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Doctor Thesis

Anaerobic Methane Production from Separated Liquid Produced in Hydrothermal Treatment of Sewage Sludge

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2014

TOKYO INSTITUTE OF TECHNOLOGY

Interdisciplinary Graduate School of Science and Engineering

Department of Environmental Science and Technology

Anaerobic Methane Production from Separated Liquid Produced in Hydrothermal Treatment of Sewage Sludge

Table of Content

General introduction 1

1.1 Background 1

1.2 Status of sludge disposal and treatment in China 1

1.2.1 Sludge generation in China and its disadvantages 1

1.2.2 Treatment and disposal of sludge in China 3

1.2.3 Characteristics of sludge in China and the challenges in treatment and disposal technologies 8

1.3 Current research on sludge hydrothermal treatment process 9

1.3.1 Principle and characteristics of sludge hydrothermal treatment process 9

1.3.2 Process and application status of sludge hydrothermal treatment 10

1.3.3 Current situation of sludge hydrothermal treatment process 20

1.3.4 Problems of sludge hydrothermal treatment technology 26

Chapter 2 39

Study on Potential of Biochemical Methane Production from Separated Liquid Produced from Sewage Sludge by the Hydrothermal Treatment under Different Operating Conditions 39

2.1 Introduction 39

2.2 Methods and materials 39

2.2.1 Experimental facility 39

2.2.2 Sewage Sludge 42

2.2.3 Experimental procedure 43

2.2.4 Analytic methods 44

2.3 Results and discussions 44

2.3.1 Component of the separated liquid under different hydrothermal treatment conditions 44

2.3.2 Biogas production from the separated liquid 51

2.4 Conclusion 60

References 60

Chapter 3 62

Performance of Anaerobic Digestion of Separated Liquid Produced from Sewage Sludge by Hydrothermal Treatment 62

3.1 Introduction 62

3.2 Experimental facility and measurements 63

3.2.1 Large-scale facility 63

3.2.2 Experimental separate liquid samples 67

3.2.3 Experimental procedure and measurement 68

3.2 Operating characteristics and effects evaluation of EGSB in a commercial plant 69

3.2.1 Influent and effluent COD changes of the EGSB reactor 69

3.2.2 Influent and effluent NH4+-N changes of the EGSB reactor 71

3.2.3 VFA changes of the EGSB reactor 73

3.2.4 Daily biogas changes with different Influent COD 75
3.4 Conclusion 78
References 78

Chapter 4 79

Energy and Mass Balance Analysis of Commercial-scale Hydrothermal Plant 79
4.1 Introduction 79
4.2 Experimental facility and procedure 79
4.3 Analysis of operative condition of the commercial-scale project 81
4.3.1 System design specifications 81
4.3.2 Effect of the hydrothermal treatment time on the operation condition 81
4.3.3 Material and energy balances 82
4.4 Process design improvement and energy-saving of the sludge hydrothermal system 85
4.4.1 Energy saving measures for the sludge hydrothermal system 86
4.4.2 Evaluation of the reaction time of each batch in the energy-saving sludge hydrothermal system 87
4.5 ERR calculation and effect contrast 92
4.6 Conclusion 96

Chapter 5 99

Acknowledgements 104

Chapter 1

General introduction

1.1 Background

The statistics of the Ministry of Housing and Urban-Rural Development of the People's Republic of China show that 1,992 urban sewage treatment plants have been constructed and that 28 billion cubic meters of sewage have been disposed. This amount of disposed sewage has produced about 20.05 million tons of sludge with 80% moisture content. According to incomplete statistics, only a fraction of urban sewage treatment plants adopt sludge treatment measures, such as sanitary landfill, land use, incineration, and building material utilization. However, most of these treatment and disposal measures are not standardized. When sludge is not effectively disposed, the pathogens, heavy metals, and organic pollutants found in sludge may cause secondary pollution to groundwater and soil and thus threaten environmental safety and public health [1].

In China, sewage treatment is developing at an unprecedented rate. However, a large portion of sludge is still disposed in landfills or simply discarded. If we do not find reasonable solutions for sludge disposal and treatment, land resources for stacking, discarding, and landfill purposes will continuously decrease. Similarly, the supervision of local environmental protection departments requires further strengthening. If these issues are not addressed, sludge disposal and treatment is bound to become a major problem.

1.2 Status of sludge disposal and treatment in China

1.2.1 Sludge generation in China and its disadvantages

Sludge production in sewage treatment plants in China is rapidly growing along with urbanization, the continuous development of social economy, and the improvement of sewage treatment capacity. The sludge treatment process is an important link that has been neglected for a long time. This disregard for such an essential process has significantly hindered sludge disposal in China. The lack of efficient techniques and the

unsound policy systems for sludge treatment and disposal have worsened sludge-related pollution. Fig. 1-1 shows the sewage sludge production in China.

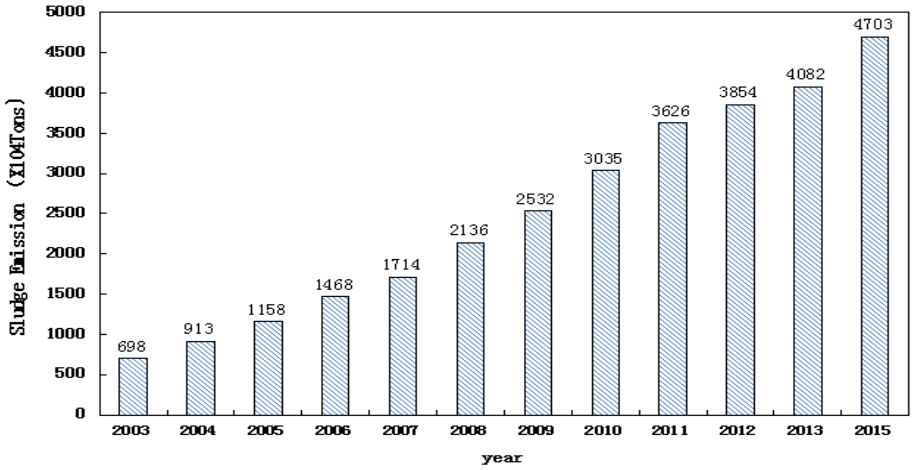

Fig. 1-1 Sewage sludge production in China

The sludge production has increased year after year. If the sewage sludge is discharged directly into the environment without appropriate treatments, it will pollute the environment and threaten people's lives. The regional imbalance of the economic development in the country has a significant impact on urban sludge discharge. Currently, sewage sludge discharge is mainly concentrated in the central region. The municipal sewage drainage system, where sewage and rainwater meet, generates sludge with high solid content and low organic matter content, particularly during anaerobic digestion; this sludge causes the severe abrasion of drying equipment [1-3]. The monitoring results of a typical urban sewage treatment plant for three consecutive years show that sludge is mainly composed of more than 60% inorganic compounds and 36% organic compounds on average [1-4]. Most heavy metals in urban sludge are non-biodegradable and may accumulate in biological bodies, leading to the heavy pollution of the ecological environment. Therefore, heavy metals are the most harmful components of sludge.

Mechanical dewatering is widely used in sewage sludge treatment plants for sludge dehydration; generally, dewatered sludge has 75% to 85% moisture content, as demonstrated by its adhesive-like appearance [1-5]. Sludge has four “high characteristics”: high moisture content, high organic matter content, high heavy metal content, and high bacteria content. Regardless of where it is disposed and whether it is disposed moderately or indiscriminately, sludge will inevitably pollute the air, soil, and water and seriously endanger human health and environmental safety. We will pay a high price when subjected to secondary pollution.

1.2.2 Treatment and disposal of sludge in China

Three main methods can be employed for sewage sludge treatment at different processing stages: sludge thickening, sludge stabilization, and sludge mechanical dewatering. Table 1-1 presents the main sludge processing technologies in China.

Table 1-1 Main sludge processing technologies in China

Number	Sludge treatment process	Proportion of application (%)
1	concentration tank–final disposal	36.50
2	two-layer sedimentation tank–final disposal	1.35
3	two-layer sedimentation tank–sludge drying bed–final disposal	2.70
4	concentration tank–wet deposition pond–final disposal	14.87
5	concentration tank–sludge drying bed–final disposal	4.05
6	contact oxidation tank sludge–sludge drying bed–final disposal	1.35
7	digester–sludge drying bed–final disposal	1.35
8	concentration tank–two-phase digester–wet deposition pond–final disposal	1.35
9	concentration tank–twin-stage digester–final disposal	2.70
10	concentration tank–digester–wet deposition pond–final disposal	6.76
11	concentration tank–digester–sludge drying bed–final disposal	1.35
12	concentration tank–digester–mechanical dewatering–final disposal	9.46
13	twin-stage digester–mechanical dewatering–final disposal	1.35
14	aerobic digestion–concentration tank–mechanical dewatering–final disposal	2.70
15	concentration tank–anaerobic digestion–concentration tank–mechanical dewatering–final disposal	1.35
16	concentration tank–twin-stage digester–mechanical dewatering–final disposal	1.35
17	concentration tank–mechanical dewatering–final disposal	14.87

In the sludge thickening process, 72% of the application used is the gravity concentration technology. Under sludge stabilization, 86% of the application used is the anaerobic digestion technology. In the sludge dewatering process, the belt filter press dewatering technology is predominantly used. Sludge treatment in most sewage treatment plants in China is based on a single mode, that is, concentration–dehydration–landfill or farmland.

Sludge disposal techniques include greening, landfill, landfill with garbage,

incineration, and agricultural land uses. Landfill is the main form of sludge disposal in China (about 65%), followed by agricultural land uses (15%), landfill with garbage (3%) and incineration (3%). At present, 11% of the sludge disposal modes in China remains unreasonable. These sludge disposal techniques can potentially harm the environment [1-6]. Fig. 1-2 shows the sludge disposal proportions in China.

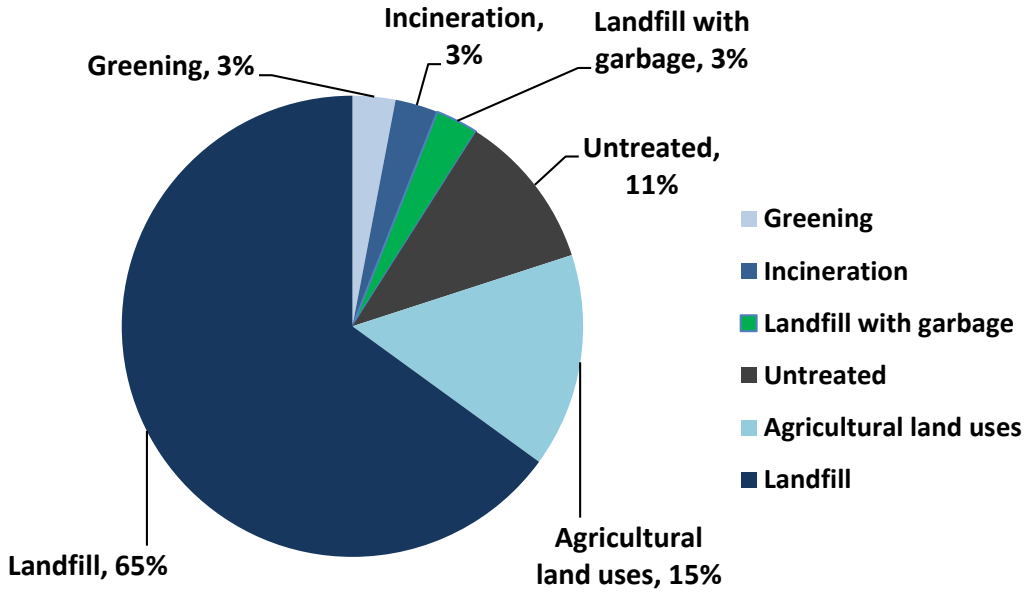

Fig. 1-2 Sludge disposal proportions in China

1.2.2.1 Main sludge treatment technologies in China

(1) Sludge thickening process

In sludge thickening, a part of water is removed from sludge through the gravity or mechanical means to reduce sludge volume. The moisture content of sludge ranges from 94% to 96% after sludge thickening. The conventional methods for sludge thickening are the gravity thickening, the mechanical thickening, and the flotation thickening. At present, the gravity thickening is the main sludge thickening technology in China [1-7].

The gravity thickening essentially involves compression precipitation and can be categorized as the batch type and the continuous type. The batch gravity thickening is mainly used for small-scale sewage treatment plants, whereas the continuous gravity thickening is used for full- or medium-scale sewage treatment plants. The gravity thickening features simple process technology, equipment structure, and operation management. However, this technique leaves a large carbon footprint and is carried out in unsanitary conditions. Such drawbacks cannot be ignored. Sludge that is left unstirred in

an aeration tank undergoes anaerobic digestion. The floating sludge in turn affects sludge thickening. After the gravity thickening, the solid content of sludge remains low. Consequently, the volume of subsequent processes, capital investment, and operation cost increase. The gravity thickening is particularly limited to waste-activated sludge disposal. Generally, solid content does not exceed 4% after sludge thickening.

The flotation concentration can be divided into the following categories according to the bubble formation: the pressure dissolved air floatation, the biological dissolved air flotation, the cavitation air flotation, the vacuum flotation, the chemical flotation, and the electroflotation. In sewage treatment, the pressure dissolved air flotation process is widely used to thicken waste-activated sludge in urban sewage treatment plants. The biological dissolved air flotation process for the concentration of activated sludge also has many applications. Meanwhile, the applications of the cavitation air flotation process and the other flotation processes for sludge thickening have not been reported.

The mechanical thickening can be divided into the centrifuge thickening, the belt thickener thickening, and the drum or the screw thickener thickening. The footprint of the centrifuge thickening is small, the cost is low, and no foul odor is generated during operation. This process can also avoid the secondary release of phosphorus in phosphorus-rich sludge, thus improving the total phosphorus removal rate of the system. However, the running cost and the mechanical repair cost for the centrifuge thickening are high, and this method is rarely used for sludge thickening. Nevertheless, the centrifuge thickening can be used to treat waste-activated sludge. The belt thickener thickening and the drum or the screw thickener thickening processes are mainly carried out in the thickening section of the integral equipment for sludge concentration and dehydration.

(2) Sludge Stabilization Process

The sludge stabilization process reduces the water and organic contents of sludge and renders the solids suitable for reuse or final disposal. The purpose of sludge stabilization is to reduce pathogens, eliminate offensive odors, damage the cell wall, and inhibit, reduce, or eliminate the potential for putrefaction. The methods for sludge stabilization include the anaerobic digestion, the aerobic digestion, and so on. Large wastewater treatment plants (WWTPs) generally use the anaerobic digestion technology [1-8].

The anaerobic digestion has the advantages of low energy consumption, low processing cost, recyclable energy, etc. Thus, this process is widely used in China for sludge stabilization treatment. Some advanced technologies have been developed to improve the stability of the traditional anaerobic digestion and to overcome its

shortcomings, including its low rate of digestion, low processing efficiency, and long hydraulic retention time (HRT). These technologies include the two-phase anaerobic digestion, the anaerobic co-digestion of organic waste and sludge, and the sludge pretreatment with the anaerobic digestion. The two-phase anaerobic digestion process is divided into the acidogenic phase-operated thermophilic condition and the methanogenic phase-operated mesophilic condition. Under this process, the HRT is reduced by 40% with similar treatment results compared with the traditional anaerobic digestion. However, this process significantly reduces the engineering investment.

The aerobic digestion occurs in the extended aeration-activated sludge process. On the one hand, this process has the advantages of high efficiency, small processing facilities, low investment, low BOD concentration of supernatants, and odorless product. On the other hand, the process has its disadvantages, including its power requirement, which increases the operating cost. Furthermore, the small digested sludge output and the degree of degradation resulting from the significant effects of temperature cannot be ignored. Researchers have attempted to improve the anaerobic digestion process through thermophilic condition, ultrasound, new strain screening, etc. The results show that the improved anaerobic digestion process has a positive effect on the aerobic digestion.

Considering the drawbacks of the anaerobic and the aerobic digestion, some academics have proposed a new sludge stabilization process called micro-oxygen digestion. Based on batch lab and pilot dynamic experiments performed in a traditional activated sludge WWTP, Hu Yinghua studied the sludge digestion with a low dissolved oxygen concentration to reduce the energy consumption of the aerobic sludge digestion [1-54]. The results show that under a low aeration, sludge mixing is the key factor because insufficient stirring results in sludge sedimentation, which influences the digestive effect. This finding may be useful for the excess sludge treatment of medium- and small-scale WWTPs.

(3) Sludge Dewatering Process

Wastewater treatment via the precipitation process generates a considerable amount of sludge. Even after the enrichment or digestion process, the moisture content is still as high as 96%. Given the difficulty in dealing with a large volume of sludge, sludge must be dewatered to increase solid content. This dewatering process reduces the sludge pile footprint. Typically, large- and medium-scale WWTPs employ a mechanical dewatering process, which can be divided into the vacuum filtration, the filter press dewatering, and the centrifugation according to the dehydration principle. Most domestic WWTPs use filter and centrifugal dewatering machines [1-9].

Most of the early WWTPs used vacuum filtration dewatering machines. However, the moisture content of sludge cake remains high after the dehydration. The dewatering device makes loud noises and occupies a large area, and its construction and performance cannot be improved further. Therefore, this device has rarely been used since the 1980s.

The filter press dewatering machine comes in the form of a plate and frame filter press dewatering machine and a belt filter press dewatering machine. The plate and frame filter press dewatering machine achieves the lowest sludge moisture content and has thus been widely used in sludge treatment. However, this machine operates intermittently, has a low operating efficiency, involves complex operation, and requires heavy maintenance. Thus, it is only used in cases that require low moisture content. Meanwhile, the belt filter press dewatering machine has also been widely used. The device applies pressure on the filter cloth, and the pressure and the tension from the filter cloth causes sludge dewatering. Hence, the filter cloth requires frequent cleaning. In addition, washing the filter cloth needs a large amount of water, which burdens the sewage treatment process and renders the dehydration effect unsatisfactory.

The dehydration effect of the centrifugal dewatering equipment is better than that of other machines. However, the device consumes a large amount of power and generates loud noises. The major drawback of this device is that it is difficult to maintain. Accurately grasping the shaft balance is particularly challenging. A balance deviation in the axis may cause equipment damage.

1.2.2.2 Main sludge disposal technologies in China

A typical sludge disposal process involves landfill disposal, composting, and incineration [1-10]. Sludge landfill disposal is performed using the trench fill (narrow ditch/wide ditch), the flat landfill (mound landfill/layered landfill), and the diking methods. The application of these methods has the following requirements: the solid content of sludge should not be less than 35%, the shear strength should be higher than 25 kPa, and the permeability coefficient should range from 10^{-6} cm/s to 10^{-5} cm/s. The moisture content of dewatered sludge is generally about 80%. If the dewatered sludge is landfilled directly, operation becomes difficult, the leachate collection system becomes clogged, and the amount of leachate significantly increases.

Sludge composting has the following features: self-generated heat; high temperatures for long periods to achieve harmless operation without external heat source, to break down cellulose, to improve composting humification, and to increase the

effective nutrient; low capital cost; easy management; simple equipment; odorless product; loose texture; and low moisture content. However, the process requires a 35% solid content after mixing, which entails the use of a large number of materials. The practical processing ability of this technique is thus limited.

Incineration can combust the combustible components of sludge at high temperatures and eventually produce a stable slag. The advantages of incineration include volume reduction, weight loss rate, fast processing speed, safety, and the use of waste heat for power generation and heating. However, residues are generated after sludge incineration, the ash produces secondary pollution, and the processing cost is high. Furthermore, the sludge drying and incineration process entails high investment and operation cost, which limits the promotion and application of the technology.

Table1-2 Comparison of investment and operating costs of the different disposal methods for wastewater and sludge in China

Project	Investment cost ($\times10^4$ yuan/t)		Operating cost ($\times10^4$ yuan/t)	
	Sludge	Wastewater	Sludge	Wastewater
Landfill disposal	3–5.5	30–55	15–30	0.015–0.03
Mechanized composting	30	300	60	0.06
Drying and incineration	35–45	350–450	500	0.5

Table 1-2 shows the comparison of the investment and operating costs of the different wastewater and sludge disposal methods in China. The statistical results show that drying and incineration has the highest investment and operating cost, followed by mechanized composting and sludge landfill disposal. Most of the methods are completely safe, and all of them require a sludge moisture content of approximately 60%. Deep dewatering treatment is the key to solving the sludge disposal problem.

1.2.3 Characteristics of sludge in China and the challenges in treatment and disposal technologies

1.2.3.1 Characteristics of sludge in China

Mud characteristics determine the technical route of sludge treatment and disposal. The development of the wastewater treatment industry draws much foreign advanced technologies and experiences. Therefore, sludge treatment, particularly the characteristics

of sludge in China, must be investigated further.

In China, the municipal wastewater piping system promotes the confluence of rainwater and wastewater. Hence, the sludge produced in China is characterized by high moisture content, low organic matter content, high sediment concentration, and large sludge flow. Low organic matter content is not conducive to digestion, high sediment concentration seriously wears out the drying equipment, and large sludge flow exacerbates equipment corrosion. Simultaneously, high sediment concentration and low carbon content are not conducive to direct incineration.

1.2.3.2 Challenges in sludge treatment and disposal technologies in China

Considering the characteristics of sludge and the sludge treatment and disposal technologies in China, we can draw the following conclusions: the moisture content of sludge is the key factor in sludge treatment and disposal in China, and the existence of microbial cells and colloidal materials is the crux of the difficulties in sludge dewatering.

Technically, the starting point of landfill disposal and composting is a sludge moisture content of 60%. When the moisture content reaches 50%, the burning point is reached. In terms of space requirements, when the sludge moisture content decreases from 95% to 80%, the sludge volume is reduced by 75%; when the content decreases from 80% to 50%, the volume is reduced by 60%. The existence of a large number of microbial cells and organic colloids in sludge could hinder mechanical dewatering. Organic matter in sludge exists mainly in solid form, which reduces biodegradability. The major challenge in sludge disposal and treatment technologies is reducing the moisture content through deep dehydration. Once the moisture content decreases below 60%, the resource potential increases exponentially.

1.3 Current research on sludge hydrothermal treatment process

The sludge hydrothermal treatment process is a type of sludge thermal chemical treatment method. The use of hydrothermal technology for sludge pretreatment before the anaerobic digestion could improve the efficiency of the anaerobic digestion; achieve the objectives of sludge stabilization, reduction, and safety; and recover the available energy in the sludge to realize waste resource and application.

