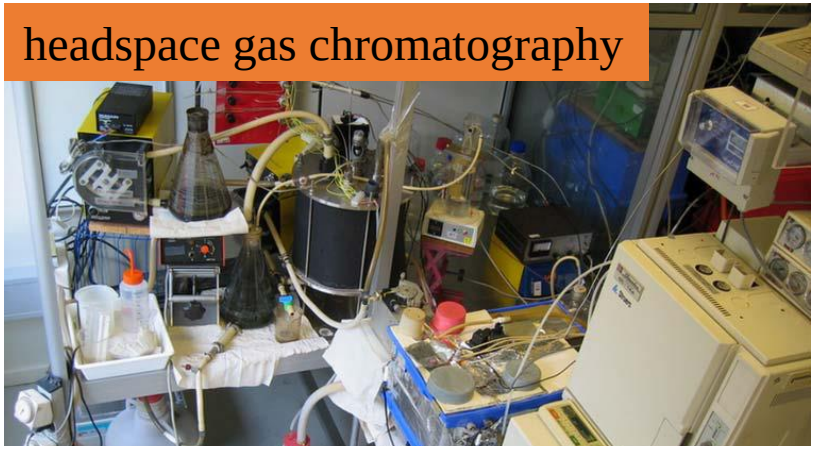
pH, Gas volume, Gas composition, Temperature, Pressure

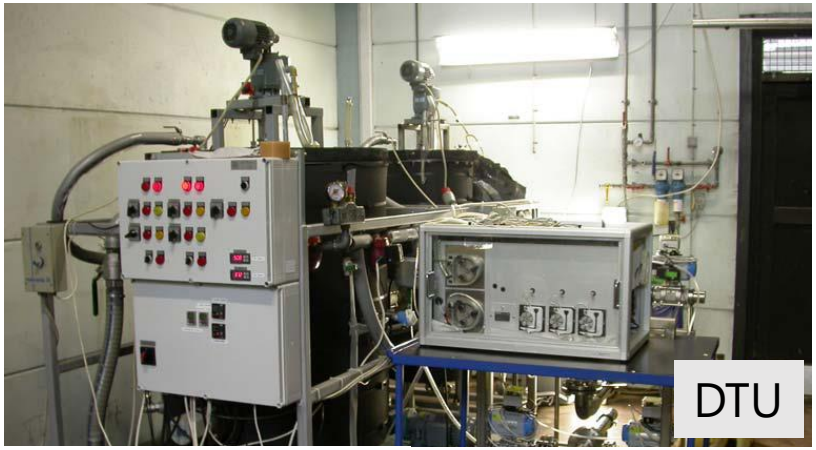
Current Monitoring Status of Anaerobic Digestion Plants in China