1.3.1 Principle and characteristics of sludge hydrothermal treatment process

The hydrothermal treatment process is usually performed in a closed container with

a certain volume. Through this process, the sludge colloidal structure is destroyed at a certain temperature and pressure. The microbial cell structure within the sludge is also destroyed, after which the intracellular organic matter is released. The insoluble macromolecular organic matter is then hydrolyzed into small molecular soluble organics, which are conducive to the anaerobic digestion. In summary, the hydrothermal treatment process is an effective sludge treatment technology.

Compared with other sludge treatments, the sludge hydrothermal treatment process has the following advantages:

(1) The cell material in the sludge is broken down to release the intracellular water after the hydrothermal pretreatment. The water molecules move fast after heating, the colloidal structure is destroyed, the viscosity of sludge is reduced, and the solid and liquid components are separated effectively. The process improves the dewaterability and settling performance of sludge.

(2) The organic matter in the sludge changes during the thermal hydrolysis process. In particular, the solid organic matter dissolves under hydrothermal conditions; thus, the organic matter can be utilized effectively by the anaerobic bacteria and then degraded into small molecular organic matter [1-11]. This process not only solves the bottleneck in sludge anaerobic digestion and greatly improves the performance of the anaerobic digestion and the biogas production but also reduces the amount of dry sludge from dissolved organic solids to some extent.

(3) The hydrothermal sludge treatment process can kill harmful microorganisms and renders sludge harmless [1-12].

(4) The water in sludge has no phase transition during the thermal hydrolysis process, thereby reducing energy consumption.

1.3.2 Process and application status of sludge hydrothermal treatment

1.3.2.1 Process and application status of sludge hydrothermal treatment abroad

(1) Porteous process

The Porteous process was invented in the 1930s and used for industrial applications in Halifax and Horsham, Britain, in 1939[1-13]. The flow of this process is as follows [1-14] (shown in Fig. 1-3): the sludge is fed into the heat exchanger and then delivered to the reactor after preheating to 160 °C. In the reactor, the preheated sludge reacts with steam at 180 °C to 200 °C and at 1.1 MPa to 1.8 MPa for 30 min to 60 min. After the reaction, the

hydrolyzed sludge is sent to the heat exchanger to preheat the input feed. The heat exchanger can effectively utilize the residual energy and reduce the hydrolyzed sludge temperature. The dewaterability of the hydrolyzed sludge is improved without the addition of chemical agents, and the moisture content can be reduced to 40%. The conditions greatly reduce sludge volume as well as the transportation and landfill costs. In the 1960s, the Porteous process was operated in 30 facilities in Europe. However, this process has some drawbacks, such as the highly concentrated supernatant generated from the hydrothermal process and high energy consumption. For example, after disposal by the Porteous process, the BOD_5 content of the supernatant of the sludge is 4,620 mg/L and could even reach as high as 20,000 mg/L. The total organic nitrogen content also reaches 1,110 mg/L. These conditions increase the difficulty of the subsequent process. With rising energy costs, the Porteous process was finally discontinued in the 1970s [1-15].

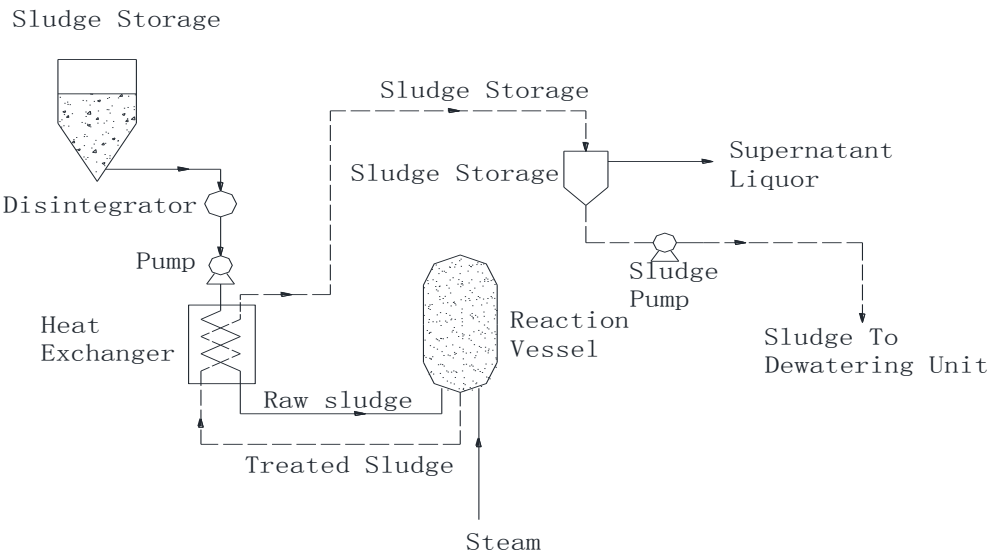

Fig. 1-3 Flow diagram of the Porteous process

(2) Zimpro process

The Zimpro process is a wet oxidation technique that was patented in the 1950s and applied in sludge disposal in the late 1950s. In the Zimpro process, sludge is treated using air as the oxidizing agent under high temperature (150 °C to 320 °C) and high pressure (10 bar to 220 bar). Under extreme temperature and pressure, more than 50% of organic matter is oxidized. The flow diagram is shown in Fig. 1-4. The Zimpro process rapidly developed in the 1960s. In 1961[1-16], the sludge disposal projects with handling capacities of 3, 5.6, and 200 $tDS \cdot d^{-1}$ were established in WI, WV, and Chicago, USA, respectively. Several years later, the process was applied in Rye, NY; Milwaukee; and in other places. During project implementation, the defects of the Zimpro process were noted; these

defects included the generation of odor and the corrosion of equipment because of high wastewater concentration. Consequently, all the projects adopting the Zimpro process broke down. In 1967, the Zimpro Company established a project in Levittown, PA, where the low pressure oxidation (LPO) process was applied to treat sludge for the first time. LPO is a technology used to improve sludge dewaterability. It is an improvement of the Zimpro process, as the processing temperature is lowered to below 200 °C. The LPO technology is still occasionally used in sludge treatment.

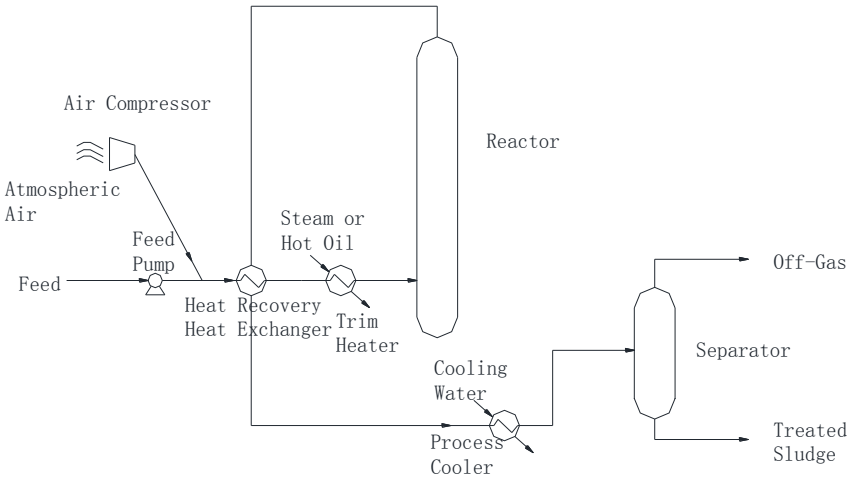

Fig. 1-4 Flow diagram of the Zimpro process

(3) Biothelys process

To reduce sludge volume and to effectively utilize the potential energy in sludge, Veolia Water in France established the Biothelys process, which combines the thermal hydrolysis pretreatment with the mesophilic anaerobic digestion. In this process, the sludge structure is destroyed, the anaerobic digestion time is shortened, and the biogas production efficiency is improved under high temperature and high pressure. Therefore, the Biothelys process centered on the hydrothermal treatment and the anaerobic digestion can effectively utilize the potential energy in sludge.

The Biothelys flow diagram is shown in Fig. 1-5. The hydrothermal treatment process is intermittently carried out in parallel. In general, the process is performed with two or three reaction tanks used alternately. The steam discharged by the first tank can be utilized to preheat the sludge in the next tank. Thus, a reaction tank performs three functions, namely, preheating, hydrothermal treatment, and decompression, to reduce investment cost. According to thermal hydrolysis conditions, a hydrothermal treatment cycle usually lasts 150 min to 160 min. Meanwhile, the biogas generated during digestion

can be used as fuel in the hydrothermal treatment. This condition in turn promotes energy self-balance in the hydrothermal treatment. The residual biogas can be used for cogeneration to maximize sludge productivity.

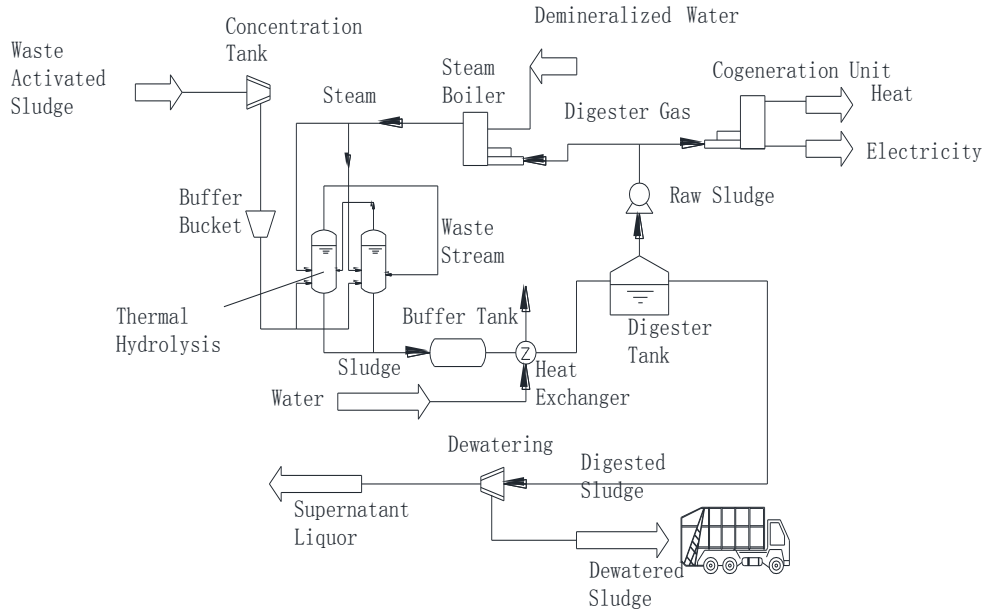

Fig. 1-5 Flow diagram of the Biothelys process

Since the introduction of the Biothelys process in 2006, six projects have adopted this process for construction or operation. France's Saumur [1-17] project is the first to adopt the Biothelys process to handle extended aeration sludge. The project has a capacity of 1,600 tDS·a^{-1} and uses two thermal hydrolysis reactors with a volume of 4.6 m^3. In this project, the sludge is fed into the mesophilic anaerobic digester after the thermal hydrolysis treatment at 160 °C for 30 min. The HRT of the anaerobic digestion is shortened to 15 d after treatment, and more than 45% of the volatile organic matter in the extended aeration sludge is removed. Today, the Esholt project established in 2013 is the largest one to adopt the Biothelys process. This project uses six thermal hydrolysis reactors with a volume of 22.3 m^3, operates in parallel, and has a maximum handling capacity of 32,730 tDS·a^{-1}. Table 1-3 shows current and future projects adopting the Biothelys process.

Table 1-3 Current and future projects adopting the Biothelys process

Project	Capacity (tDS/a)	Sludge properties	Reactor volume (m^3)	Digester volume (m^3)	Start-up
Saumur, France	1,600	Extended aeration sludge	4.6 × 2	500 × 1	2006
Chateau Contier, France	1,000	Extended aeration sludge + grease	3.1 × 2	300 × 1	2007
Le Pertuiset,	2,000	Extended	4.9 × 2	940 × 1	2008

France		aeration sludge			
Tergnier, France	1500	Extended aeration sludge	3.9 × 2	588 × 1	2009
Monza, Italy	10,200	Extended aeration sludge	12.5 × 4	7000 × 2	2010
Esholt, United Kingdom	32,730	Extended aeration sludge	22.3 × 6		2013

(4) CambiTM Process

Cambi™ technology is a sludge disposal process developed by Norway Cambi company and is used to enhance digestion through the hydrolysis [1-18]. The process includes the sludge thickening, the hydrothermal treatment (the core unit of the Cambi™ process), the digestion, the dewatering, and thethermal drying.

The Cambi™ process can be described as follows [1-19]. First, sludge is treated until its solid content reaches 15% to 20%, after which it is continuously fed to a pulper for preheating. The preheated sludge is sent to a batch reactor for the hydrothermal treatment reaction, which occurs at an operating temperature of 150 °C to 160 °C and an operating pressure of 0.8 MPa to 0.9 MPa. Second, the sludge is hydrolyzed and then cooled to 100 °C in a flash tank. Finally, the hydrolyzed sludge is fed into an anaerobic digester for the mesophilic anaerobic digestion with an HRT of 10 d to 12 d, after which it is cooled to 35 °C and diluted. The released steam from the flash tank is recirculated to the pulper for the preheating of the incoming sludge. Part of the biogas generated from the anaerobic digestion is delivered to the steam boiler to serve as fuel; the remaining portion is used for cogeneration. Fig. 1-6 is a flow diagram of the Cambi™ process; it shows that the Cambi™ process differs from the Biothelys process in that the former uses stirred and flash tanks.

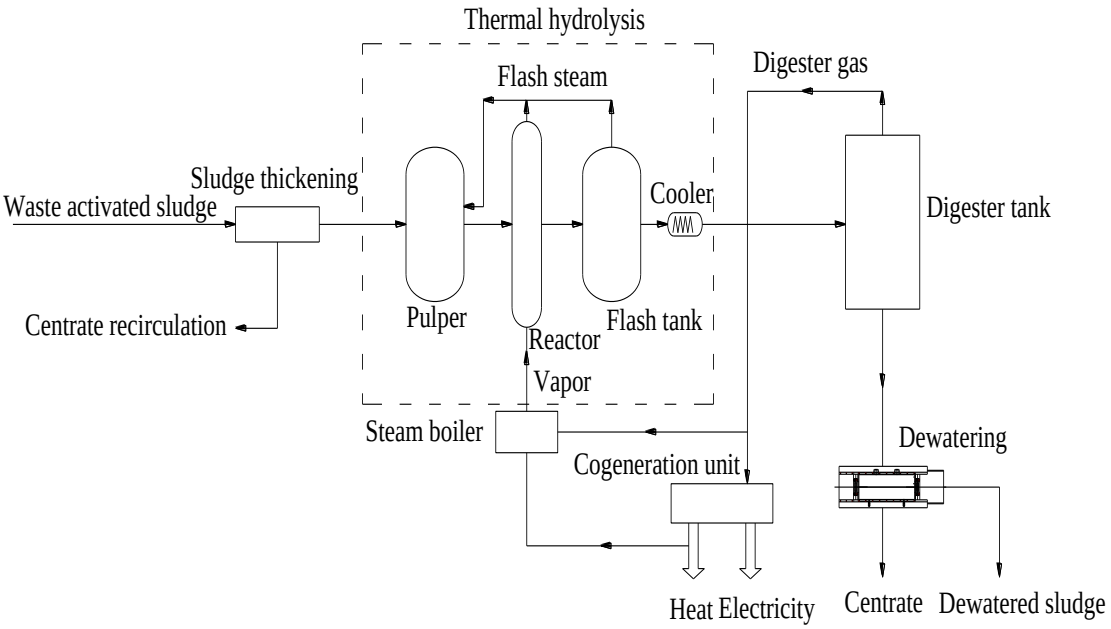

Fig.1-6 Flow diagram of the Cambi™ process

Unlike other conventional anaerobic digestion processes, the Cambi™ process offers the following advantages through its hydrothermal treatment of pretreatment sludge: improvement in the dissolution rate of organic solids, nearly twofold increase in biogas production, reduction in the volume of sludge cake, improvement of sludge dewatering performance, reduction in the volume of anaerobic digester by half, and reduction in the anaerobic digestion time to 10 d to 12 d. However, the process also suffers from certain disadvantages, including the difficulty of handling the hydrolyzate generated from the hydrothermal treatment, the need for frequent inspection and maintenance of equipment, high preheating temperature in the pulper, and other demanding requirements of the device. Moreover, the heat loss of the steam is large, the volume of the sludge hydrolysis apparatus is too small, and the process requires several reactors operating in parallel.

In 1996, the HIAS WWTP in Norway developed a sludge treatment process with a capacity of 3,600 tDS/a and successfully achieved the first application of the Cambi™ process [1-20]. By the end of 2009, this technology had been applied in Britain, Japan, Australia, Germany, the United States, and other countries. It has been applied in 23 completed projects and 7 projects under construction with a sludge treatment capacity ranging from 3,600 tDS/a to 37,000 tDS/a and good operating results. Table 1-4 shows some of the actual applications of the Cambi™ process.

Table 1-4 Some of the actual applications of the Cambi^{TM} process

Project	Capacity (tDS/a)	Devices	Digester volume (m^3)	Start-up
Cardiff (Britain)	35,000	6	2 × 7,500	—
Chertsey (Britain)	9,600	2	2 × 1,600	1998
Aberdeen (Britain)	16,500	4	2 × 4,000	2001
Brussels (Belgium)	20,000	5	2 × 3,600	2006
Whitlingham (Britain)	20,000	4	2 × 4,000	2007

(5) ExelysTM Process

The Exelys^{TM} process is a continuous sludge treatment technology developed by Veolia Water [1-21]. The process combines the hydrothermal treatment technology and the anaerobic digestion. It has the following advantages: reduction of dry sludge by 25% to 35%, increase in biogas production by 30% to 50%, odorless product, and a pasteurized digestate that is directly applicable in agriculture. The Exelys^{TM} process is applicable to all types of sludge.

Unlike the Cambi^{TM} technology, the Exelys^{TM} process uses a continuous reactor. The hydrothermal treatment unit can run all day, and the feeding and removal levels are adjustable in real time. In the process, the sludge is dehydrated to 22% solid content and is sent into the sludge/steam mixer for preheating. The preheated sludge is then delivered to the hydrothermal treatment reactor at the operating temperature of 165 °C and the operating pressure of 0.9 MPa for 30 min. The hydrolyzed sludge is then made to flow through two heat exchangers and is cooled to 60 °C to 100 °C. Afterward, it is diluted with water and fed into an anaerobic digester. In the process, the condensed water in the heat exchanger and its heat can be reused. Fig. 1-7 is a flow diagram of the Exelys^{TM} process.

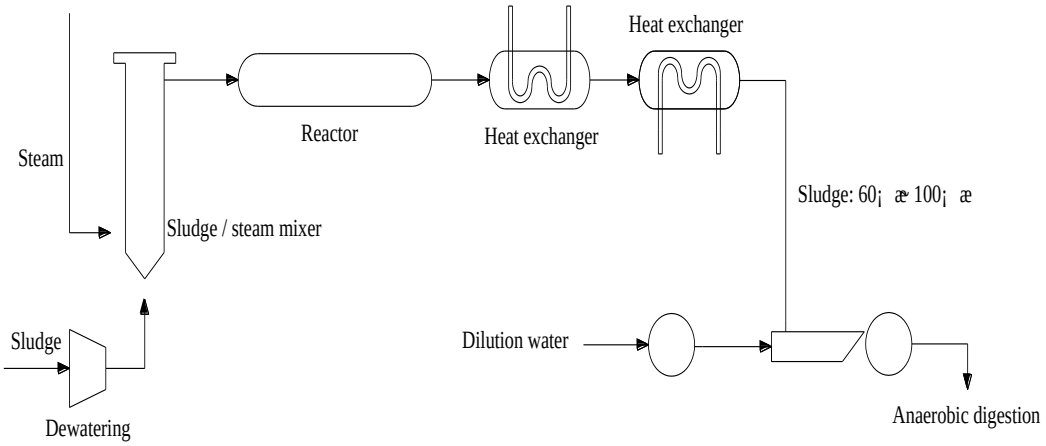

Fig. 1-7 Flow diagram of the Exelys™ process

Veolia developed the Lysis/Digestion (LD), Digestion/Lysis (DL), and Digestion/Lysis/Digestion (DLD) configurations, which are based on the combination of the processes of Exelys™ and the anaerobic digestion. The DLD configuration is the optimal process, for which a patent is being sought. This technology is currently being applied in 1 completed project and 2 projects under construction. In 2012, it was housed in a sludge treatment facility with a capacity of 300 tDS/a in Bonneuil, France. By 2015, sludge treatment facilities with capacities of 22000 and 8300 tDS/a will have been designed and built by Marquette-lez-Lille and Versailles, respectively.

(6) AthosTM Process

The Athos™ process developed by Veolia Water is a sludge treatment and disposal process based on the theory of the wet oxidation [1-22]. This process combines the processes of the hydrothermal treatment of Cambi™, anaerobic digestion, and the wet air oxidation (WAO) and thus minimizes sludge volume while fully utilizing renewable energy. The advantages of this process include zero emission of polluted fumes or harmful by-products, an easily biodegradable liquid that can be returned to the biological treatment process, and high solid mineralization. It effectively reduces sludge mass and volume.

The Athos™ process of the sludge treatment at the WWTP in Brussels, Belgium, can be described as follows: the sludge is dewatered by centrifugation and gravity concentration to a solid content of 15% to 16%, after which it undergoes the hydrothermal treatment of the Cambi™ process. The hydrolyzed sludge is then fed into a mesophilic anaerobic digester for 15 d. The digested sludge is finally sent to the Athos™

WAO process reactor for thermal oxidation treatment.

The Athos^{TM} WAO process reactor is considered as a completely stirred reactor. The reaction occurs under mild operating conditions of 250 °C and 5.4 MPa using homogeneous copper (II) ion catalyst and pure oxygen as the oxidizing agent. In the WAO step, the removal rate of COD reaches 75% to 80%, the removal rate of SS reaches 48%, and the global SS removal of the sludge treatment line is 71% at the Brussels WWTP. It effectively reduces sludge mass. From 600,400 m^3/a of thickened sludge, the final cake volume is 5,700 m^3/a, and the volume reduction factor is close to 100. The effect of volume reduction is remarkable. Fig. 1-8 is a flow diagram of the Athos^{TM} WAO process.

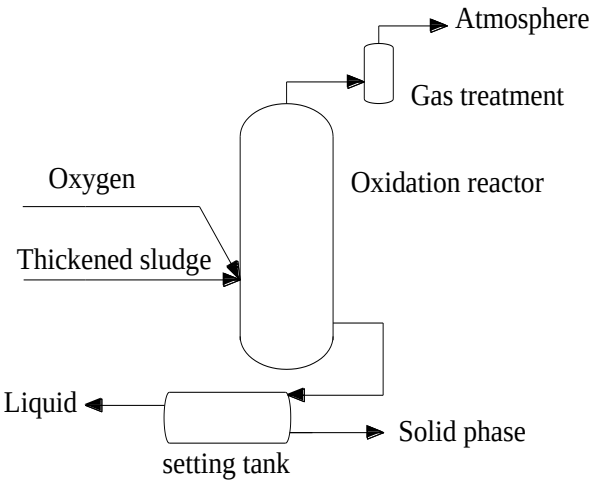

Fig. 1-8 Flow diagram of the Athos^{TM} WAO process

By the end of 2010, the Athos^{TM} technology had been applied for six sludge disposal projects. The Toulouse WWTP in France combines a biological treatment process with the Athos^{TM} process for sludge treatment. The WWTP in Brussels adopts the hydrothermal treatment–anaerobic digestion–Athos^{TM} process. Others adopt the anaerobic digestion treatment–Athos^{TM} process. Table 1-5 shows the actual applications of the Athos^{TM} process.

Table 1-5 Actual applications of the Athos^{TM} process

Project	Capacity (tDS/a)	Devices	Start-up
Toulouse (France)	1,000	1	1998
Truccazzano (Italy)	5,100	1	2005
Epernay (France)	2,200	1	2005
Brussels (Belgium)	15,000	2	2006
Aixen Provence (France)	3,200	1	2007

Rennes (France)	5,500	1	2010

1.3.2.2 Process and application of domestic sludge through the hydrothermal treatment

(1) Sludge hydrothermal drying treatment technology

Jiang Zili et al.[1-23] of BMEI Co., Ltd. conducted research on the sludge hydrothermal drying treatment technology through small and pilot-scale experiments and commercial operations. In their experiments, wet sludge (with a moisture content of 80%) was used as the research object, and the hydrothermal treatment process was completed through the direct contact of wet sludge and steam in a steam hydrolysis reaction reactor. Their results showed that after 24 h of natural air drying, when the moisture content of the hydrothermally dehydrated sludge was below 30%, the sludge moisture content decreased to 20%, and about 10% of the solid substances were dissolved in the liquid phase under the reaction temperature of 190 °C and the reaction time of 30 min. At present, this process is employed in the Hohhot 100 t/d sludge treatment projects and the Qingdao Lvjie 100 t/d activated sludge treatment renovation project. The flow diagram of the project is shown in Fig. 1-9.

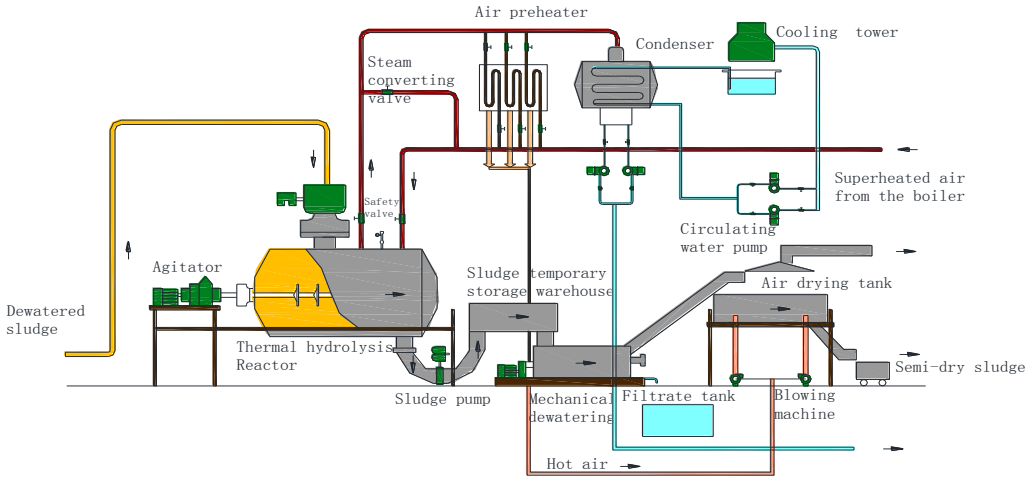

Fig. 1-9 Flow diagram of the water sludge thermal drying process developed by BMEI Co. Ltd.

(2) The hydrothermal drying combination technology for sludge treatment developed by Tsinghua University.

Domestic researchers in Tsinghua University studied the hydrothermal drying combination technology, which combines the mechanical concentration, the hydrolysis reaction, the secondary concentration, the dehydration, the heat–cold sludge heat transfer, burning, and so on. The technology optimizes the treatment system and increases the overall processing efficiency of the system. After the treatment, the

concentration of harmful substances in the sludge and the water load in the subsequent dehydration process are reduced, and a dewatered cake with a high calorific value is obtained[1-24]. This technique is being applied in demonstration projects of sludge thermal hydrolysis treatment in the Dongguan Sewage Disposal Plant and the Wuxi Shuofang Sewage Disposal Plant.

The pilot reaction process of the hydrothermal drying combination technology is outlined in the diagram below.

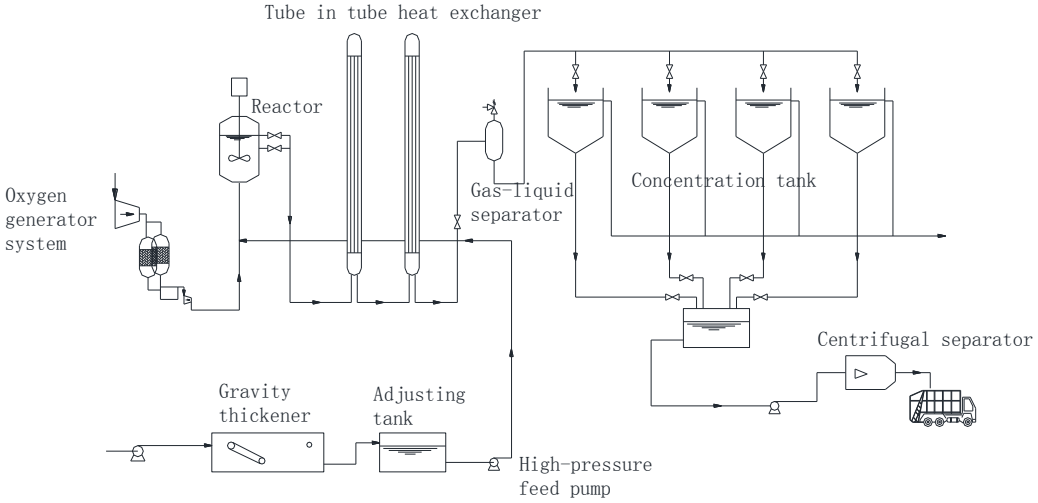

Fig. 1-10 Pilot reaction process of the hydrothermal drying combination technology

(3) HiROS sludge disposal technology

The HiROS sludge disposal technology [1-25] was developed independently by Beijing LuChuang Ecological Company. This technology uses partial wet oxidation combined with activation and puffing technology. The moisture content of sludge can be reduced from 80% to around 30%. This process uses all closed and continuous processing technology through continuous feeding and discharging. No secondary pollution is produced, and the process offers high-speed treatment and disposal, on-the-spot disposal, and remarkable resource benefits. The heat energy produced in the reaction is reasonably utilized to reduce the energy consumption of the system [1-26]. The Beijing Nankou sewage sludge disposal project currently employs this process.

1.3.3 Current situation of sludge hydrothermal treatment process

1.3.3.1 Research on sludge hydrothermal treatment pretreatment

Tae-Young Jeong et al.[1-27] conducted research on the hydrothermal treatment processing technology for excess sludge. In their process, sludge was treated at a

temperature of 120 °C for 30 min. Through the hydrothermal treatment process, biogas production quantity increased by more than 25%.

Perez-Elvira et al.[1-28] found that the thermal treatment of sludge at 170 °C for 30 min under hydrolysis conditions increased the biogas production volume by about 50% and shortened the HRT to 12 d when the pilot test was conducted on the sludge hydrothermal treatment reaction.

Bougrier et al.[1-29] evaluated the hydrolysis effect of municipal sludge subjected to the hydrothermal treatment at the temperatures of 130 °C, 150 °C, and 170 °C and the processing time of 30 min through a semi-continuous anaerobic digestion device. The hydrothermal treatment process at 130 °C was conducted in an alkaline pH of 10. The results of the anaerobic digestion showed that the anaerobic digestion effects at 130 °C and 170 °C were better than those at 150 °C, whereas the removal rate of TS from the pyrolysis sludge at 130 °C in the anaerobic digestion process was lower than that at 170 °C because of the effects of the alkaline conditions. Under the optimal conditions, the removal rate of organic matter and biogas production increased by 80% relative to that of the original sludge. In addition, the anaerobic digestion pretreatment was conducted on excess sludge [1-27]. The treated sludge was heated at 135 °C and 190 °C for 30 and 15 min. The results of the semi-continuous anaerobic digestion showed that the effect of the anaerobic digestion of the hydrolysis sludge was better at 190 °C than at 135 °C and that the yield of methane could be increased by 25% under the optimal conditions.

Nges et al.[1-30] investigated dewatered sludge using hydrolysis pretreatment before the anaerobic digestion and performed experiments at 25 °C, 50 °C, and 70 °C for 48 h. Their experimental results showed that high SCOD (Soluble Chemical Oxygen Demand) concentration does not lead to high methane gas production. In their work, the heat treatment time was extended from 12 h to 24 h at 50 °C, and methane gas production increased by 11%. The removal rate of VS (Volatile solid) increased from 42% to 51%, and the methane content in the gas composition reached the average of 65% to 69%. Sludge was disposed by hydrolysis pretreatment at 50 °C, but this process did not shorten the total time of the anaerobic digestion. Nevertheless, the output time of 90% of the biogas production improved by 2 d to 5 d relative to that of the hydrolysis and untreated sludge at 25 °C and 70 °C, respectively.

Climent et al.[1-31] handled secondary sludge through pyrolysis pretreatment at a high temperature of 134 °C for 90 min and a low temperature of 70 °C for 9 h and investigated the performance of hydrolysis sludge in the anaerobic digestion at 55 °C. The results for

the anaerobic digestion showed that biogas production did not significantly increase at 134 °C, but methane gas production increased by about 50% at 70 °C.

Jeongsik Kim et al.[1-32] tried various sludge pretreatment methods to determine the most suitable pretreatment method for the anaerobic digestion of sludge. They found that the effect of the anaerobic digestion of sludge with hydrolysis was the best, particularly at 121 °C and a high pressure of 1.5 MPa for 30 min. The biogas production rate of sludge anaerobic digestion increased by 34.3%, and the removal rate of SCOD increased by 67.8%.

Lise Appels et al.[1-33] studied the effects of sludge heat treatment at low temperatures on the performance of sludge anaerobic digestion. They compared the effects of the anaerobic digestion of sludge on hydrolysis at 70 °C, 80 °C, and 90 °C for 15, 30, and 60 min. The experimental results showed that the high temperatures and long reaction times contributed to the release of organic and inorganic compounds, which are conducive to the anaerobic digestion. The hydrolysis conditions of 90 °C and 60 min led to a biogas yield that is 10 times that of untreated sludge.

Zhou Xia, Wang Wei et al.[1-34] conducted a pilot-scale experiment at low pressure oxidation conditions on city sludge obtained from a city sewage treatment plant in north China. Their experimental results showed that at a test run at 180 °C and low pressure oxidation conditions, the effect of modified sludge was ideal. The SCOD in the sludge supernatant increased from 1,972 mg/L to 10,000 mg/L, and the sludge settling effect and the dewatering performance improved. The low calorific value of the dewatered cake was 8,021 kJ/kg, and the solid content ranged from 45% to 50%. The solid organic matter ratio decreased from the original range of 0.70 to 0.72 to 0.504; thus, the solid inorganic content of the sludge was high.

Dong Bin et al.[1-35] conducted the hydrothermal pretreatment on sludge at a low temperature and a short reaction time. To reduce the high energy consumption and cost of heat treatment at high temperature and the high requirements of the equipment, the optimal conditions for the low-temperature and short-time hydrothermal treatment were determined through the test results for the biochemical methane potential in the experiment. The performance of the sludge anaerobic digestion was optimal at the heating temperature of 110 °C and the reaction time of 20 min. The research data showed that the sludge cell ruptured and that the intracellular organic matter was released at 100 °C. At 110 °C, the mass concentration ratio of SCOD/TCOD and the mass fraction of carbohydrates and proteins in the supernatant increased from 1.20%, 1.38%, and 0.81%

before the hydrothermal treatment to 27.59%, 14.33%, and 7.81%, respectively. The proportion of the dissolved organic matter also increased. The biochemical methane potential test results showed that at 110 °C, the total volume of methane increased from 2,522 mL to 4,027 mL, the volume of biogas production increased by about 59.67%, and the removal rate of VS increased from 27% to 38%. The study results showed that the hydrothermal treatment at a low temperature enhances the methane production and organic matter degradation rates of sludge anaerobic digestion, whose peak is at 110 °C.

Wang Zhijun et al. of Tsinghua University conducted extensive research on how the hydrothermal pretreatment improves the performance of sludge anaerobic digestion [1-36]. They realized that the best solution temperature and retention time for the hydrothermal treatment was 170 °C and 30 min, respectively. Under this condition, the COD removal rate of the anaerobic digestion of sludge increased from 38.11% (non-hydrothermal treatment) to 56.78%. The TCOD biogas yield in the sludge increased from 160 mL/g to 250 mL/g.

Fisher et al.[1-37] showed that the performance of sludge dehydration significantly improves when the hydrothermal treatment is conducted at the temperature of at least 150 °C. They studied the changes in the properties of 12 different sludge samples that were subjected to the hydrothermal treatment at temperatures of 170 °C, 210 °C, and 230 °C. They found that the hydrolysis temperature higher than 180 °C significantly improves the sludge dewatering effect, whereas the hydrothermal treatment temperature of 180 °C transforms the protein and carbohydrates in the sludge into complex cyclic organic matter, thereby decreasing the biodegradability of the hydrolyzate; one-third of COD in the generated hydrolysis solution was difficult to handle. Anderson et al.[1-38] argued that the sludge dewatering effect after the hydrothermal treatment at 180 °C is better than that at other temperatures. Valo et al.[1-39] studied the hydrothermal treatment of sludge at 170 °C and 60 min. In the case of the sludge treated in a batch reactor for 24 d, the biogas production of the anaerobic digestion of the sludge increased by 45%. In the case of the sludge treated in a CSTR reactor for 20 d, the methane production increased from 88 mL/gCOD to 142 mL/ gCOD.

R. B. Brooks et al.[1-40] found that some organic matter is dissolved in the hydrolysis reaction of excess activated sludge in the hydrothermal treatment process. The effect of the hydrolysis of sludge was best at 170 °C to 180 °C in the hydrolysis experiments conducted on city sewage sludge. The reaction time showed little effect on the hydrolysis of sludge.

Haug and Stuckey et al. [1-41–43] studied the hydrothermal pretreatment of primary and activated sludge at a low temperature. The effect of sludge treatment improved with the hydrothermal treatment of activated sludge at a temperature of 175 °C. The methane content of the gas in sludge anaerobic digestion also increased by more than 60% after the treatment. The sludge digestion performance improved because the increase in the surface area of the sludge particles after the hydrolysis treatment promoted the biodegradation.

Hiraoka et al.[1-44] studied the treatment of excess activated sludge at a low temperature (<100 °C) and found that sludge hydrothermal treatment at temperatures ranging from 60 °C to 80 °C increases the gas production of anaerobic digestion by 30%. Pretreatment at a low temperature requires more time than that at a high temperature.

Li and Noike et al.[1-45] claimed that the hydrothermal pretreatment of excess activated sludge at 170 °C and 60 min yields the best anaerobic digestion effect. In their work, the anaerobic digestion cycle of sludge could be reduced by 5 d, and the COD removal rate and biogas production of sludge significantly increased after the hydrothermal treatment.

1.3.3.2 Experimental study on the combined thermochemical pretreatment of sludge

Guan Baohong[1-46] investigated the influence of the heat treatment of sludge on sludge dewatering when $CaCl_2$ solution was added at 50 °C to 90 °C. In their work, the addition of $CaCl_2$ significantly improved the sludge dewatering performance.

Honglin Zhang et al. used the method of the hydrothermal treatment to solve the problem of excess activated sludge in the Sanbaotun WWTP in Fushun. A two-step anaerobic reaction process was used to deal with the excess activated sludge [1-47]. The surplus sludge was anaerobically digested after pretreatment at 70 °C for 2 d. The removal rate of COD and VSS (Volatile suspended solid) increased by 11.3% and 12.3%, respectively, compared with that obtained for untreated sludge. After the anaerobic digestion for 16 d, the total gas yield increased by 74 mL, the sludge retention time was shortened to 12 d, and the settling performance of sludge significantly improved.

Yuanyuan Yan et al. investigated sludge with a high solid content (10%) and a low organic matter content (VS, /TS < 0.5) and the effect of alkali and heat pretreatment on its lytic processing [1-48]. Their results showed the degree of SS reduction and the digestion results of COD. The protein and carbohydrate contents increased with an increase in the temperature and hot alkali treatment, and the change was considerably obvious at 100 °C.

A. G. Vlyssides et al.[1-49] found that a VSS concentration of 6.82% at 90 °C and pH = 11 after the pretreatment of activated sludge at mid-temperature (50 °C to 80 °C) and pH = 8 to 11 decreased the SCOD to 70.00 mg/L in 10 h. The methane production rate was 0.28 L/gVSS in the study on the performance of the anaerobic digestion of activated sludge after pretreatment by alkali under heat conditions.

Qiao Wei et al. studied the microwave thermal hydrolysis treatment combined with the anaerobic digestion of sludge[1-50] and found that the speed of temperature increase by the microwave heating is fast, VSS and SS dissolve in sludge, the concentration of liquid COD, TOC, ammonia nitrogen, TN, and TP increases, and the pH value decreases. The addition of alkali was also found to be effective in promoting the process [1-51].

Li Yangyang et al. investigated the effects of alkali heat treatment on the drying characteristics of sewage sludge [1-52] and found that alkaline thermal pretreatment significantly improves the drying efficiency and the drying performance of sludge. The humic acid content in the sludge dewatering solution was 8.69 g/L under the following conditions: 140 °C, 60 min, and NaOH/TS = 0.25. The sludge dewatering solution can be used to manufacture foliar fertilizer containing humic acid after increasing the concentration four times.

Lai Xianjiao et al. conducted research on the separated liquid produced by the steam hydrolysis of sludge. They proposed the pretreatment technology of micro-electrolysis combined with electric Fenton [1-53]. In their work, the removal rate of COD_{Cr} of the sludge removal solution reached 98.3%, the removal rate of BOD_5 reached 96.4%, the chroma removal rate reached 99.6%, the ratio of BOD_5/COD_{Cr} increased to 0.56, and the biodegradability was significantly enhanced.

1.3.4 Problems of sludge hydrothermal treatment technology

The characteristics of the sludge hydrothermal treatment process at home and abroad are shown in Table 1-6.

Table 1-6 Main characteristics of the sludge hydrothermal treatment process at home and abroad

Process	Investigator	Time	Project application	Advantages	Disadvantages
Porteous Process	William K. Porteous	1939	Horsham, Halifax, Colorado Springs, Pudsey, and others in Europe	No sludge regulation, no chemical reagents added, easily implemented process	Needs several sets of individual treatment facilities, difficult to operate and control, high energy consumption
Zimpro Process	Zimpro Company	1954	UK Hockford	Strong oxidation ability, can destroy the organic composition of sludge, can remove 65% of organic matter in sludge	Produces odor, causes equipment corrosion, produces a high concentration of organic waste liquid, high energy consumption
Biothelys Process	Veolia Water	2006	2006 Saumur, France 1,600 tDS·a^{-1}; 2008 LePertuiset, France 2,000 tDS·a^{-1}; 2010 Monza, Italy 10,200 t DS·a^{-1}; 2013 Esholt, UK 32,730 tDS·a^{-1}	Meets the requirement of the process of energy balance, supplies heating and power to external, maximizes energy output	Hydrothermal treatment reaction for intermittent operation, needs multiple parallel reactors, high initial investment, difficult disposal of hydrolyzate; a large amount of residue remains after digestion
Cambi™ Process	Cambi Corporation in Norway	1995	Cardiff, UK 3.5 wt/y; Chertsey, UK 9,600 t/y; Aberdeen, UK 1.65 wt/y; Brussels, Belgium 2 wt/y; Whitlingham, UK 2 wt/y	Enhances sludge degradability, reduces cake volume, improves the efficiency of anaerobic digestion and dewatering performance, high efficient sterilization	Difficult disposal of hydrolyzate, easily damaged equipment, uses a sludge hydrolysis device volume that is too small, needs multiple parallel reactors
Exelys™ Process	Veolia Water		Carré-de-Réunion, France 8,250 t/y; Marquette-lez-Lille, France 2.2 wt/y; Bonneuil, France 365 t/y; Hillerød, France	Can run continuously for 24 h, equipment is easy to operate and maintain, equipment covers a small	

			1,140 t/y	area, high energy utilization, reduces the volume of solid waste, good system flexibility	
Wet oxidation process Athos™	Veolia Water	1998	Brussels, Belgium 110 wP.E.; Epernay, France 15 wP.E.; Truccazzano, Italy 30 wP.E.; Aixen-Provence, France 19 wP.E.; Toulouse-Ginestous, France 5 wP.E. (P.E.: population equivalent)	Flexible operation process, suitable for all types of sludge, compact and continuous processes, suitable for large capacity	
hydrothermal drying sludge treatment combination process	Tsinghua University	1980 s	2003 Beijing north river 40 t/d; 2009 Dongguan 30 t/d; Wuxi 10 t/d	Direct mixing of heat steam flow, enhances heat transfer and mass transfer processes to avoid local overheating, carbonized coking, effectively recovers system energy	High system energy consumption and cost, easily scalable heat exchanger and heat transfer surface, low thermal efficiency, complicated equipment maintenance
Hydrothermal drying	BMEI Co., Ltd.		Hohhot 100 t/d sludge treatment projects, Qingdao Lvjie 100 t/d renovation project of activated sludge treatment	Low power consumption of mechanical dehydration, steam heating	High energy consumption
HiROS Process	Beijing LuChuang Ecological Technology Co., Ltd.	2006	Nankou project 50 t/d	Closed continuous processing technology, high processing speed, can realize on-site processing, equipment covers a small area, automated system, easy to operate, low energy consumption	Complex process equipment

In conclusion, domestic studies on the hydrothermal treatment of sludge mainly focus on improving the capacity of sludge anaerobic digestion, whereas foreign research focuses on treating excess sludge through the thermal drying process. Given the high moisture content of excess sludge, the energy consumption of the hydrothermal treatment process is high. The hydrothermal treatment of dewatered sludge can somehow reduce energy consumption after the moisture content of mechanical dewatering sludge (80%) is decreased, Moisture forms are mainly interstitial and bound water. Thus, studies on excess sludge and sludge dewatering should be clearly distinguished. Through the hydrothermal technology for dewatered sludge treatment, research on hydrolyzed sludge composition and the treatment effect of subsequent anaerobic digestion contributes greatly to the development of dewatering sludge treatment technologies.