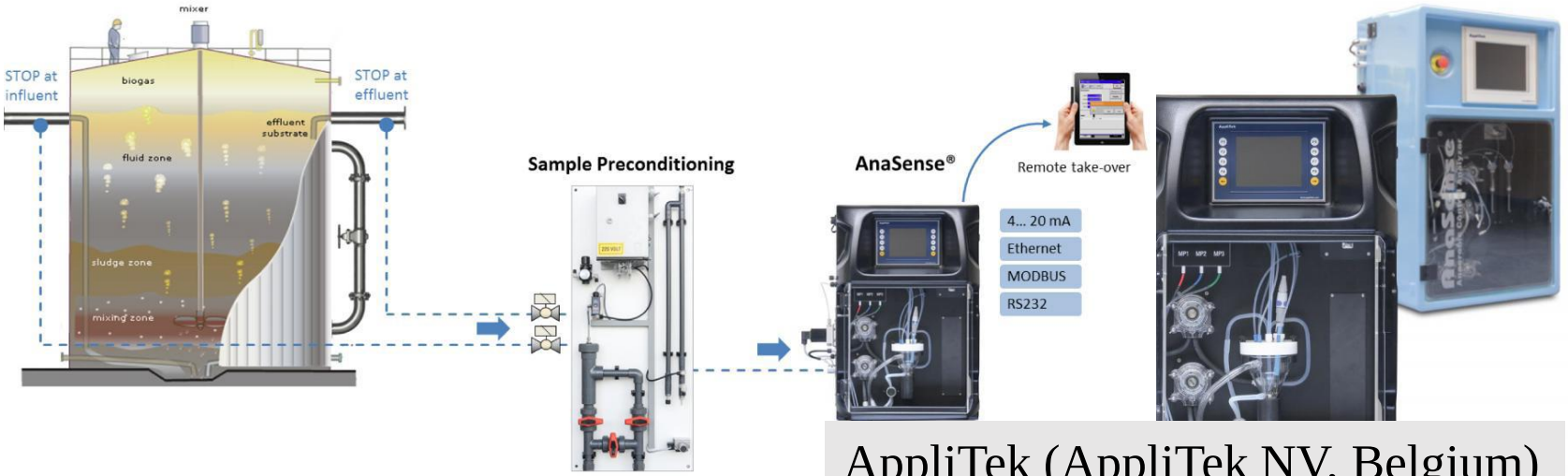


Advanced equipment is really good, but maybe quite expensive for farmers

headspace gas chromatography







AppliTek (AppliTek NV, Belgium)

[1].Boe, K., D.J. Batstone and I. Angelidaki, An innovative online VFA monitoring system for the anerobic process, based on headspace gas chromatography. Biotechnology and bioengineering, 2007. 96(4): p. 712-721.

Titration methods are relatively simple, cost effective, robust

Table 1. Techniques for determination of VFAs in AD processes.

Techniques	Advantages/Disadvantages
Distillation	- High quantification limit and low precision [23].
Colorimetric test	- Complex and vulnerable to interference [23].
Chromatography (GC, Head Space GC, HPLC)	- High precision and accuracy [16]; - Measurement of individual VFAs concentration [15, 17]; - Time consuming, require specialized equipment and skilled operators [14].
Spectroscopy (Fluorescence Spectroscopy, IR Spectroscopy, NIR Spectroscopy)	- Online monitoring [22]; - High accuracy and sensitive [21]; - Require specialized equipment and maintenance [18–20].
Titration	- Simple, cost-effective, robust [8]; - TVFAs concentration measurement [8].