1.4 Objectives and Outline

Tokyo Institute of Technology and State Environmental Engineering Centre for Sludge Disposal and Resource have been investigating the sludge hydrothermal treatment system. The main objective of the previous study was to investigate the optimum operating conditions of the hydrothermal drying for obtaining RDF from sewage sludge by experimentally comparing the performance of the pilot-scale and commercial-scale hydrothermal reactors. Now, the hydrothermal drying technology of sewage sludge was successfully in pilot production. According to the previous research, the separated water treatment and recycling problems still exist associated with the application process of this technology.

The main objective of this study is to investigate the optimum operating conditions of the hydrothermal drying for obtaining the best mass and energy balances of the hydrothermal system through the dehydrated water treatment and the recycling from sewage sludge by experimentally comparing the performance of the pilot-scale and commercial-scale hydrothermal reactors. The contents of this study are the following:

To study the characteristics of the separated water from the hydrothermally treated sewage sludge under different operating conditions of the hydrothermal treatment. And to evaluate by the Biochemical Methane Potential (BMP) test as well as the guidance for a biochemical methane potential project.

One of the objective of this research is to study the performance of the biochemical methane potential of the separated water from the hydrothermally treated sewage sludge and sewage sludge product after the hydrothermal treatment. And another objective is to optimize the parameters for the anaerobic digestion reactor as well as to analyse the energy benefit.

Next, study on the performance of the commercial-scale reactor of optimally designed condition and operation condition was conducted by taking into account the mass and energy balances. It includes the energy of biogas which was obtained from wastewater anaerobic digestion treatment. Then the optimization of the hydrothermal drying treatment system and the maximization of the system energy efficiency were carried out.

This thesis is divided into the following five chapters.

Chapter1 [Introduction]: In this chapter, the sewage sludge treatment and disposal technologies are reviewed and the research progress of the hydrothermal drying is summarized to clarify the object of this thesis.

Chapter2 [Study on methane-producing potential and engineering application of sludge dehydrated water through hydrothermal drying treatment]: In this chapter, to study the characteristics of the sewage sludge dehydrated water of different operating conditions of the hydrothermal treatment. By changing the organic loading, pH value and the reaction temperature during the anaerobic digestion treatment process of dehydrated water and property change of the dehydrated water before and after the anaerobic digestion treatment were investigated for each kind of sludge to clarify the optimum operating parameters of the hydrothermal treatment.

Chapter3 [Commercial-scale demonstration of the hydrothermal treatment of sewage sludge]: In this chapter, the performance of the biochemical methane potential of sewage sludge product after the hydrothermal treatment including sludge dehydrated slurry and dewatered sludge was investigated. The difference of the anaerobic methanogenesis efficiency between sludge dehydrated slurry and pyrolytic sludge was studied. Then the optimization of parameters on the anaerobic digestion reactor and the analysis of the energy benefit were conducted. At last, the operation characteristic of the anaerobic methanogenesis was carried out to evaluate its effectiveness.

Chapter4 [Energy efficiency and economy analysis of commercial-scale hydrothermal drying system]: In this chapter, the performance of the commercial-scale reactor with optimal design condition and operation condition by taking into account the mass and

energy balances and economy analysis was investigated. It includes the energy of biogas which was obtained from wastewater anaerobic digestion treatment. Then the optimization of the hydrothermal drying treatment system and the maximization of the system energy efficiency were done.

Chapter5 [Conclusion]: The main achievements of this thesis are summarized.

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Chapter 2

Study on Potential of Biochemical Methane Production from Separated Liquid Produced from Sewage Sludge by the Hydrothermal Treatment under Different Operating Conditions

2.1 Introduction

From the results of chapter 1, it is believed that the hydrothermal treatment technology of sewage sludge has advantages in energy saving. Previous studies on the hydrothermal treatment were aimed at improving the dehydration ability of sewage sludge and drying them to produce solid fuel. However, the potential usage of the liquid product associated with the hydrothermal process was not well investigated. Therefore, the liquid product of sewage sludge from the hydrothermal treatment would be researched in this chapter.

The objective of this part was to a) investigate the effect of different operating conditions of the hydrothermal treatment on the separated liquid characteristics; b) to evaluate the methane-producing potential of the separated liquid from the hydrothermal treatment at different reaction conditions; c) to discuss the characteristics of the separated liquid by comparing their COD, volatile fatty acid (VFA), soluble COD (SCOD), ammonia nitrogen (NH_4^+-N), total nitrogen (TN), and total organic carbon (TOC).

2.2 Methods and materials

2.2.1 Experimental facility

2.2.1.1 Hydrothermal reactor

The parameters and structure of the hydrothermal reactor of the small-scale facility are shown in Table 2.1 and Figure 2.1, respectively. The hydrothermal reactor with a horizontal agitator whose rotation speed is adjustable is made of stainless steel and its total volume is 20 L.

Table 2.1 Parameters of the small-scale reactor

Volume	20 L (u260×377 mm)
Rated Operating Pressure	3.0 MPa
Design Temperature	240 ° 4
Jacket Rated operating Pressure	1.0 Mpa
Jacket Temperature	187 ° 8

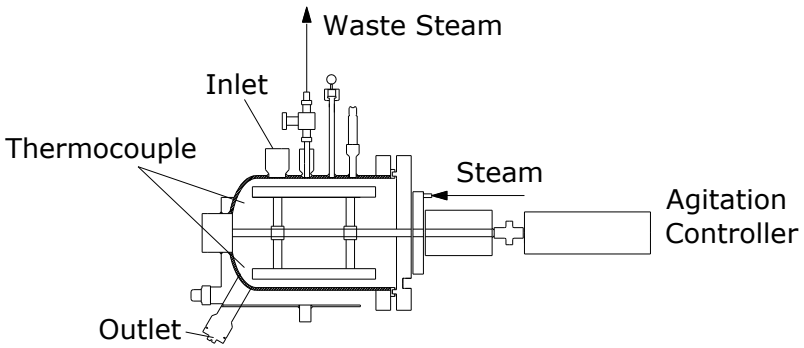

Fig. 2.1 The hydrothermal reactor of the small-scale facility

2.2.1.2 Electric Steam Boiler

The electric steam boiler of the small-scale facility is shown in Fig. 2.2. The specified evaporation rate of the boiler is 12 kg/h. The power of the electric steam boiler is 10 kW.

Fig. 2.2 The electric steam boiler used in the hydrothermal treatment

2.2.1.3 Dehydration facility

The small three-foot centrifuge shown in Fig. 2.3 is the dehydration equipment used in the small-scale facility. The volume of the equipment is 2.5 L (Φ200 × 100 mm), and the revolution speed is 1900 rpm. The hydrothermal product was dehydrated by centrifugation at 1900 rpm for 30 min and the separated liquid was collected for analyzing.

Fig. 2.3 Small centrifuge

2.3.1.4 Stirred Tank Reactor

The volume and stirring rate of the stirred tank reactor (STR) tanks used in the research (Figure 2.4) is 2.5 L and 20 rpm, respectively.

Fig. 2.4 Stirred tank reactor

2.2.2 Sewage Sludge

Sewage sludge samples were collected during winter and summer, respectively. The characteristics of sludge samples are shown in Table 2.2.

Table 2.2 Sewage sludge properties

Item	Unit	Summer sludge sample	Winter sludge sample
Water content	%	79.5	84.3
HHV	MJ/kg	9.3	10.9
	Proximate analysis (d.b.)		
Ash	Wt%	43.1	41.1
V.M	Wt%	51.7	53.3
F.C	Wt%	5.2	5.6
	Ultimate analysis (d.a.f.)		
C	Wt%	46.0	48.4
H	Wt%	5.7	5.9
N	Wt%	7.6	7.8
O	Wt%	40.7	37.9

The characteristics of separated liquid samples after the hydrothermal treatment at 190 ℃ are shown in Table 2.3. According to the research of Jiang [2-6], for different kinds of sewage sludge, the hydrothermal products showed similar dehydration and drying characteristics. Likewise, the results of this study indicated that the source, organic matter, sand content and moisture content fluctuations of the sludge hardly influenced the hydrothermal drying of sewage sludge (Table 2.2, and Table 2.3). Thus, the hydrothermal technology for sewage sludge treatment can be widely applied in the whole China.

Table 2.3 Characteristics of separated liquid

Sludge sources	TCOD (mg/L)	SCOD (mg/L)	TN (mg/L)	Ammonia Nitrogen (mg/L)	TOC (mg/L)
Winter	70600	55000	3224	1198	14590
Summer	69200	54200	3130	1162	14000
Average	69900	54600	3177	1180	14295

2.2.3 Experimental procedure

The experimental procedure is shown in Figure 2.5. Thirteen kilograms of raw sludge with the moisture content of approximately 82% was supplied in the hydrothermal reactor. Afterwards, the saturated steam generated in the electric boiler was injected into the reactor to heat the sludge. In the reactor, the sludge completely mixed with steam by the action of the horizontal agitator. The conditions of this study were minimal: no co-reactants, catalysts, or other materials were used. After 30 min of the reaction at the pressure of 2.0 MPa, the steam was exhausted into the buffer tank and then discharged to the atmosphere. The sludge product was extruded from the reactor and mechanically dehydrated at 1900 rpm for 30 min by the small three-foot centrifuge [2-6]. After that, the separated liquid from sewage sludge was collected for the anaerobic digestion in STR tanks.

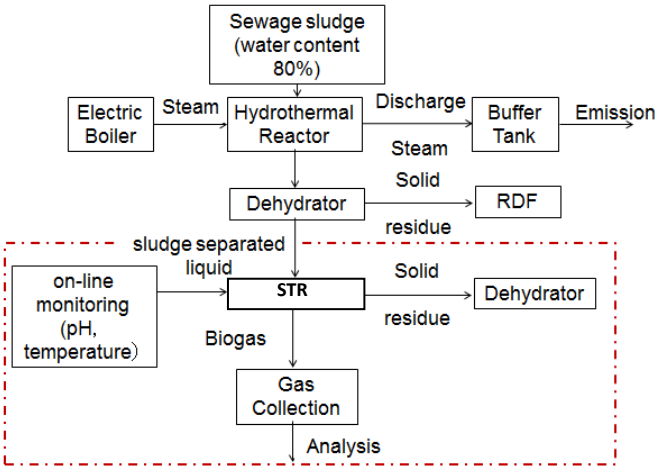

Fig. 2.5 The experimental procedure

According to the above experimental process, the research was divided into two parts. On the one hand, the effect of the reaction temperature employed in sludge hydrothermal treatment on the composition of sludge separated liquid which could be digested by anaerobic microorganisms producing biogas was investigated by analysing COD, SCOD, VFA,

TN, Ammonia and TOC. On the other hand, the separated liquid from the hydrothermal treatment at different reaction temperatures was digested in the STR anaerobic tanks to evaluate its biochemical methane potential. Meanwhile, the biogas producing efficiency, methane purity, and methane conversion rate were assessed to provide data support for the subsequent engineering application.

2.2.4 Analytic methods

The methods for analysing the parameters were as following:

(1) Total chemical oxygen demand (TCOD): The COD was determined by the potassium dichromate/ferrous ammonium sulfate method.

(2) The soluble chemical oxygen demand (SCOD): The supernatants separated from sludge by filtering were used for soluble COD (SCOD) determination.

(3) Ammonia nitrogen (NH_4^+-N): The content of NH_4^+-N in the sludge was analysed by the titration.

(4) Total nitrogen (TN) [2-3]: Alkaline potassium persulfate oxidation-UV spectro photo metric method was used to determine TN in sludge effluent。

(5) Total organic carbon (TOC) [2-2]: The TOC was evaluated by the dilution heat method.

(6) Volatile fatty acid (VFA): Gas chromatograph was used to analyse VFA.

2.3 Results and discussions

2.3.1 Component of the separated liquid under different hydrothermal treatment conditions

Jiang et al [2-6] selected China's urban sludge as the research object and studied the preparation of RDF fuel using the hydrothermal treatment for sludge recycling. They established the optimal technological parameters of RDF, which access to maximize the energy fuel. The results indicated that the optimum temperature and the reaction time for the hydrothermal treatment were 190 °C and 30 min, respectively. With these optimum operating conditions, the moisture content of the solid residue was less than 40% after the mechanical dehydration. It could be reduced down to 10% after 48 hours of natural drying. And the energy recovery ratio (ERR) was 39.9%. While the separated liquid in Jiang’s

research was not further utilized, this study focuses on the recycling of the separated liquid.

According to the results of Jiang et al [2-6], when the reaction temperature was more than 190°C, the amount of RDF obtained from sludge would be reduced with the increase of the reaction temperature. In this research，it had been demonstrated that the dewatering performance of sludge after the hydrothermal treatment at 190°C was significantly improved. Meanwhile, a higher reaction temperature would increase the energy consumption. Therefore, the reaction temperatures used in this study were 160, 170, 180 and 190°C,respectively, and the reaction time was fixed at 30min in all hydrothermal treatments (Table 2.4).

Table 2.4 Conditions for the hydrothermal reaction

Experimental No.	1	2	3	4
Temperature (°C)	160	170	180	190
Time (min)	30	30	30	30
Hydrothermal reactor stirring speed (rpm)	22			
Centrifuge speed (rpm)	1900			

The separated liquid from the hydrothermal treatment was collected for analysing and the research of the biochemical methane potential by investigating its variation tendency at different reaction temperatures and particularly studying its COD, SCOD, VFA, TN, TOC, NH_4^+-N, and TN.

The operating principle of the hydrothermal treatment is that sewage sludge and high temperature/pressure saturated steam will react to rupture the cell wall and membranes of organics in the sewage sludge, and at the same time it will improve the dewatering ability of the sludge and the improvement of the anaerobic digestion ability of the sludge effluent. The anaerobic digestion efficiency of sludge effluent can be evaluated by the concentration of soluble COD (SCOD).

As one of the most important parameters for the process control of the anaerobic digestion, the concentrations of VFAs in sludge effluent have direct correlation with the digester performance. Thirty to forty percent of SCOD in sludge effluent were VFAs including acetate, propionate, butyrate, and valerate in this research. Methanogenic bacteria mainly use the VFA to form methane, only a small part of the methane is generated by CO_2 and H_2. It can be confirmed that VFA is the necessary substrate for methane production, however, high VFA concentration will inhibit the activity of methanogens. Therefore, the VFA variation at different reaction conditions and its effect on the anaerobic digestion were investigated.

Nitrogen in the liquid phase mainly comes from protein hydrolysis in solid phase. Microbial cell contains rich protein which can be hydrolyzed to polypeptide, dipeptide, and amino acid under heated conditions. Amino acid will be further hydrolyzed to low molecular organic acids, ammonia, and carbon dioxide which cause the increasing of TN and NH_4^+-N in liquid phase. There into, the C/N ratio and the content of NH_4^+-N are the most important factors that affect subsequent anaerobic reaction, and their variation trend against the hydrothermal treatment at different temperature conditions was studied.

2.3.1.1 COD variation tendency of the hydrothermal treatment at different operating conditions

Figure 2.6 shows the concentrations of TCOD, SCOD and SCOD/TCOD of the separated liquid obtained under different hydrothermal temperature conditions. When the reaction temperature was increased to 160 °C, 170 °C, and 180°C, respectively, the concentrations of TCOD was 47.3g/L, 49.9g/L, 51.1g/L, respectively, and the concentrations of SCOD was 31.2g/L, 35.6g/L, and 36.6g/L, respectively. When the reaction temperature was increased to 190 °C, TCOD and SCOD concentrations increased significantly which was 69.9g/L and 54.6g/L, respectively.

Sludge is the organic aggregates which are composed of variety of microorganisms, organic compounds and inorganic particles, and these substances are surrounded by a gel network structure formed by extracellular polymeric substances (EPS). Organic ingredients in sludge are mainly microbial flocs and polymers which are produced from microbial growth and metabolism and excretion, and adsorbed organic matters in waste water. These organic constituents mainly contain protein, carbohydrates, lipids, and DNA [2-16, 2-17]. During the process of the hydrothermal treatment, heat can destroy the floc structure formed by EPS and further damage the structure of microbial cells which causes the water within the cells to be adsorbed in the floc, which are macromolecules in cells such as proteins, polysaccharides and fats releasing. A high temperature promotes the dissolution of organic and the hydrolyzation of macromolecular organic. For instance, protein, carbohydrates and fats in the sludge will continue to be hydrolyzed into peptide, amino acids, fatty acids, low molecular polysaccharose, and monosaccharides and so on. This results in the dissolution of solid organics in the sludge. And elevated temperature accelerates the dissolution and hydrolysis of organics ingredients in sludge which decreases the content of organic components and reduces quantity of sludge. The content of organic compounds in separated liquid is also enhanced which increases the value of TCOD and SCOD.

The COD concentration of the separated liquid generated by the hydrothermal process is very high and requiring further treatment. In some domestic sewage treatment plants, the SCOD of influent is often insufficient to provide carbon resource for the removal of phosphorus and nitrogen by biological treatments. While the separated liquid can be used to increase the SCOD content of the influent by reflowing the separated liquid to sewage treatment plant and mixing with influent to provide carbon source required in the biological treatment and thus reducing or removing the necessity of adding external carbon source. Because of the changes of solid stalemate structure of sludge after the hydrothermal treatment, organic molecules come into the liquid phase. This study analysed the effects of the hydrothermal temperature on the components and the anaerobic digestion of the separated liquid. In the anaerobic digestion, the organic loading is one of the key factors. SCOD represents the level of dissolved organic matter and is one of the main criteria evaluating available organics which can be used by anaerobic microorganisms in the anaerobic digestion. In this research, COD solubility was used to determine available ratio of organic compounds in separated liquid. The ratio of COD dissolution rate is defined as shown in the formula 2-1. Figure 2.6 showed that COD dissolution rate increased with the increase of the reaction temperature and reached the maximum of 78.11% when the hydrothermal temperature was 190°C. This result indicated that the ratio of soluble organic compounds which was available for anaerobic microorganisms in the separated liquid increased with the rising of the hydrothermal temperature, and the separated liquid was more conducive to the anaerobic digestion.

The ratio of COD dissolution rate =SCOD/TCOD [2-7] (eq. 2-1)

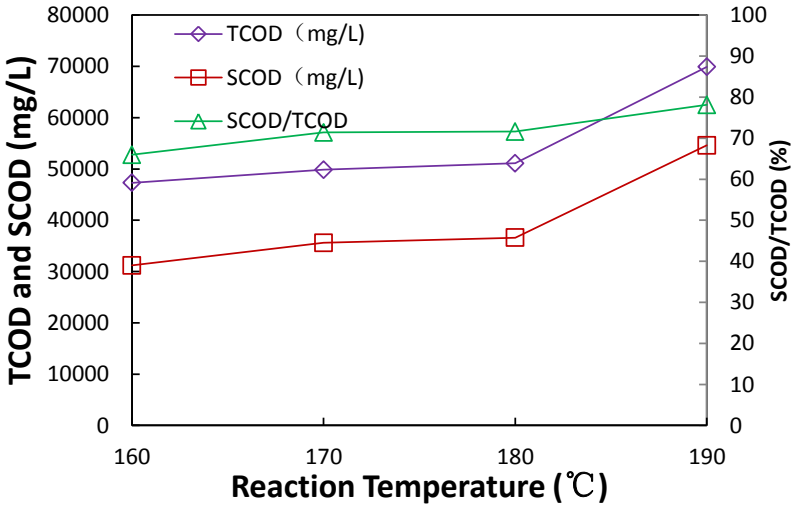

Fig. 2.6 Tendencies of TCOD, SCOD, and SCOD/TCOD in the separated liquid under different reaction temperatures

2.3.1.2 VFA variation tendency of the hydrothermal treatment at different operating conditions

Volatile fatty acids (VFA) mainly composed of acetate, propionate, butyrate, and valerate, are an important parameter in the anaerobic digestion, and there is a direct correlation between the concentration of VFAs in the liquid phease and the anaerobic digestion characteristics [2-8]. Figure 2.7 shows that The quantity of total volatile fatty acid (TVFA) was almost constant (VFA, 180℃=3206 mg/L, 190℃=3090 mg/L) and more than 80% (acetic acid,180℃=2821 mg/L, 190℃=2874 mg/L of them were acetate which was a major organic intermediate of degradation of most organic matter. The concentration of acetate increased, while those of propionate, butyrate, and valerate decreaseed when the digested temperature was increased. Butyrate and valerate are frequently observed during degradation of amino acids and protein. A concentration of VFA above 2000 mg/L (or 33 mM as acetate) is considered to be inhibitory to the anaerobic digestion. Nevertheless, the TVFAs concentrations in sludge effluent were all higher than 2000 mg/L after the hydrothermal treatment (Fig. 2.7) and above the inhibitory level. Therefore, sludge effluent from the hydrothermal treatment should be diluted to a concentration of TVFA below the inhibitory level when it was used for the anaerobic digestion.