Time consumption and low precision

Overview of Classification of Titration Methods Developed in the Past Decades

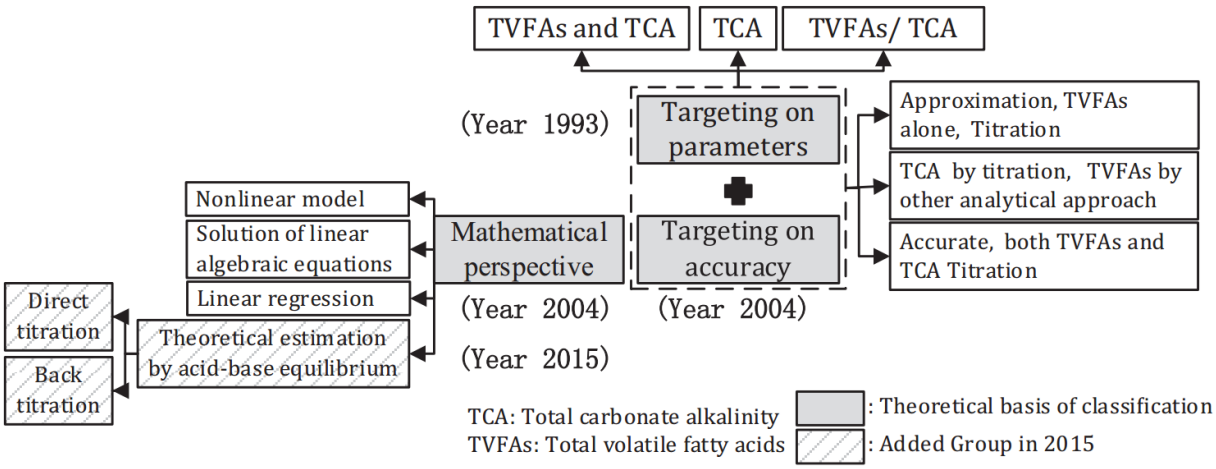


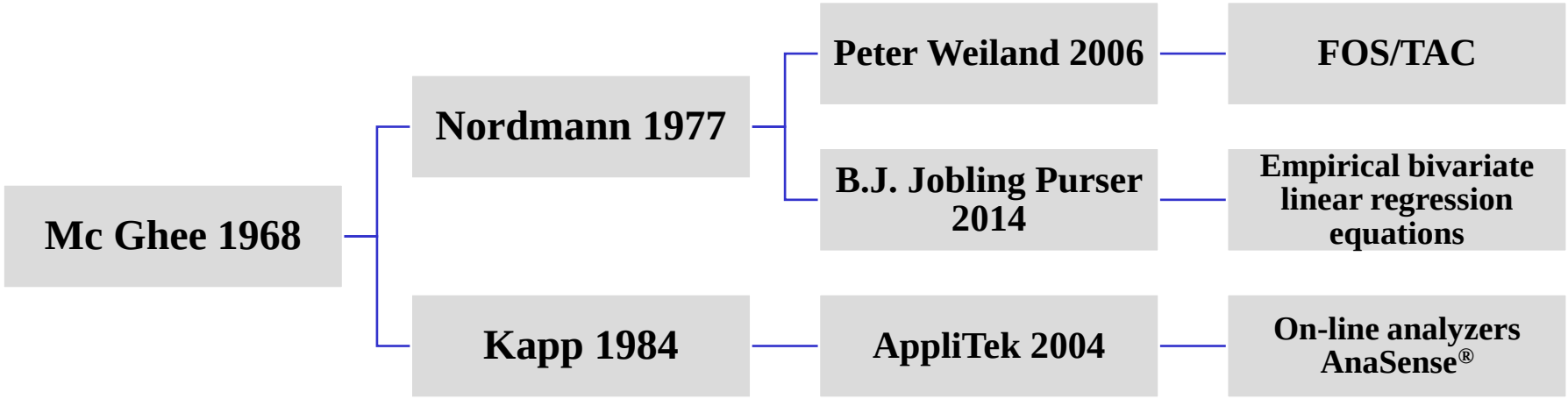
Figure 3. Overview of the classification of titration methods developed in the past decades.

Table 4. Titration methods belonging to the group of linear regression.

Author	Year	Parameter	pH points	Characteristics	Ref.
McGhee	1968	TVFAs	5.0, 4.0	Rough approximation; gives the TVFAs concentration changes	[39]
Nordmann	1977	TVFAs, TCA	5.0, 4.4	Titration from initial pH to 5.0 for TCA; titration between pH 5.0 and 4.4 for TVFAs	[49]
Kapp	1984	TVFAs, TCA	Initial pH, 5.0, 4.3, 4.0	Four-point titration; algorithm based on empirical relations	[40]
Møller and Ward	2011	TVFAs	Initial pH, 5.1, 3.5	A purely empirical linear model; TVFAs range from 38 up to 30 056 mg L^{-1}	[32]
Purser et al.	2014	TVFAs	5.75 and 4.3, 5.0 and 4.4	Empirical bivariate linear regression equations	[1]

Hao Sun, Shubiao Wu*, Renjie Dong. Monitoring Volatile Fatty Acids and Carbonate Alkalinity in Anaerobic Digestion: Titration Methodologies [J]. Chemical Engineering & Technology. 2016. 39(4): 599-610.

Nordmann method is a very popular method with very simple procedures



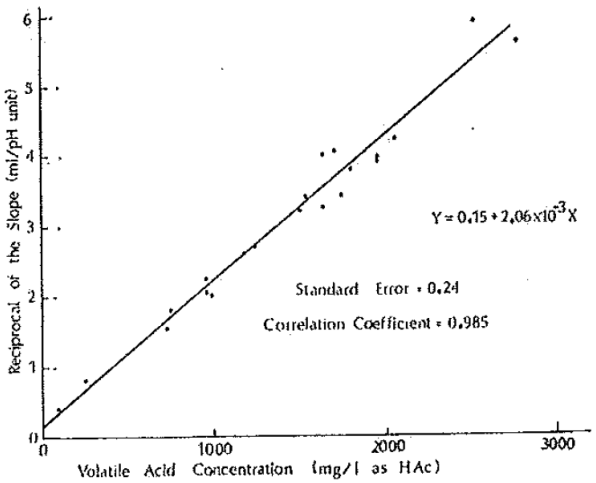


Figure 8: Variation of the slope of the titration curve for cleared digester mixed liquor.

$$\text{(FOS)}\ \ \text{VFA} = [V_{5-4.4} \times 1.66 - 0.15] \times 500\ \text{mg HAc/L}$$

$$\text{(TAC)}\ \ \text{TIC} = V_5 \times 250\ \text{mg}\ CaCO_3/\text{L}$$

Nordmann (1977) proposed a similar titration method just using two endpoints to estimate carbonate alkalinity, VFAs, and the VFA/alkalinity ratio, simultaneously.

(Adam et al., 2015; Allen et al., 2014; Browne et al., 2014; Kim and Kafle, 2010; Pagés-Díaz et al., 2015; Rugele et al., 2015; Schwede et al., 2013)

The Goal of This Study

However, **differences** between VFAs measured using the Nordmann method and lab-instrument methods have been noted in few studies (Kujawski and Steinmetz, 2009; Purser et al., 2014). Consequently, the Nordmann method is better and more representative when developing a new method, based on the original procedure of Nordmann titration method, as it achieves **considerable accuracy with reduced or simplified sample pretreatment**.

- undertakes the development and validation of a simplified Nordmann titration method for VFA measurement.
- The influence of ion interfering and solid interfering subsystems in titrated samples using the Nordmann titration method was first analyzed.
- The relationship between the different VFAs measured by gas chromatography and the traditional Nordmann method was then correlated with the content of total removal solids in the titrated samples.

The Goal of This Study

Generally, the system **interfering with the determination of VFAs** in the AD process is very complex, often containing various interfering components, but can be classified into two categories: **ion interfering systems** and **solid interfering systems**.

Ion interfering systems comprise several subsystems of bicarbonate, sulfide, phosphate, ammonium, and others.

These ion interfering subsystems participate in a reaction with the titrant, affecting titrant consumption during the titration process, thereby influencing titration results to different extents.

Influence of ion interfering subsystems

Titrant consumption during the titration process was calculated theoretically to investigate the influence of ion interfering subsystems in the Nordmann method.

Table 1. Titrant consumption from pH 5 to pH 4.4 by theoretical calculation

Concentration	HCO_3^-	Ac^-	NH_4^+	HS^-	H_2PO4^-
1	0.0125	0.0725	0.0060	0.0079	0.0060
5	0.0386	0.3384	0.0060	0.0156	0.0060
10	0.0712	0.6709	0.0061	0.0253	0.0060
50	0.3320	3.3306	0.0064	0.1027	0.0063
100	0.6579	6.6553	0.0068	0.1994	0.0066
500	3.2657	33.2524	-0.0102	0.9730	0.0089
1000	6.5255	66.4989	-0.0145	1.9400	0.0119

Titrant: 0.1 N H_2SO_4; $V_{solution}$: 20 mL; The unit of concentration is mmol/L.

Therefore, the influence of ion interfering subsystems on the titration results can be ignored.