The source of VFAs in the anaerobic treatment system contained those in the original separated liquid and produced in the anaerobic digestion, such as acetic acid, propionic acid, and so on. This section analysed the VFA concentration and its effect on the anaerobic digestion of the separated liquid. The results demonstrated that the toxicity of VFA to methanogenic bacteria was influenced by the pH value. When the pH value is lower in the anaerobic reactor, the methanogenic bacteria did not grow and VFA cannot be converted into biogas and continue to accumulate within the system. Otherwise, when the pH value was 7 or slightly higher than 7, VFA was relatively nontoxic. The toxicity of volatile acids to methanogenic bacteria at lower pH values was reversible. Methanogenic bacteria stayed alive in the waste water containing VFA for two months when the pH value was approximately 5 and recovered the activity in several days to weeks after the pH value in the system was normal. If the condition of low pH value only kept less than 12 h, the activity of methanogenic bacteria could be resumed immediately after the pH value was adjusted. If the VFA concentration in the separated liquid was higher than 15 mmol/l (equivalent to 900mg/L), it needed to adjust the pH value to avoid the acidification inhibiting the growth of methanogens. The pH in the range of 6.5 to 7.8 was best for the growth of methanogens. Therefore, the separated liquid obtained from the hydrothermal treatment containing high

content of VFA should be diluted to a concentration of VFA below the inhibitory level when it was used for the anaerobic digestion.

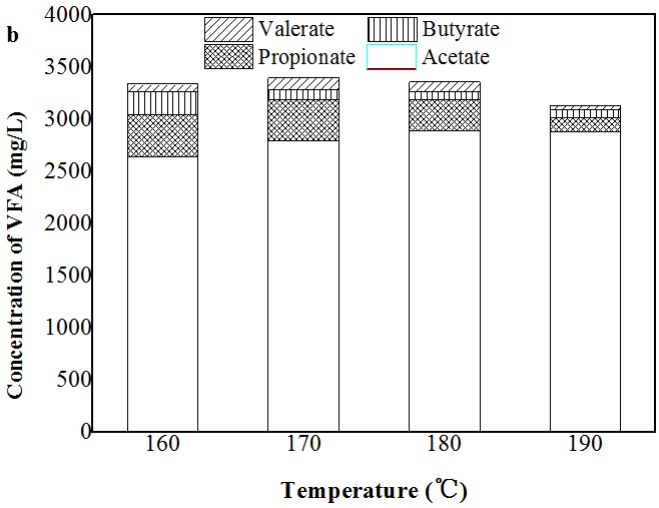

Fig. 2.7 Tendencies of VFA in sludge separated liquid under different reaction temperatures

2.3.1.3 C/N variation tendency of the hydrothermal treatment at different operating conditions

The bacterial composition in sludge can be characterized by $C_5H_7O_2NP_{0.1}$. The content of organic carbon, organic nitrogen, and ammonia nitrogen in liquid phase increased with the dissolving of VSS in the hydrothermal treatment. As shown in Figure 2.8, the concentration of TOC and COD in the separated liquid enhanced with the increase of the reaction temperature in the hydrothermal treatment. Therefore, the reaction temperature affected the TOC concentration significantly. The TOC concentration was approximate 12393 mg/L, 13289 mg/L, and 13583 mg/L at 160 °C, 170 °C, and 180 °C, respectively. It reached to 14295 mg/L when the reaction temperature was 190 °C. The concentrations of TN and NH_4^+-N remained little changed when the reaction temperature was lower than 180 °C and were approximate 2300 mg/L and 700mg/L, respectively. Whereas they increased obviously when the reaction temperature was increased to 190 °C and were up to 3177mg/L and 1180mg/L, respectively. The reasons of the high concentrations of N and TOC in the liquid phase was that the organic matter dissolved into the liquid phase with the hydrolysis of organic matter. Dissolved into the liquid, nitrogen comes mainly from the hydrolysis of proteins. Microbial cells contain abundant protein which can be hydrolyzed to polypeptide, dipeptide, and amino acid in the heated conditions. Amino acid will be further hydrolyzed to low molecular organic acids, ammonia, and carbon dioxide which cause the increase of TN and NH_4^+-N in the liquid phase.

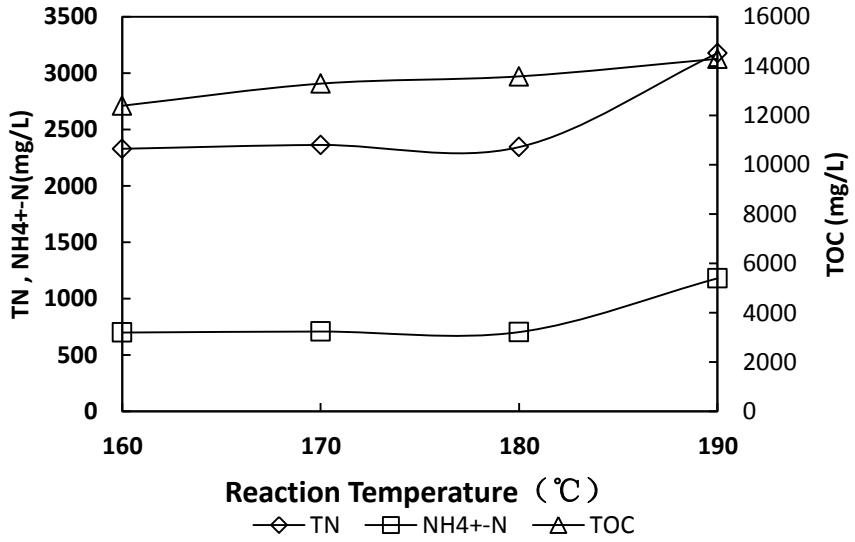

Fig. 2.8 Effect of the reaction temperature on TN, NH_4^+-N and TOC contents

Ammonia nitrogen is coming from the free ammonia and the ammonium ion in water. The total nitrogen is the amount of various forms of nitrogen (the ammonia nitrogen, the nitrate nitrogen, the nitrite nitrogen and the organic nitrogen). Theoretically，the total nitrogen is the sum of ammonia N, organic N, nitrate N and nitrite N [2-18]. The total nitrogen is the sum of the ammonia N and the organic N in wastewater. It was determined that the ammonia nitrogen in the sample was of about 37 % of the total nitrogen, organic nitrogen accounted for about 55%, nitrate + nitrite accounted for about 8%. In the process of anaerobic treatment, ammonia will be accumulated in the process of organic nitrogen can be converted to ammonia. In the process of anaerobic treatment, ammonia nitrogen is the key factor in the anaerobic digestion because the ammonia nitrogen is poisonous to anaerobic bacteria in the anaerobic digestion process by reducing the efficiency of the anaerobic digestion and interference with the anaerobic digestion process. When the influent ammonia <200 mg/L, the anaerobic reactor is not conducive to microbial growth and reproduction; When the influent ammonia concentrations in 200-500 mg/L, the ammonia no adverse effects on microorganisms; influent ammonia concentration of 500 -2000 mg/L, the inhibitory effect of ammonia would be produced by microorganisms, the stage will affect the stability of the system operation; especially, when the concentration of the ammonia nitrogen was higher than 2000mg/L, the activity of microorganisms was inhibited significantly[2-19]. In this study, the ammonia nitrogen concentration in the separated liquid at the different reaction temperature was always lower than the limit concentration. According to the results of previous research, the optimum reaction temperature of the sludge hydrothermal treatment was 190 °C and the ammonia nitrogen concentration was higher than that at lower temperatures. Meanwhile, in order to obtain

better methane production in the anaerobic digestion, it still needed to consider the relationship between the ammonia nitrogen concentration and the anaerobic digestion in the subsequent research.

The optimal C/N ratio for the best growth of microorganisms should be in the range of 20%-30% in the anaerobic digestion [2-11]. Therefore, in the process of the anaerobic digestion, the C/N ratio of the system could be increased through the backflow to improve the yield of methane [2-9]. Thus, it was necessary to analyze the C/N ratio in the separated liquid under different reaction temperatures. As shown in Figure 2.9, the C/N ratio in the separated liquid was all in the range of 20%-22% which was suitable for the anaerobic digestion and the highest C/N ratio was approximately 22% at 190 °C. The C/N ratio should be increased to enhance the biogas production in the anaerobic digestion of the separated liquid.

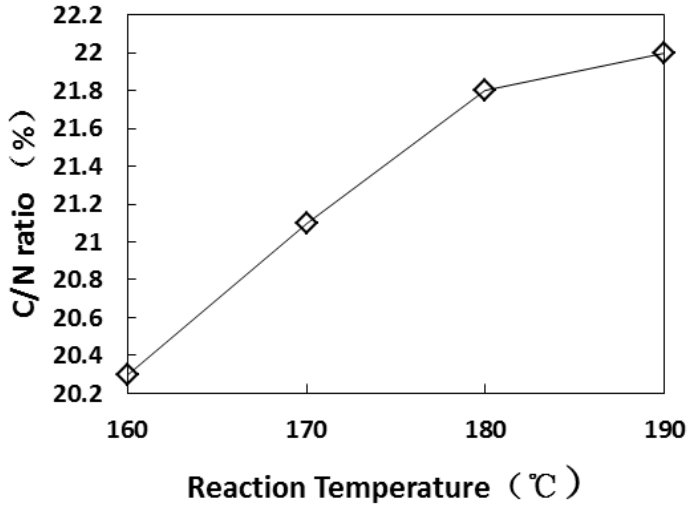

Fig. 2.9 The C/N ratio under different reaction temperatures

2.3.2 Biogas production from the separated liquid

In the hydrothermal treatment process, energy used for heating could be provided by RDF fuel and biogas produced by the anaerobic digestion of the separated liquid. From the results of the analysis the COD, VFA, NH_4^+-N, and TOC of the separated liquid under different reaction temperatures, it was indicated that organic matters in sludge transferred to the liquid phase after the hydrothermal treatment which caused the increase of organic matters and the COD concentration in the separated liquid. These organic matters in the separated liquid were easily utilized by microorganisms which were beneficial to the anaerobic digestion for biogas production.

Temperature is one of important factors for the control of the anaerobic digestion

because of its effect on the enzyme activity in the digestive process which can change the microbial metabolic activity and influnce the quantity of biogas produced. Generally, methanogens have strong temperature adaptability and their anaerobic digestion can be carried out in the range of 4-65 °C. A large number of studies have shown that metabolism of anaerobic microorganisms is optimum when the temperature is in the range of 35-38 °C and 50-65 °C. Therefore, the anaerobic digestion temperature is generally controlled within two scopes, namely, medium temperature digestion (35-38°C) and high temperature digestion (50-65°C) [2-20]. Furthermore, the temperature of the anaerobic process also needs to be kept relatively stable. While the high temperature digestion compared with the medium temperature digestion consumes energy more with higher operation cost and more complex managing [2-21]. At the same time, according to the local situation of Qingdao demonstration project, this research chose the medium temperature digestion where the optimum temperature was 35 °C.

The STR tank was used for the anaerobic fermentation in this part. The anaerobic digestion process aimed for the treatment of the separated liquid and producing methane by comparing methane-producing effectiveness and the COD removal rate before and after the anaerobic reaction. These studies would explore the possibility of anaerobic methanogenesis and provide a technical support for the subsequent demonstration project.

2.3.2.1 Biogas production from the separated liquid under different reaction temperatures

In this part, the separated liquid obtained under different reaction temperatures was treated directly by the anaerobic digestion. Biogas-producing effectiveness and the COD removal rate before and after the anaerobic reaction were studied. STR digesters with working volume of 2.5 L were utilized in this research and the temperature was maintained at 35 °C. 1.5 L separated liquid from 160 °C, 170 °C, 180 °C and 190 °C reaction conditions was added to the four different STR reaction vessels. The amount of biogas production, the content of methane, pH, and the COD concentration were measured every day.

(1) Cumulative biogas production and methane content

The important purpose of the anaerobic digestion is to transfer biodegradable organic matter to methane to recovery energy. Gas producing rate is a sensitive indicators in the operation of the anaerobic treatment because it is the easiest way to monitor to reflect the running condition of the reactor. Biogas-producing effectiveness can be performed by testing the gas composition and its variation law of biogas quantity. Figure 2.11 shows the gas

change laws of the accumulative gas production of the separated liquid under different temperature conditions in the STR anaerobic reaction process in 30 days. The content of methane at the corresponding reaction conditions is shown in Figure 2.12.

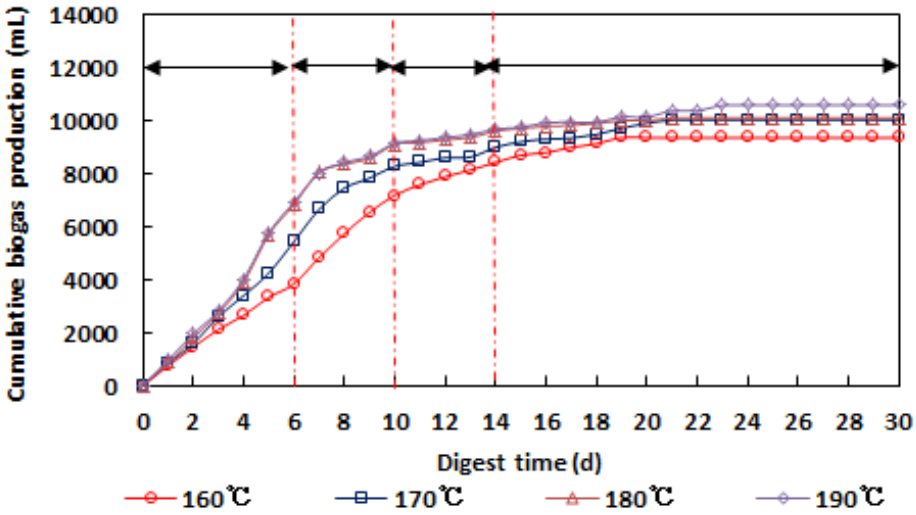

Fig. 2.11 Cumulative biogas production of the separated liquid under different reaction temperatures

As shown in Figure 2.11, the cumulative gas production of the separated liquid at 190 °C was the highest. Under the condition of 180 °C and 170 °C, anaerobic cumulative gas production from the separated liquid trended to similar results. It was the least when the temperature in the hydrothermal treatment was 160 °C. The rate of gas producing was faster in the first six days, slowed down after ten days, and terminated in fourteen days. Finally, the maximum accumulative gas production reached to 10552.4 mL. Eventually, the COD concentration of the fermented liquid according to the cumulative gas production was as following: 190 °C > 180 °C > 170 °C > 160 °C. The separated liquid obtained from the hydrothermal treatment at 190 °C with a high SCOD concentration and rich carbon source was utilized easily by anaerobic microorganisms and produced more biogas. The result of methane content showed that the unit methane production for 190 °C and 180 °C was 210 mL/gCOD and 205 mL/gCOD, respectively. With the proceeding of the anaerobic fermentation, methanogens stopped producing more methane because sulfate reducing bacteria and nitrate reducing bacteria increased with the cumulative VFA in the system and no more carbon source could be utilized by methanogens. The efficiency at the startup stage, the unit methane production efficiency, and the cumulative gas production of the separated liquid of 190 °C were significantly superior to the separated liquid of 180 °C, 170 °C and 160 °C. It had important guiding significance for the engineering application of the separated liquid.

As shown in Figure 2.12, the methane content was 59.2%, 59.3%, 60.8%, and 62.2% when the hydrothermal temperature was 160 °C, 170 °C, 180 °C and 190 °C, respectively. During the process of the hydrothermal treatment, heat can destroy the floc structure formed by EPS (Extracellular Polymeric Substances). Temperature promotes the dissolution of organic and the hydrolyzation of macromolecular organic. For instance, protein, carbohydrates and fats in the sludge will continue to be hydrolyzed to peptide, amino acids, fatty acids, low molecular polysaccharose, monosaccharides and so on. Therefore, there were more low molecular organic matters which were favored by microorganisms in the separated liquid of 190 °C. Thus, the accumulative gas production and methane content of 190 °C was higher than others. Furthermore, the calorific value of RDF fuel obtained from the hydrothermal treatment at 190 °C was better. Therefore, the separated liquid under the heating condition of 190 °C was selected for the subsequent anaerobic digestion.

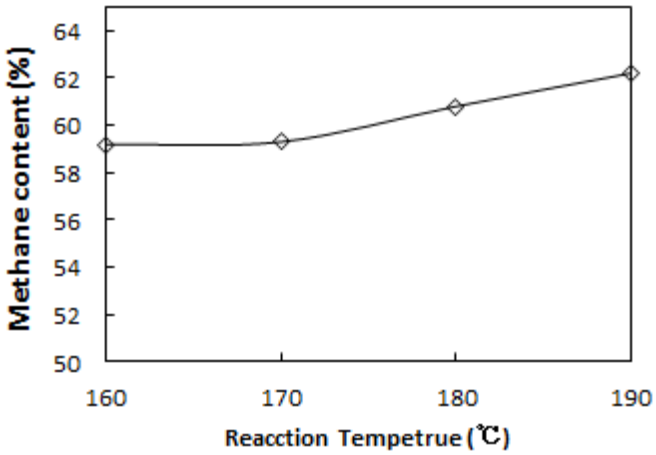

Fig. 2.12 The methane content of biogas product from the separated liquid under different reaction temperatures

(2) COD change before and after the anaerobic digestion

The COD concentration is a conventional indicator for evaluating the organic matter content in sewage during the wastewater treatment and its changes before and after the anaerobic reaction can be used to estimate the removal of the organic loading in the reactor. As shown in Figure 2.13, the order of the COD removal rate after the anaerobic treatment was as following: 160 °C >170 °C >180 °C >190 °C.

The typical characteristics of the anaerobic digestion is the methanation, namely the anaerobic digestion is the process that the methanogens convert the organic carbon to the lowest oxidation state of CH_4 which will escape from water and reduce the COD concentration by the removal of organic matter in wastewater. The results of the anaerobic treatment showed that the highest removal rate of COD was 41% when the hydrothermal

temperature was 160 °C. On one hand, the removal of COD in the separated liquid mainly depended on the implementation of microbial cell synthesis, releasing of CO_2 and H_2, and production of methanation. While most of the COD which was converted to volatile acid remained in the water, the COD removal rate of system was relatively low. On the other hand, because the initial concentration of COD, VFA, and ammonia nitrogen in separated liquid under the condition of 190 °C was 69.9 g/mL, 3000 mg/L, and 1000 mg/L, respectively, the activity of the methanogens was inhibited for this concentration. Therefore, the removal rate of organic matter was lower than others. Although the COD removal rate of 160 °C was higher, the accumulative gas production and the methane content were lower. The diluted separated liquid under the condition of 190 °C would be chosen for further study because of its higher accumulative gas production and methane content and to provide more data support for the engineering application.

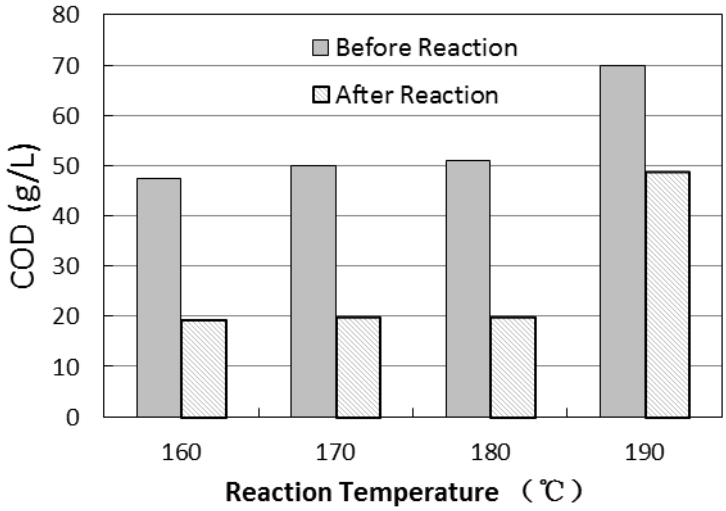

Fig. 2.13 COD changes before and after the anaerobic digestion

2.3.2.2 Biogas production from the diluted separated liquid

The separated liquid obtained from the hydrothermal treatment with a high COD and an ammonia nitrogen concentration needed to be diluted to satisfy the growth of methanogens [2-12, 2-13]. In the process of the anaerobic fermentation, the production quantity and composition of biogas are important indicators for running the reactor and also indirectly reflect the variety regulation of the sludge activity in producing methane. This part would study the effect of the production quantity and the composition of biogas of the separated liquid with different dilution gradient to provide data supporting for the engineering application.

As shown in Table 2.5, the separated liquid obtained from the hydrothermal treatment

at 190 °C was diluted with water in the ratio of 1:0, 1:1, 1:3, and 1:7, respectively, and added into STR tanks named #1, #2, #3, and #4, respectively. The temperature of the anaerobic digestion was 35 °C. The quantity and methane content of biogas and the changes of COD value before and after the anaerobic digestion were recorded every day.

Table 2.5 STR reaction condition

No.	Dilution Rate	COD(g/L)
#1	1	69.90
#2	2	34.95
#3	4	17.48
#4	8	8.74

(1) Cumulative biogas production of the diluted separated liquid

In the process of the anaerobic fermentation, the quantity and composition of biogas are mainly restricted by two factors. The first factor is the microbial species. The distribution proportion of degradated organic matter in synthesizing cells varies according to the bacterium species. The more degraded organic compounds are used to synthesize microbial cells, the less matters are utilized to produce methane which leads to lower quantity and methane content of biogas. The second factor is the COD concentration of the influent. The biogas quantity increases with the addition of the COD concentration in a certain concentration range. Meanwhile, the ammonia nitrogen also influences anaerobic digestion. Higher concentration of the ammonia nitrogen can inhibit the microbial anaerobic metabolism and the amount of biogas is reduced. When the influent ammonia <200 mg/L, the anaerobic reactor is not conducive to microbial growth and reproduction; When the influent ammonia concentrations in 200-500 mg/L, the ammonia no adverse effects on microorganisms; influent ammonia concentration of 500 -2000 mg/L, the inhibitory effect of ammonia would be produced by microorganisms, the stage will affect the stability of the system operation; especially, when the concentration of the ammonia nitrogen was higher than 2000mg/L, the activity of microorganisms was inhibited significantly[2-19].

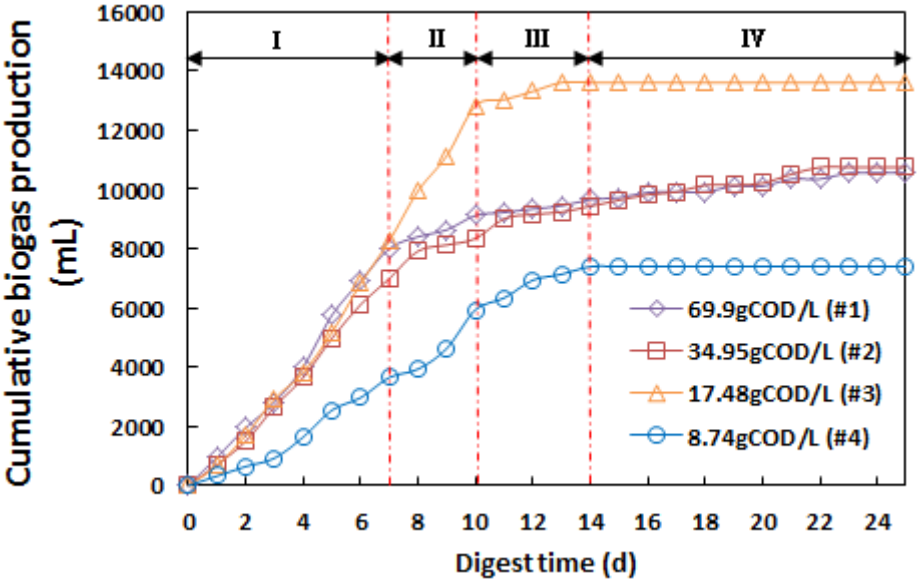

Fig.2.14 Cumulative biogas production of separated liquid with different dilution rate

As shown in Figure 2.14, the cumulative gas production under different COD loadings was monitored for 24 days. The period of the anaerobic digestion can be divided into four stages, namely stage I, II, III, and IV, respectively.

In stage I (1-7d), which was the initial phase of anaerobic digestion, the speed of methane production of #1, #2, and #3 was fast because the VFA concentration of them was high and transformed into methane directly while that of #4 was slow for its low VFA concentration.

In stage II (7-10d), as the process of anaerobic fermentation, the inhibition of ammonia and the reducing and shortage of VFA of #1 and #2 lead to the increasing of methane production in stage II (7-10d). However, the efficiency of methane production of #3 and #4 was still higher and not restrained because the organic matters of #3 and #4 was continually digested into VFA.

In stage III (10-14d), the biogas production was reduced with the decreasing of COD concentration.

In stage IV (14-24d), the anaerobic stage of gas producing was terminated by the lack of organic matters and the accumulation of volatile acids. Therefore, one cycle of the anaerobic digestion producing biogas was 14 days. The cumulative gas production sequence of the separated liquid with different dilution gradients in the anaerobic reaction is as following: #3>#2>#1>#4. The final cumulative gas production of #3 was highest and reached to 13607.8 mL and its methane content was 64%.

(2) Unit biogas production

The unit for the methane production and methane conversion rate was shown in Figure 2.15. Unit methane production represents for the amount of methane production per degrated COD. At 35°C, 101.3 KPa, 395mL pure methane generates with the degradation of 1 g COD in theory [2-15]. Thus the methane conversion stands for the ratio of COD transferred to methane in the total degradated COD.

Unit methane production was calculated as following :

(eq. 2-2)

G(mL/g)—unit biogas;

G_0(mL/g)—cumulative methane production;

C_0(mL/g)—COD value of separate liquid before anaerobic;

C_1(mL/g)—COD value of separate liquid after anaerobic;

V_0(L)—volume of separate liquid (1.5L);

The calculation of methane conversion was as following:

(eq. 2-3)

The theoretical methane production is 395 mL/gCOD.

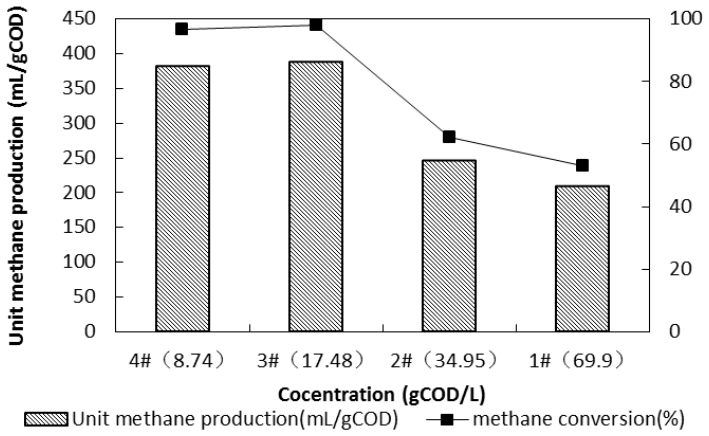

Fig. 2.15 Unit methane production and methane conversion

As shown in Figure 2.15, the unit methane production and the methane conversion increased and then decreased with the increase of the COD concentration and they were up to the maximum value (388 mL/gCOD gas production and 98.2% methane conversion) in #3 (COD=17.48g/L). The order of unit gas production from high to low was: #3>#4>#2>#1.

The ammonia nitrogen concentration of #3 was 295mg/L (less than 400 mg/L) which was suitable for the methane production and the activity of methanogen was highest which leaded to the maximum transformation of low molecular organic (as acetic acid, and ethanol) to methane. The ammonia nitrogen concentration in the seperated liquid increased with the addition of the COD content and inhibited the activity of acid and methane producing bacteria [2-14]. When the concentration of the ammonia nitrogen was too low (#4), the organic compounds in the liquid was consumed by the growth and metabolism of anaerobic microorganisms and short-chain fatty acids was in short of supply. The ammonia nitrogen concentration of #1 and #2 was higher than 800 mg/L which performed the inhibitory for the methane production.

(3) The changes of COD before and after the anaerobic digestion

The COD changes in the separated liquid before and after the anaerobic digestion is shown in Figure 2.16. The COD removal efficiency of #1, #2, #3, and #4 was 30%, 50%, 86% and 93%, respectively. High COD concentration of #1, #2 severely inhibited the activity of acid-producing bacteria. Relatively neutral environment was benefit for the growth of methanogenic bacteria. Therefore, methanogenic bacteria well transformed acetic acid produced from fatty acids (propionic, butyric acid, valeric acid) and ethanol at the function of acetogen. Although #3 and #4 had better anaerobic digestion, dilution multiples of #4 was high which meant the large consumption of water and the dilution multiples of #3 was confirmed as the optimal one.

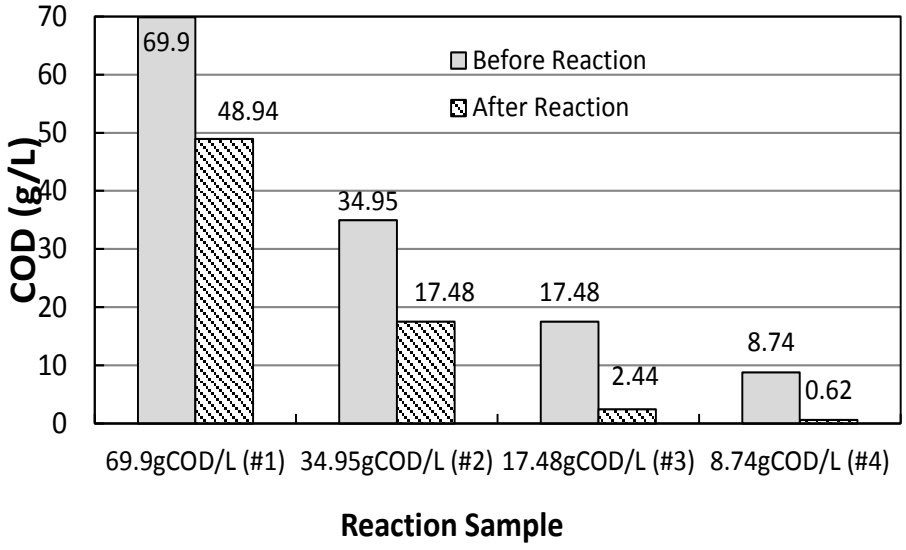

Fig.2.16 The changes of COD before and after the anaerobic digestion

2.4 Conclusion

This chapter investigated the impact of the hydrothermal reaction temperature on the characteristics of the separated liquid obtained from the hydrothermal treatment. The characteristics of the separated liquid were discussed in view of COD, VFA, SCOD, TN, NH_4^+-N, and TOC. The methane producing potential of the separated liquid was carried by STR tanks and evaluated the biogas producing efficiency, methane content, and methane conversion. The following conclusions were obtained.

(1) The results of the analysis of components showed that sludge separated liquid contained large amounts of organic matter, which could be digested by anaerobic microorganisms to produce biofuel. The biogas produced from the anaerobic digestion could be used as an energy source for the production of steam for heating sewage sludge in hydrothermal treatment.

(2) The accumulative gas production, the methane content, and the unit methane production at 190 °C was 10654.2 mL, 62.2%, and 210 mL/gcod, respectively. Furthermore, the calorific value of the RDF fuel obtained from the hydrothermal treatment at 190 °C was better than others. Therefore, the separated liquid under the heating condition of 190 °C was selected for the subsequent anaerobic digestion.

(3) The separated liquid obtained from the hydrothermal treatment at 190 °C was diluted with water in the ratio of 1:0, 1:1, 1:3, and 1:7, respectively, and added into STR tanks named #1, #2, #3, and #4, respectively. The dilution multiples of #3 was confirmed as the optimal one. The final cumulative gas production, unit gas production, methane conversion, and COD removal efficiency of #3 were 13607.8 mL, 388 mL/gCOD, 98.2%, and 86%, respectively.

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Chapter 3

Performance of Anaerobic Digestion of Separated Liquid Produced from Sewage Sludge by Hydrothermal Treatment

3.1 Introduction

The separated liquid studied in this research is different from conventional wastewater. The liquid is of high concentration organic waste liquid after the hydrothermal treatment of sludge followed by the dehydration.

In Chapter 2, the STR experiments verified the feasibility of the anaerobic treatment and evaluated the performance of biogas production. After the anaerobic digestion experiment of the separated liquid obtained by 30-minute hydrothermal treatment at 190 ℃ and diluting it four times (sample #3), sample #3 (17.48 gCOD/L) yielded the highest methane production (388 ml/gCOD), the conversion rate of methane reached 98.2%, and the removal rate of COD reached 86%. The experiments provided the basic data to support the engineering study in this section.

In view of the analysis and research on the separated liquid, an anaerobic reactor is selected, including expanded granular sludge bed (EGSB), UASB, etc. EGSB is a new kind of an anaerobic reactor that belongs to the third generation of anaerobic reactors [3-1] and is used in wastewater anaerobic treatment processes. Compared with UASB, EGSB increases the effluent backflow and speeds up biochemical reactions in the reactor. EGSB has a high ascending velocity, a small floor space, and a high treatment efficiency. EGSB also has the advantages of homogeneous mixing of sludge and water, small dead zone, and high biomass in sludge. In addition, the dilution effect of the effluent backflow helps to increase the reactor load and enhance the withstanding capability of the reactor to toxic and harmful substances. EGSB can be used for different kinds of wastewater treatment [3-2].

Therefore, to explore the engineering feasibility of the anaerobic treatment of a separated liquid and the energy recovery effect, this study employs the EGSB reactor using

the technology of mesophilic anaerobic digestion to deal with the separated liquid.

The synergistic effect of microorganisms in the reactor, the structure and operating conditions of the reactor itself, and the selection of various operation parameters in the actual operation play key roles in the reactor operation effect. This study mainly discusses the factors of the COD concentration, the residence time, the ammonia nitrogen, and VFA of the influent and effluent water work in concert with EGSB processing effectiveness. The study also evaluates the efficiency of the gas yield, the methane purity, the methane conversion rate, and other indicators. The analysis and comparison of the practical computational results, compared with the laboratory research results, confirm the optimum operating conditions, which provide the basis and reference for subsequent engineering practical applications.

3.2 Experimental facility and measurements

3.2.1 Large-scale facility

3.2.1.1 Hydrothermal reactor

Figure 3.1 shows a picture of the hydrothermal reactor of the large-scale facility. The specifications of the hydrothermal reactor of the large-scale facility are shown in Table 3.1.

Figure 3.1 Hydrothermal reactor

Table 3.1 Specifications of the large-scale reactor

Volume (Φ1,800 × 6,000 mm)	7.8 m^3
Rated Operating Pressure	3.0 MPa

Design Temperature	240 °C
Jacket Rated Operating Pressure	1.0 MPa
Jacket Temperature	187 °C

3.2.1.2 Boiler

Photos and the specifications of the hydrothermal boiler of the large-scale facility are shown in Figure 3.2 and Table 3.2, respectively.

Table 3.2 Specifications of the boiler

Specified Evaporation Rate	2 T/h
Rated Operating Pressure	3.0 MPa
Grate Area	3.2 m^2
Rated Evaporation Temperature	235 °C
Design Efficiency	85%

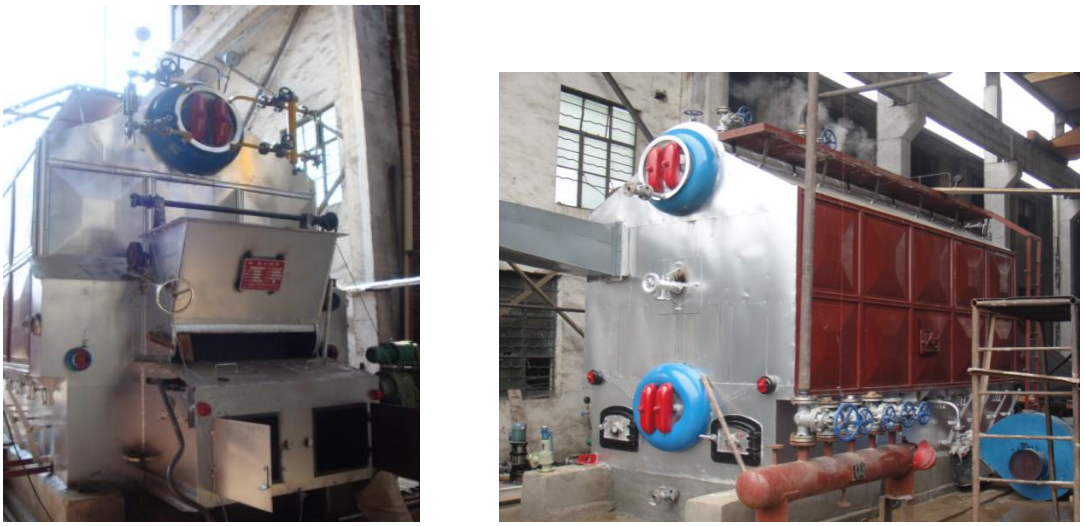

Figure 3.2 Hydrothermal boiler

3.2.1.3 Dehydration facility

A photo and the specifications of the flame filter for dehydroration of the large-scale facility are shown in Figure 3.3 and Table 3.3, respectively.

Table 3.3 Specifications of the frame filter

Each batch processing	12.13 t
Operation mode	Intermittent

Each batch processing time	120 min
Inlet time	80 min
Processing batches	10

Figure 3.3 Frame filter

3.2.1.4 Large-scale commercial plant facility—EGSB

A drawing, a photo, and the specifications of the EGSB of the large-scale facility are shown in Figure 3.4, Figure 3.5, and Table 3.4, respectively.

The separated liquid enters the bottom of the EGSB reactor through a sewage pump, passes the reaction zone, and is separated into gas, liquid, and solid via a three-phase separator. The wastewater is discharged via the outlet after the processing. Most of the anaerobic granular sludge automatically returns to the bottom of the reaction zone because of gravity. When the gas production is large enough, part of the sludge follows the two phases of gas and liquid and rises to the top of the reactor through the lift leg, and then reenters the bottom of the reactor through the sludge circulation tube. Large amounts of gas mixture of CH_4 and CO_2 are produced from the biochemical reactions, which would be collected by a three-phase separator, enter the water seal, and then enter the wet gas flow meter to determine the gas production. Based on the principle of the fluid dynamics and differential pressure, the reactor itself can also form the self-circulation.

The EGSB reactor is composed of the following five parts:

(1) Influent system: In the influent system, as shown in Figure 3.4, the water intake is located at the center of the reactor bottom to evenly distribute the wastewater throughout the EGSB reactor, which is in favor of sufficient contact with wastewater and microorganisms,

thereby raising the utilization ratio of the reactor volume.

(2) Reaction zone: As shown in Figure 3.4, the reaction zone of the EGSB reactor is the core of the EGSB reactor. This region is where most of the anaerobic granular sludge and the organic matter decomposed by anaerobic bacteria, and is the site for the anaerobic microorganism cultivation and enrichment. Considering the demand on temperature of microorganisms, the reactor preservation insulation jacket is designed outside the reaction zone to ensure that the reactor works under the constant temperature of 35+2 °C.

(3) Three-phase separator: As shown in Figure 3.4, a three phases separator is the key structure of the EGSB reactor. The main purpose of the separator is to separate the three phase of water, methane gas, and sludge and keep the sludge in the reactor effectively. The three-phase separator is composed of a gas-collecting chamber and a subsidence area. The gas enters the gas-collecting chamber, and the two phase of gas and liquid are separated and discharged through the water seal. The height of the interface between the gas and liquid phases is the key. The gas-collecting scum or the froth may form between the gas and liquid phases, which would hinder the release of bubbles. When the interface is too high or fluctuated, the scum or froth would clog the exhaust pipe, especially when the gas production in the reactor is small. Thus, to keep the interface in the gas-collecting chamber in a relatively stable and low position, adjusting the liquid level height in the water seal is particularly important. The solid is brought to the gas-collecting chamber by gas and begins to sink to the reaction zone after the separation of the liquid and gas. When the solid and liquid are separated in the subsidence area, the solid returns to the reaction zone because of gravitational force and the liquid is discharged through the outlet (7 - Effluent).

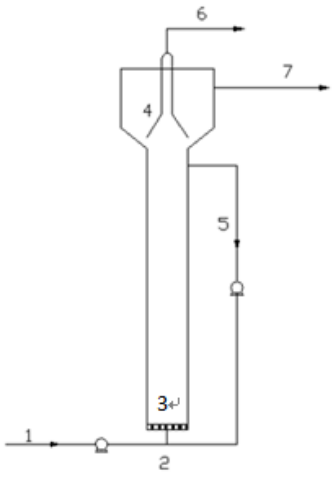

Figure 3.4 Schematic of the EGSB

1 - Influent system; 2 - EGSB reactor; 3 - distributing system;

4 - Settler; 5 - inner circle system; 6 - gas collection system; 7 - effluent

(4) Effluent water recirculation systems: As shown in Figure 3.4, the inner circle system employs effluent water recirculation systems. A greater flow rate means that to keep the water distribution systems uniform is easier. The effluent water recirculation systems improve the liquid flow velocity inside the reactor, fully inflate the granular sludge bed, ensure that the wastewater and microbes are in sufficient contact, enhance the mass transferring effect, and avoid dead ends and shortage produced in the reactor.

Table 3.4 Specification of EGSB

EGSB quantity	2
HRT design value	10 d
Volume (Φ5×16.8 m)	330 m^3

Figure 3.5 The EGSB reactor

3.2.2 Experimental separate liquid samples

According to the test results shown in Chapter 2, the separated liquid after the hydrothermal treatment at 190℃ was used as a sample for the EGSB treatment. The separated liquid was diluted four times and supplied into the EGSB reactor process, where the sample is average. Related properties of the influent separated liquid are shown in Table 3.5.

Table 3.5 Properties of influent separated liquid in EGSB

Reaction condition	TCOD (mg/L)	SCOD (mg/L)	NH_4^+-N (mg/L)	VFA (mg/L)	pH Value
Separated liquid average	69900	54600	1180	2792	7.1
four times dilution average	17475	13650	295	698	7.1

3.2.3 Experimental procedure and measurement

The process flow diagram of the large-scale commercial plant is shown in Figure 3.5. The construction scale is 100 t/d. This commercial plant includes at least the sludge storage and pumping system, the hydrothermal treatment system, the dehydration system, the wastewater treatment system, the waste gas treatment system, the RDF utilization system, and so on.

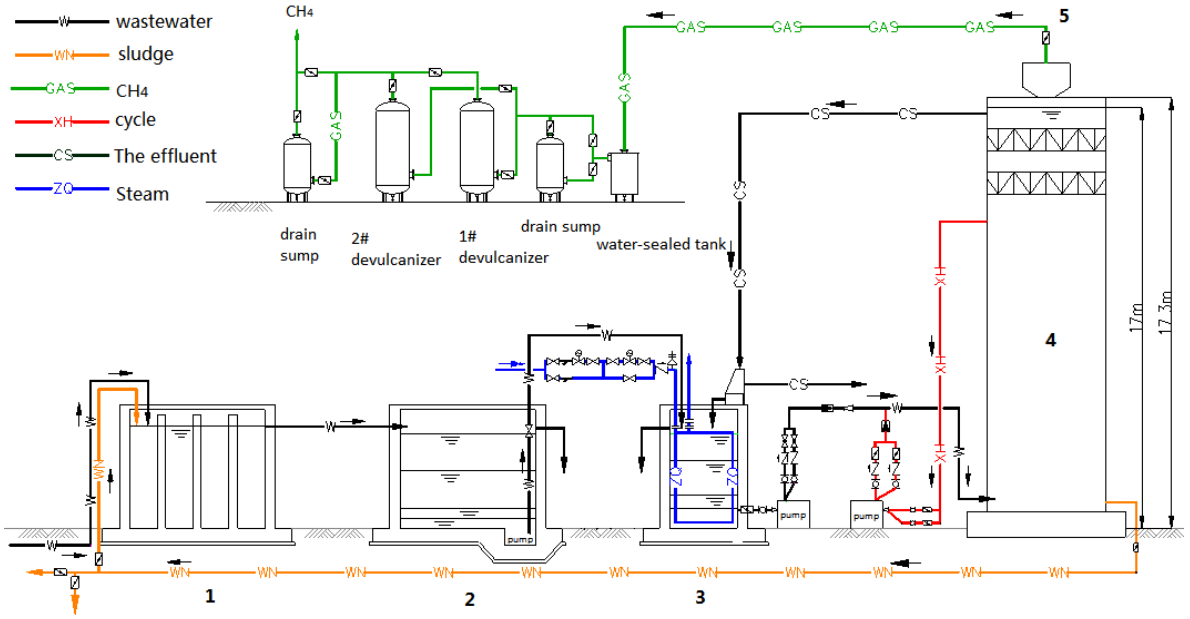

Figure 3.6 Process flow diagram of methane production from sludge

1 - water collecting basin; 2 - conditioning tank; 3 - distribution reservoir; 4 - EGSB anaerobic reactor; 5 - gas refining

Figure 3.6 shows the EGSB process flow diagram of the anaerobic reaction and methane production of the separated liquid. The separated liquid after the hydrothermal treatment at 190℃ passes through the grate canal first, wipes off the sundries, and then

enters the water collecting well. The effluent from the water collecting well and part of the aerobic pool backflow sewage enters the adjusting pre-acidification pool ("regulating reservoir" for short) to dilute the separated liquid four times and to stabilize the quality and quantity of the water. The effluent is pumped up to the service reservoir, where heat exchanges with high temperature steam take place and the temperature rises to 35 ℃. The effluent of the service reservoir is pumped up to the EGSB anaerobic reactor. Under the action of anaerobic microorganisms (methanogens, etc.), the organic matter in the separated liquid decomposes and produces methane. The sewage enters the three-phase separator after the treatment. The granular sludge is trapped in the service reservoir and then brought into the EGSB reactor by the inflow water once again. The effluent then enters the follow-up system. The biogas is used for the heat recycling after being refined.