Influence of solid interfering subsystems

Solid interfering system mainly includes subsystems of suspended solids (e.g., cellulose and hemicellulose) and precipitated solids.

The potentially important solid precipitants in anaerobic digesters include:

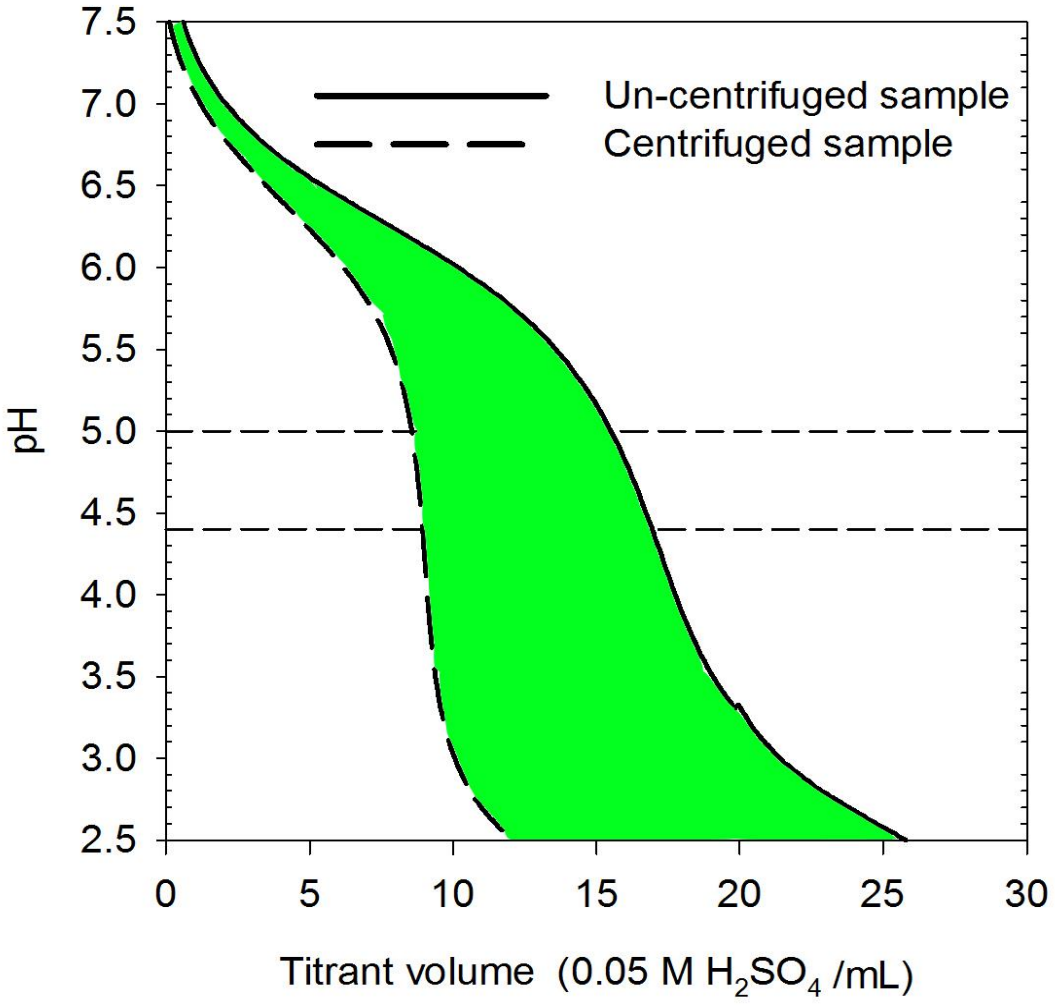
- calcium carbonate ($CaCO_3$, pKso=8.2–8.5)
- calcium phosphate ($CaPO_4$)
- magnesium carbonate ($MgCO_3$, pKso=7.5–8.2)
- metal sulfide precipitates (particularly FeS and Fe_2S_3)
- newberyite ($MgHPO_4$
- magnesium ammonium phosphate hexahydrate (struvite, $MgNH_4PO_4.6H_2O$) .