3.2 Operating characteristics and effects evaluation of EGSB in a commercial plant

Based on the commissioning and the operating stability of the EGSB reactor and given that the granular sludge has reached a good running state, the operation characteristics and the influencing factors of EGSB are evaluated and researched in this paper. The composition of the separated liquid processed in this project is different from that of the conventional high-concentration organic wastewater. The anaerobic action and methane production are referred to in Chapter 2, and the EGSB reactor is debugged in the demonstration project. Researches on the influence factors (the COD concentration, the residence time, the ammonia nitrogen, VFA, etc.) and the efficiency of the separated liquid processing are carried out. The indicators of the gas production efficiency, the methane purity, the methane conversion rate, etc. are also evaluated.

3.2.1 Influent and effluent COD changes of the EGSB reactor

The HRT (Hydraulic Retention Time) is the retention time of the separated liquid in the EGSB reactor, which represents the duration of exposure of microorganisms and the separated liquid in the reactor. While designing the anaerobic reactor, the retention time was an important control parameter. Exorbitant residence time leads to waste in effective volume of the reactor, thereby increasing cost and easily causing the inadequate nutrition of microorganisms. A residence time that is too short causes insufficient exposure time of microorganisms and wastewater and a high level of organic loading in the reactor, thereby influencing the katabolism effect of microorganisms to contaminants and leading to the deterioration of the effluent quality. This experiment explores the proper retention time of

the separated liquid in the EGSB reactor and inspects the COD change of the inlet and outlet water as a reference for engineering application.

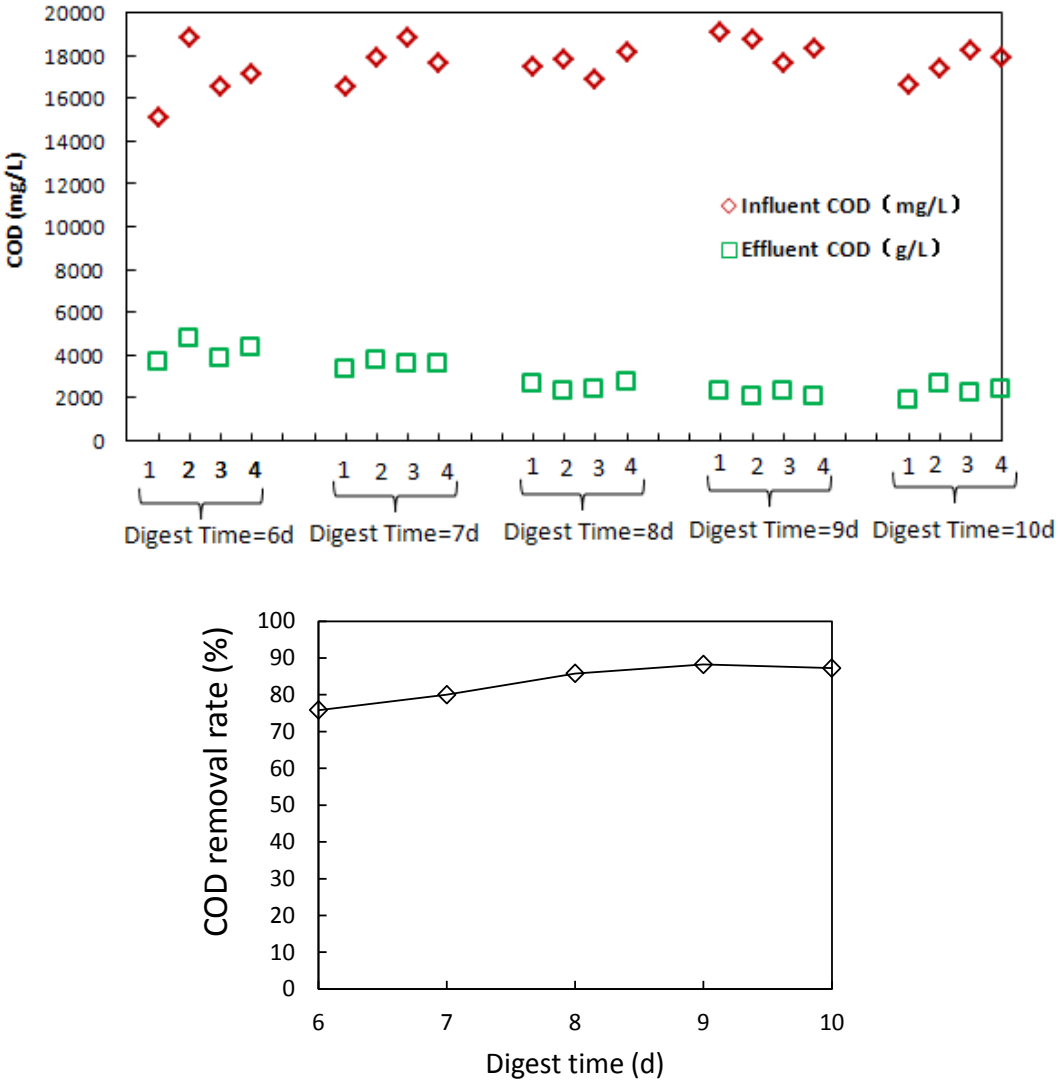

Figure 3.7 Influent and effluent COD changes of the EGSB reactor with different digest times

Based on the test results shown in Chapter 2, the separated liquid that was diluted four times is used as the object of the study. The COD level of the inflow is controlled between the ranges of 15,000 mg/L to 18,000 mg/L. The HRT is separately set up in five stages of 6, 7, 8, 9, and 10 d. The change in the four-day COD values of the inlet and outlet water is recorded and measured. The computational results are shown in Figure 3.7. When the HRT is 6 d, the COD removal rate is about 75.8%. When the digestion retention time is extended, the removal rate increases. When the HRT is 8 d, the COD removal rate is about 85.8%. When the HRT is 9 d, the COD removal rate is about 88.25%. When the HRT is 10 d, the COD removal rate is close to 87.25%.

Therefore, the values of COD removal rates were obtained when the digestion time was more than 8 d. The COD removal rate was 86% in the laboratory-scale test when the digestion time was 12 d and about 85.6% when the digestion cycle was 8 d, because microbial degradation into separated liquid needed longer retention time. The retention time of 6 and 7 d was short and resulted in deficient microbial degradation into separated liquid. The COD removal rate reached 85.6% when the HRT was increased to 8 d. The COD removal rate was about 87.25% when the HRT was prolonged to 10 d, which is only 1.65% more than that when the HRT was 8 d.

The HRT reduced by 4 d compared with laboratory-scale STR test because the process of fermentation and gas production was completed in a closed tank in the STR test. The reaction between the separated liquid and the microorganism inoculate was triggered only by stirring. EGSB is a complete system composed of a water distributor, three-phase separator, gas-collecting chamber, and an external inflow system. The separated liquid entered the EGSB reactor by the slush pump. Its organic matter came in sufficient contact with the sludge at the bottom of the anaerobic reactor, and most was absorbed. The high hydraulic loading and gas yield caused the sludge to mix with the organic matter intensively. The sludge was in a full expansion state and the mass transfer rate was high, which greatly improved the anaerobic reaction rate and the organic load as well as reducing the HRT.

The exorbitant residence time would lead to the waste of effective reactor volume and consequently increase costs, easily cause inadequate nutrition for microorganisms, and influence the treatment effect on the EGSB reactor. Therefore, the digestion time HRT of 8 d is the best considering the actual project running cost.

3.2.2 Influent and effluent NH4+-N changes of the EGSB reactor

Ammonia is the key factor that affects the anaerobic digestion. Excessively high ammonia concentration would restrain the metabolism of anaerobic microorganisms, decrease gas production, and cause difficulties in the operation of the reactor. Research results indicate that the environment would not benefit from microbial growth and reproduction if the influent ammonia concentration is less than 200 mg/L; the ammonia concentration is not harmful for microorganisms when the influent ammonia concentration is 200 mg/L to 500 mg/L; ammonia would restrain metabolism of microorganisms and harm the stability of the system if the influent ammonia concentration is 500 mg/L to 2000 mg/L; and the inhibition effect on microorganisms from the ammonia nitrogen is more obvious and activity is reduced by half when the influent ammonia concentration is more than 2000 mg/L [2-19].

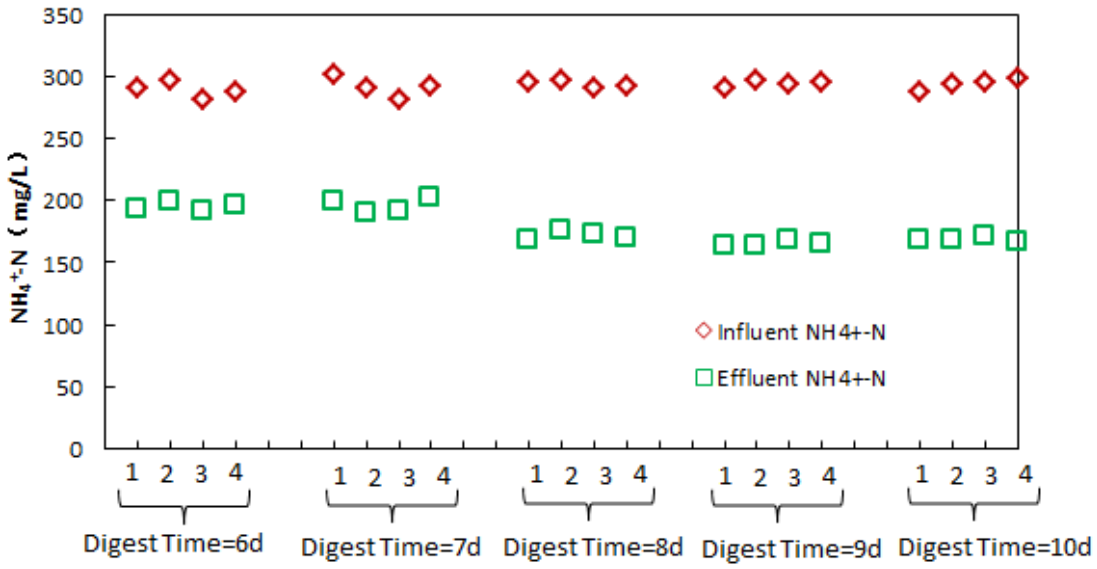

Fig. 3.8 Influent and effluent NH_4^+-N changes of the EGSB reactor with different digestion times

Fig. 3.8 shows the variation of the ammonia nitrogen concentration with different digestion times in the influent and effluent water. However, the ammonia nitrogen removal rate stabilized at around 44% at the beginning of this period when the digestive cycle was 8 d. Imports of the ammonia nitrogen concentration was around 300 mg/L or so and the ammonia concentration was around 200 mg/L to 500 mg/L because of the prolapse of the diluted liquid #3, which affected the system performance for promoting methane production, thereby making methanogenic microbial communities grow and reproduce intensely, and ensuring that anaerobic acidogenic and methanogenic bacteria co-transform organisms in fermentation liquid better; the result was similar to that shown in Chapter 2. The degradation of the ammonia nitrogen concentrations was partly due to the anaerobic treatment systems. The synthesis of methanogenic bacteria required NH_4^+ as ammonia source for its cell synthesis, consuming part of the ammonia nitrogen on the other. At the same time, the organic nitrogen is simultaneously reduced to NH_4^+-N. The anammox reaction simultaneously exist in the reaction process in the EGSB, that NO_3^- or NO_2^- as electron acceptor, the NH_4^+ oxidation of gaseous N_2 or nitrides, making prolapse liquid ammonia has been part of the degradation.

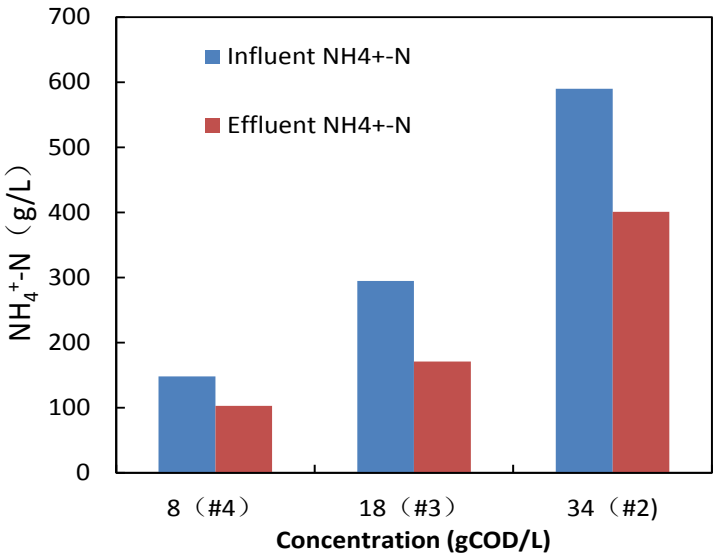

Fig. 3.9 NH_4^+-N changes of different influent CODs

Fig. 3.9 shows the different inlet COD concentration digestion cycles for 8 d changes of ammonia concentrations. Removal rates were low when imported COD load was 8 g/mL because the ammonia nitrogen was 149 mg/L < 200 mg/L, which was not conducive to the growth and reproduction of microorganisms in anaerobic reactors, because methanogenic bacteria itself requires ammoniacal nitrogen to synthesize the basic substance of synthetic cells. The ammonia nitrogen would not adversely affect microorganisms if the imported COD load is 18 g/mL and separated liquid imports the ammonia nitrogen concentration of 295 mg/L, in 200 mg/L to 500 mg/L. The enrichment of the anaerobic ammonia oxidation bacteria increased the ammonia nitrogen conversion rate, which improved the removal effect. Ammonia nitrogen would restrain microorganisms if the imported COD load is 34 g/mL, while the separated liquid imported ammonia nitrogen concentration is 590 mg/L, in 500 mg/L to 2000 mg/L, thereby making the removal rate less effective than if imported COD load is 18 g/mL. Therefore, for 3#(18gCOD/L), the ammonia nitrogen removal rate stabilized at around 44% at the beginning of this period when the digestive cycle was 8 d, which has better removal while not inhibiting the anaerobic biogas reaction.

3.2.3 VFA changes of the EGSB reactor

The volatile fatty acid (VFA) is used in the intermediate production in the anaerobic digestion process. Organic matter under the action of hydrolysis acidification bacteria is decomposed into short chains of organic acids from complex organic matter. Subsequent methanogens mainly use VFA for the substrate to form methane. Volatile fatty acids mainly refer to acetic, propionic, isobutyric, butyric, isovaleric, and valeric acids. Methanogenesis of methanogens cannot occur without the participation of VFA. However, VFA will accumulate

in the reactor when the methanogen activity declines for some reason, the reactor organic load is too high, or VFA production is too much (more than the capacity of the methanogen processing). This condition is characterized by the increased VFA concentration while detecting. The pH value of the reactor may decline when the VFA concentration is constantly higher than the reactor buffering capacity, which has adverse effects on methanogenesis.

The anaerobic treatment process of the EGSB reactor can be simplified to involve two groups of microorganisms, namely, acid- and methane-producing bacteria. In the degradation process, glucose under the action of methanogens is transformed into VFA, and VFA under the action of methanogens is converted to CH_4 and CO_2.

The effect of the basicity and VFA methanogenic process can be represented in the following two equations:

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错误!未找到引用源。 （3-2）

CO_2 in the reactor came from two channels: from organic compounds metabolized by acid-producing bacteria and from neutralizing alkalinity and HAC. The equilibrium pressure of CO_2 fluctuated in a certain range because of digestion in the EGSB reactor. The equilibrium partial pressure of CO_2 and pH increased at an early reaction period because of the acetic acid production process and alkalinity neutralization. Acetic acid was used as substrate during a later reaction period. Biochemical processes that occurred at this time were mainly for methane production, as shown in Formula 3-2.

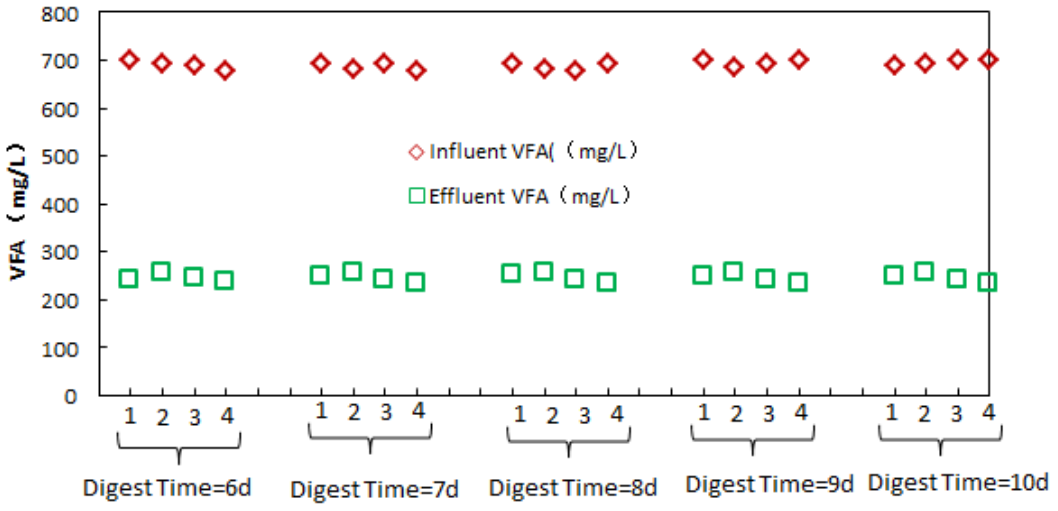

Fig. 3.10 VFA concentration changes of the EGSB reactor with different digestion times

Fig. 3.10 shows the VFA concentration changes of the EGSB reactor with different digestion times in this experiment. The VFA concentration of the effluent is low (< 300 mg/L) in the reactor. Alkali is added to buffer VFA to maintain the pH of the system in the reaction process between 7.2 and 7.6 and reduce the free VFA concentration of the reactor, so that methanogenesis process is not restrained and the reactor maintains the normal gas production and removal rate. Excessive free VFA is toxic to the methanogens because two forms of VFAs are present in the reactor, namely, the free and the ion state combined with other materials. It can go through the cell membranes of methanogens and dissociate in the cell, thus interfering with the formation of the proton motive force in the methane production process, thereby suppressing the methanogenesis. VFA will be inhibited only when the concentration of VFA is high, which is also significantly related to the buffering capacity of the reactor. A high VFA concentration in the reactor can be neutralized by alkali if the alkali concentration and the buffer capacity of the reactor are also high, then the reactor can maintain a normal pH value. Therefore, the general alkalinity requirement of the reactor is 1500 mg/L [3-8]. However, an excess in the buffering capacity may cause the reactor pH to decline and VFA free molecules to increase, thereby suppressing the methanogenesis process.

3.2.4 Daily biogas changes with different Influent COD

Changes in the gas volume directly reflect the operation state of the system. It is also a key indicator that reflects the operation situation of the EGSB reactor; the methane gas production is higher when methane-producing bacteria in the reactor are abundant and the treatment efficiency of the reactor is better [3-5]. This test used a wet-type gas flow meter to measure gas flow rate. Liquid sludge removal in the anaerobic process was exploded and transformed into methane and carbon dioxide. Most of the COD was converted into methane and a few was used for the proliferation of anaerobic microorganisms.

We recorded the daily gas production changes of the EGSB reactor in an experiment under different volume load regulations, as shown in Fig. 3.11. We recorded the daily gas production changes on the condition of different influent COD concentrations at 8 gCOD/,18 gCOD/L, L, 34 gCOD/L while the EGSB stably operated because the separated liquid of the EGSB reactor had a treatment scale of 100 t/d. The figure shows that the average daily gas production rate was 397.2 m^3 when the influent COD concentration was 8 gCOD/L under an 8 d digestive cycle. The average daily gas production rate became 817.6 m^3 with the increase of the influent COD concentration to 18 gCOD/L. The gas system efficiency increased with the increase of the influent concentration when the system adapted to low influent

concentrations. However, when the influent concentration reached 34 gCOD/L, which exceeded the dissolution load of the system, the methane-producing activity reduced, which affected the gas production efficiency and the daily gas production (573.8 m^3).

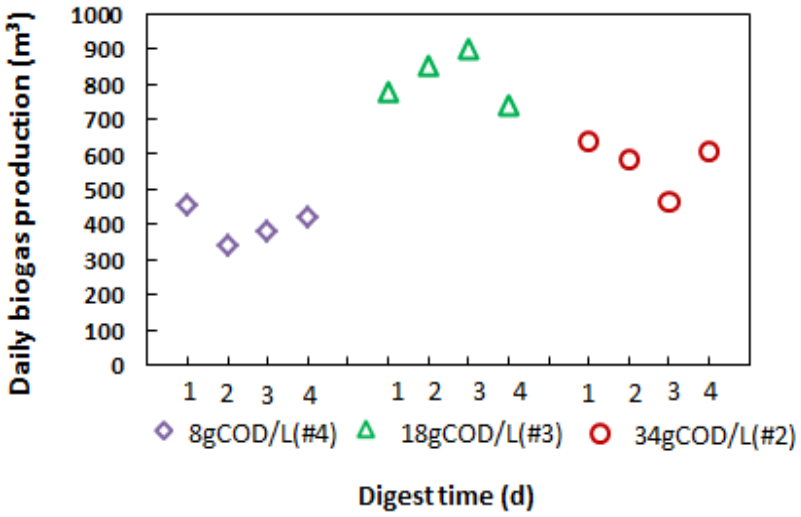

Fig. 3.11 Daily gas production of the EGSB reactor under different volume load regulations

The unit removal COD of gas production is another indicator that could reflect the essence of the anaerobic process based on the actual amount of influent water and gas production as shown in Fig. 3.12. Inaccurate data caused by the line block or meter damage were not counted when gas production were calculated by using the actual daily intake volume and the COD concentration. The diagram shows that methane gas production was the maximum up to 345 mL/gCOD, the methane conversion was 87.3%, and the methane purity was 60% when the imported COD concentration was 18 gCOD/L.