These suspended or precipitated solid subsystems can adsorb or react with titrant during the titration process, resulting in increased titrant consumption.

Influence of solid interfering subsystems

Firstly, two titration curves of one sample taken from a mesophilic AD plant, **with and without centrifugation** pretreatment, were compared by conducting a continuous titration process with an automatic titrator (ZDJ-5 China)

The results clearly showed that the thoroughly mixed sample without pretreatment clearly increased the titrant consumption in comparison with the centrifuged sample.

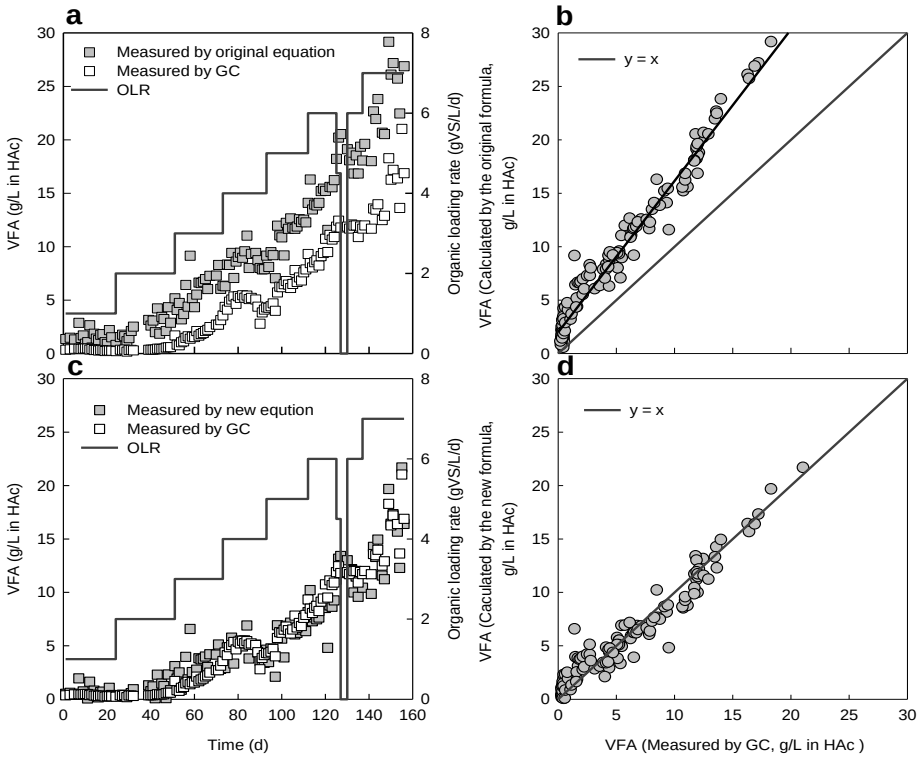


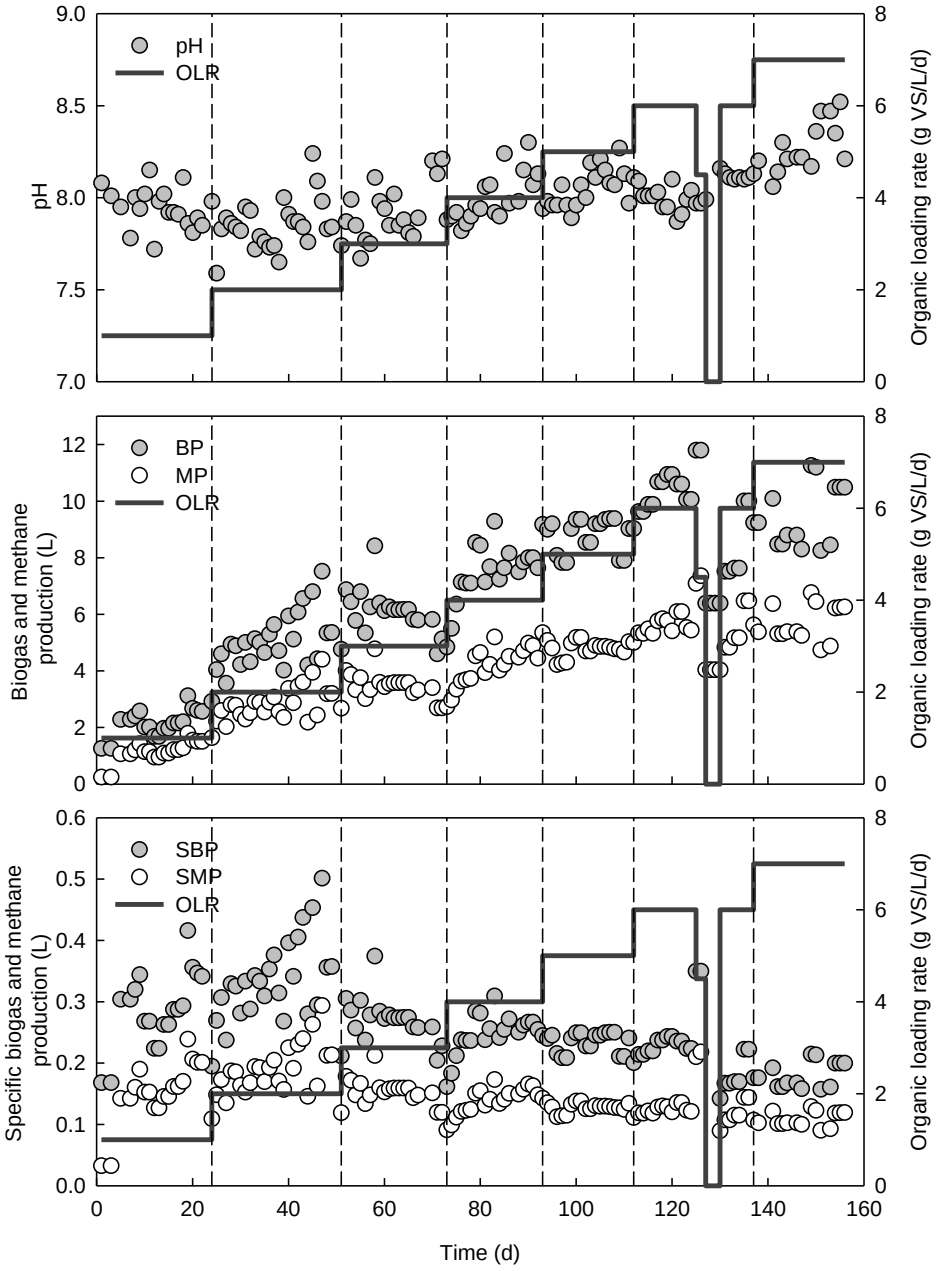
Development of a simplified Nordmann method

No Pretreatment

TS measurement

Validation of the simplified Nordmann method





Conclusions

- The influence of ion and solid interfering subsystems on the VFA measurements accuracy was discussed. The content of TS in titrated samples was found to be the main contributing factor.
- A high linear correlation was established between the TS contents and differences in VFA measurements by the original Nordmann equation and the GC method.
- A simplified Nordmann method was developed and finally validated using a semi-continuous experiment with various organic loadings. The good fitting of the results obtained by this method compared with GC results strongly supported the potential application to VFA monitoring in the AD process.
- This new method could be used for on-site AD plant operators

Acknowledgements

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北京市科学技术委员会
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National Key Technology R&D Program

Also thanks to my colleagues



生物能源环境科学与技术研究室

Bioenergy and Environment Science & Technology Laboratory

谢 谢!

Thanks very much

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