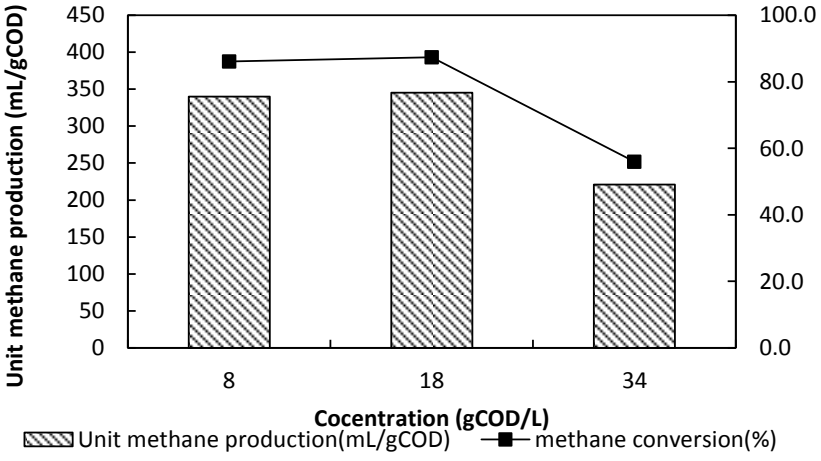

Fig. 3.12 Unit methane production and methane conversion with different influent CODs

Sample #3 (COD = 17.48 g/L) had the highest gas production (unit gas production was 388 mL/gCOD; the methane conversion rate was 98.2%) compared with the STR test results shown in Chapter 2, which was a little lower, but the trend results are similar. This result is due to the long digestive cycle of the lab test. Although follow-up gas production during the digestive period was small, the methanogenesis period was extended. In addition, the utilization of organic compounds in waste water was enhanced. Cumulative gas production increased in the reaction cycle as a result, making unit gas production and methane conversion rate slightly higher.

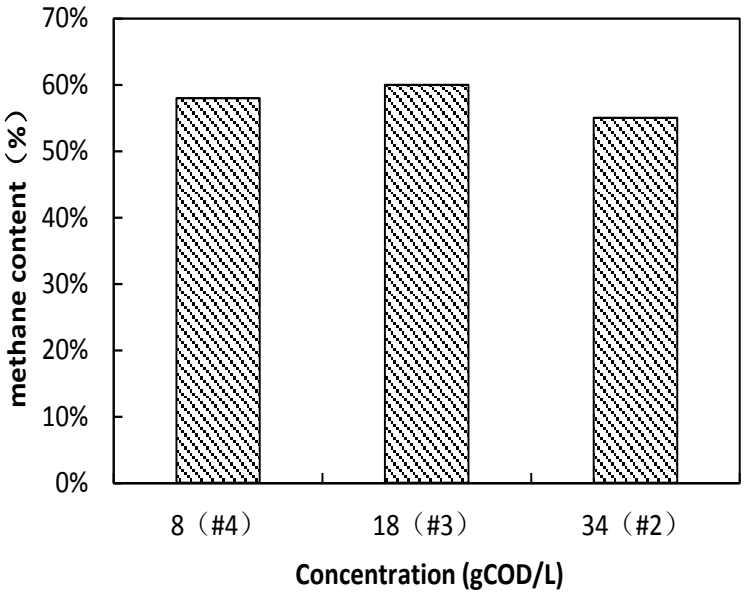

Fig. 3.13 Methane content with different influent CODs

3.4 Conclusion

The commercialization model project of the EGSB reactor using the mesophilic anaerobic digestion technology to treat separated liquid was investigated. Influencing factors such as the inlet COD concentration, the retention time, the ammonia nitrogen, and VFA were analyzed to evaluate the efficiency of the gas production, the methane purity, and the methane conversion index. Actual runtime results were compared with lab test results. The main conclusions are as follows:

(1) The research results indicate that the optimal digestion time of the separated liquid treated by the EGSB reactor was 8 d, the COD removal efficiency was about 79%, the removal efficiency of the ammonia nitrogen was 44%, VFA was less than 300 mg/L, the methanogenic process was not too constrained, and the reactor maintained normal gas production and removal rate.

(2) We conclude (through research on daily gas production of different intake COD concentrations: 8, 18, and 34 gCOD/L) that the unit of methane gas production was the maximum 345 ml/gCOD, the methane conversion rate was 87.3%, and the methane purity was 60% after the stable operation of the EGSB.

(3) The unit gas production, the conversion of methane, the methane purity, and the COD removal efficiency in this chapter were similar to the test results shown in Chapter 2. The data from the study can provide data support for the practical application of this technology and have certain significance.

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Chapter 4

Energy and Mass Balance Analysis of Commercial-scale Hydrothermal Plant

4.1 Introduction

In this chapter, energy and mass balance calculations are conducted to investigate the energy efficiency of the commercial-scale hydrothermal treatment system, which includes the hydrothermal, dehydration, and the anaerobic digestion treatment systems. The Energy Recovery Ratio (ERR) is the most important parameter used to evaluate the energy efficiency of the hydrothermal treatment system. The ERR is defined as follows: ERR = (Energy content in RDF + Energy content in separated liquid − Energy requirement of steam generation − Energy requirement of drying) / Energy content in the raw sludge. To increase the ERR value, the biogas produced from the separated liquid is recycled, whereas the discharged steam from one reactor is recovered into another reactor to reduce the exhaust loss. Comparison of the ERR value of this system with that of other sludge treatment processes enables the analysis of the feasibility and advantages of the present system.

4.2 Experimental facility and procedure

Through a laboratory-scale experiment on the research object in China, a demonstration project was established in Qingdao according to the Hohhot project operation result. This chapter took the demonstration engineering project that was in commercial operation as the research object, and an experimental study was conducted. The process scale of this demonstration engineering project in commercial operation was 100 t/d. Three hydrothermal reactors were adopted to conduct an intermittent alternant type of the reaction, with each reactor capable of disposing 4.17 t for each batch. The processing time for each batch was approximately 105min, and each reactor ran 24 h a day. The steam required in the reaction was supplied by a steam boiler. After the hydrothermal treatment, sludge was transported to the buffer tank and then mechanically dehydrated by the plate and frame presser after the temperature dropped below 80 °C. After the dehydration, the sludge was transported to the boiler for burning as RDF fuel.

The separated liquid was discharged after the anaerobic treatment, whereas the biogas generated from the anaerobic process was transported to the steam boiler for recycling. The spent steam generated in the system was discharged after the deodorization treatment.

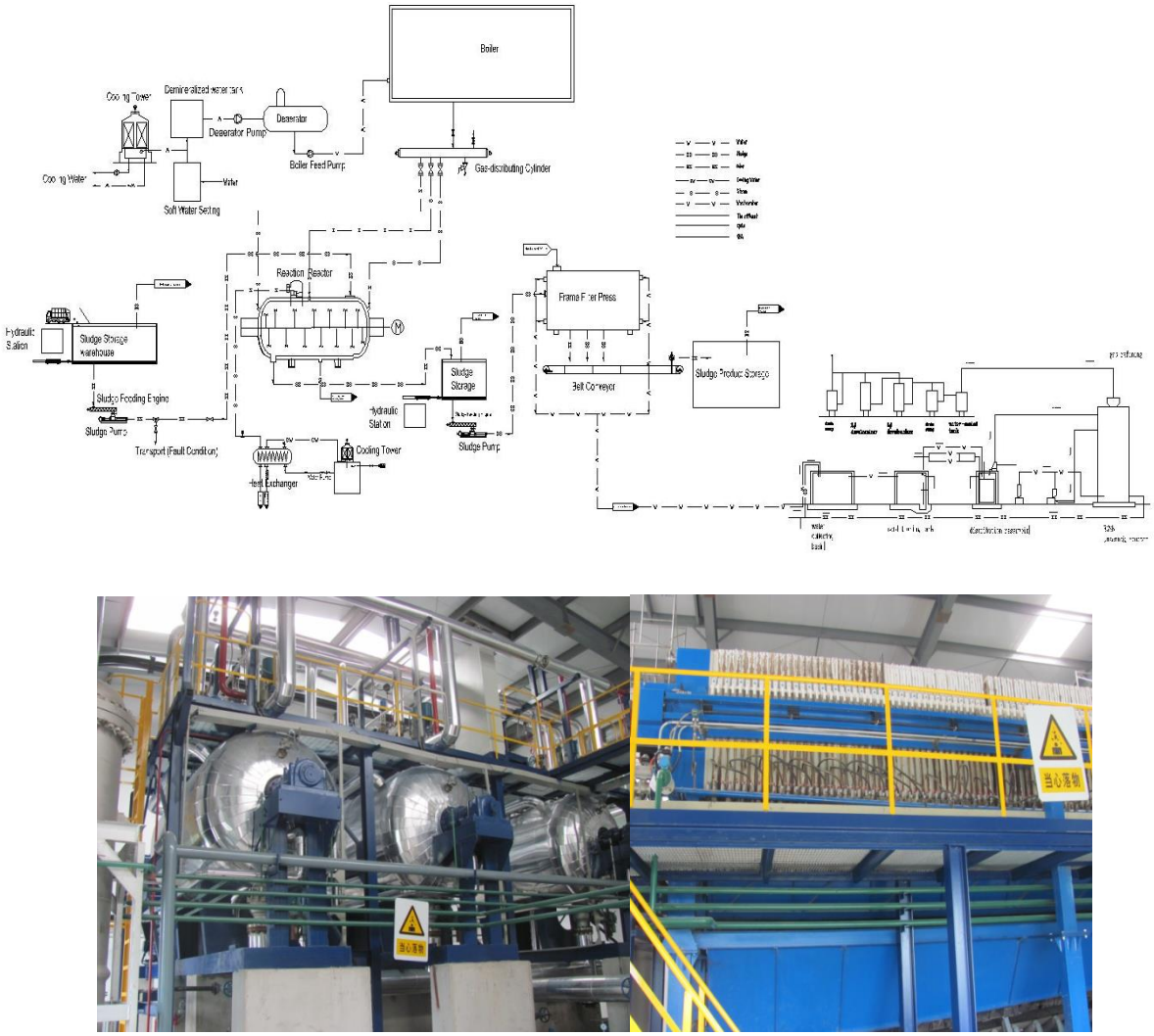

Fig. 4.1 Process flow diagram of the commercial plant

4.3 Analysis of operative condition of the commercial-scale project

The hydrothermal reaction temperature and the reaction time are major factors affecting the hydrothermal treatment and the dehydration of sludge [4–2]. This section examines the actual operation conditions affecting the hydrothermal treatment effectiveness.

4.3.1 System design specifications

The process scale of this demonstration engineering project was 100 t/d. The equipment continuously ran for 24 h each day, and the handling capacity throughout the year was calculated at 330 d of operation. After the hydrothermal treatment, the sludge was mechanically dehydrated. After the dehydration, the sludge was recycled as RDF fuel. The separated liquid was discharged after disposal by the EGSB, whereas the biogas was recycled for further use.

Table 4.1 Main design parameters

Project	unit	
Sludge handling capacity	t	100
Moisture content	%	80
Rated capacity each single Reactor each batch	t	4.2
Reaction time each batch	min	30
Sludge moisture content After dehydration	%	≤40
Saturated steam temperature	centigrade	200

4.3.2 Effect of the hydrothermal treatment time on the operation condition

Given that the hydrothermal reaction time of each batch was a key factor influencing the handling capacity of each reactor for each day, this parameter was also among the factors affecting the steam consumption. Thus, this section focuses on the reaction time required in different stages of the hydrothermal treatment.

The experience values obtained through small-scale and pilot-scale tests under the design conditions are shown in Fig. 4.2. The reaction time of each hydrothermal reaction for each batch is 120 min [4–1].

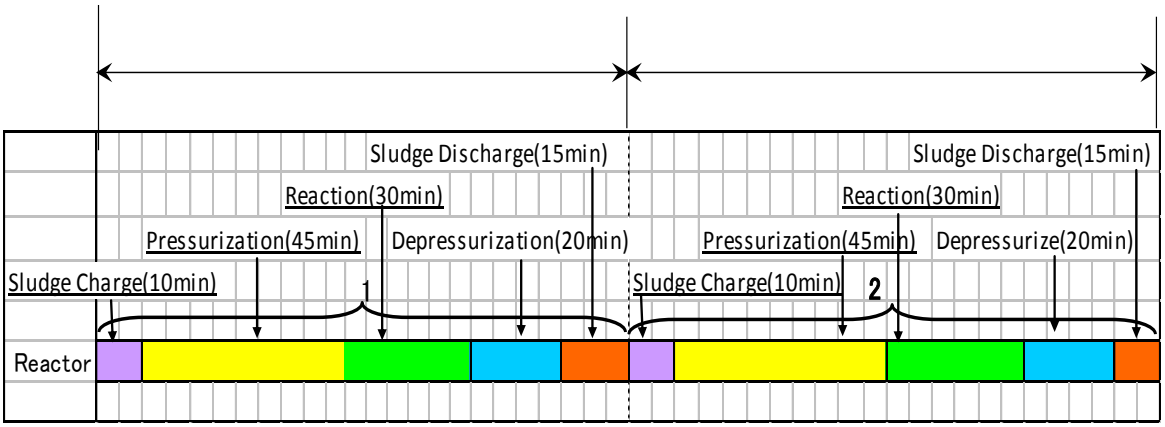

Fig. 4.2 One cycle time of the batch reactor under the design conditions[4–1]

Under the actual operation conditions, the whole experiment could be completed in 120 min according to the design requirements. In the process of subsequent design and development, the reaction time of each batch was increased to enhance the handling capability further.

4.3.3 Material and energy balances

(1) Material balance

Under the actual operation conditions of the commercial project, where the target process condition of 190 ℃ reacted for 30 min, moisture content was expected to be below 50% after the dehydration. The saturated steam supplied was 200 ℃. The data and results of the demonstration project under commissioning conditions are shown in Table 4.2, with the average of five sets of calculated data taken as the value.

Table 4.2 Data records under operation conditions

Serial	Handling capacity of each batch [t]	Reaction temperature [°C]	Reaction time of each batch [min]	Measured steam consumption [t]	Sludge moisture content after dehydration [%]	H.H.V. of sludge after dehydration [MJ/Kg]
1#	4.2	193	117	1775	35.7	13.72
2#	4.1	190	120	1755	34.2	14.42
3#	4.2	187	123	1766	37.1	13.6
4#	4.3	195	120	1740	35.2	15.11
5#	4.2	188	120	1754	36.3	14.1
Average	4.2	190	120	1758	35.7	14.19

The material and energy balances of the demonstration project under the designed operation conditions are shown in Table 4.3 and Figure 4.3, respectively. The actual operation data show that the actual steam consumption was 1758kg of each batch. The reaction time of each batch was 120 min. Sludge moisture content was 35.7% after the mechanical dehydration. This value is lower than 40% and thus meets the design requirements. According to the actual measured data, the dissolution rate of the solid materials was approximately 9.9%, which is in line with a previous research result that the dissolution rate of solid matter was below 10%.

Table 4.3 Material balance of the demonstration project under the designed operation conditions

Input			
	Weight [Kg]	Water [Kg]	Dry Weight [Kg]
Raw Sludge	4200	3457	743
Steam	1758	1758	0
Sum	5958	5215	743

Output			
	Weight [t]	Water [t]	Dry Weight [t]
Dehydrated Solid product	1041	372	669
Waste Steam	1482	1482	0
Liquid	3435	3361	74
Sum	5958	5215	743

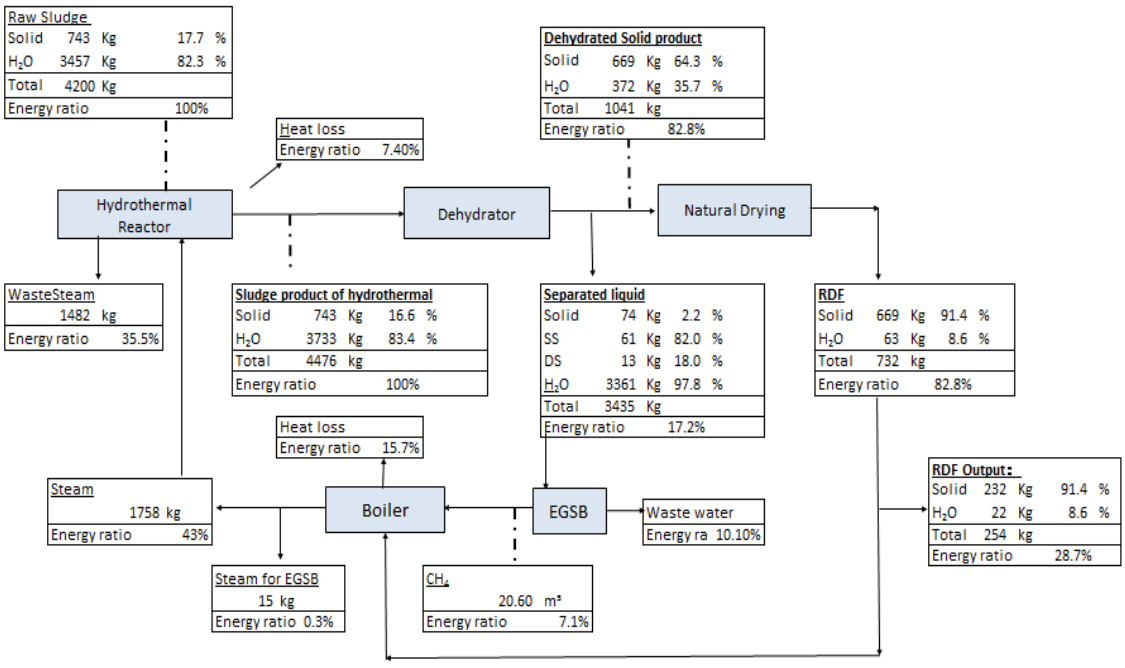

Fig. 4.3 Energy balance with RDF and CH_4 recycles

1) Sludge hydrothermal system

First, the handling capacity of each batch was 4200kg; 4200 kg of sludge with 82.3% moisture content was placed in the hydrothermal reactor to facilitate a reaction through the sludge pump. Second, 4200Kg of sludge was preheated in the jacket, and temperature rose from room temperature (20 °C) to 95 °C. Steam was added, and the hydrothermal treatment proceeded. The sludge temperature rose from 95 °C to 190 °C. The saturated steam at 200 °C was used to heat the sludge, and the enthalpy value was 2798 kJ/kg. Measured steam consumption was 1758 kg.

2) Sludge dewatering system

The solid attrition rate of the mechanical dehydrator was 9.9% according to the measured value. The moisture content of sludge cake was 35.7% after the dehydration, and the amount of sludge that entered the mechanical dehydrator after the hydrothermal treatment was 4476 kg. The dehydrated product of sludge was 1041kg, and the separated liquid was 3435 kg.

3) EGSB anaerobic digestion unit

The amount of the separated liquid produced by the mechanical dehydration was 3435 kg. According to the operation results of EGSB in Chapter 3, the obtained separated liquid of 4.2 t could produce 20.06 m^3 of biogas with the methane purity of 60%.

The calorific value of methane is 39580 kJ/m^3, so the converted energy is approximately 20.06 m^3 × 39580 kJ/ m^3 × 60%=815506.32kJ.

4) RDF product

After the mechanical dehydration, the amount of the solid product was 732 kg. If the calorific value of the dry basis was 14.19 x 10^3 kJ/kg, the sludge moisture content was 35.7%. After the natural drying, the moisture content of RDF was 8.6%. The calorific value was: 732kg×(1-0.086)×14.19×10^3 kJ/kg=9490434kJ.

5) System energy recycles

The RDF product generated from the sludge after the dehydration and the natural drying was recycled, and the biogas generated from the separated liquid was recycled.

As is shown in Fig.4.4, 4200kg sewage sludge with the moisture content of 82.7% about 500kg of RDF fuel energy by way of recycling and methane can be prepared saturated steam 1773Kg of 200 ℃, where about 1758kg for heating sludge and about 15kg for EGSB. There are still about the rest of 245Kg RDF can be output can create additional value.

4.4 Process design improvement and energy-saving of the sludge hydrothermal system

According to the above actual operation condition analysis of the 100 t/d sludge hydrothermal treatment of the demonstration project and under the optimal process condition of 190 °C maintained for 30 min, the sludge moisture content could be reduced to below 40% after the mechanical dehydration. The separated liquid and the sludge product could both meet the design criteria. The RDF could be recycled, and the separated liquid could produce biogas through the anaerobic reaction. However, the spare steam was not considered for the direct recycling and discharge. Based on the above problems, a further analysis was conducted with consideration of the effects of the operation conditions of the commercial project. The analysis, design, and research mainly focused on the steam supply process, the spare steam recycling, and the shortening of the reaction time. The water heat and the waste steam were analyzed to realize the utilization of resources and the reduction of system energy consumption, ultimately to reduce the operation cost.

4.4.1 Energy saving measures for the sludge hydrothermal system

The concept map for energy-saving in the sludge hydrothermal system is shown in Fig. 4.4. This type of energy-saving requires an optimization of the design and steam pipeline renovation on the basis of the original process design. The hydrothermal reactors are still used for the batch intermittent reaction. The spent steam is fully utilized to reduce energy consumption. Part of the spent steam discharged from one reactor is used by another, whereas the remaining part is directly discharged into a subordinate cooling tower to condense. Noncondensing gas is discharged after the deodorization. The alternate continuous reaction of the three reactors increased their revolutions, accelerated the contact between sludge and saturated steam, and improved the reaction efficiency.

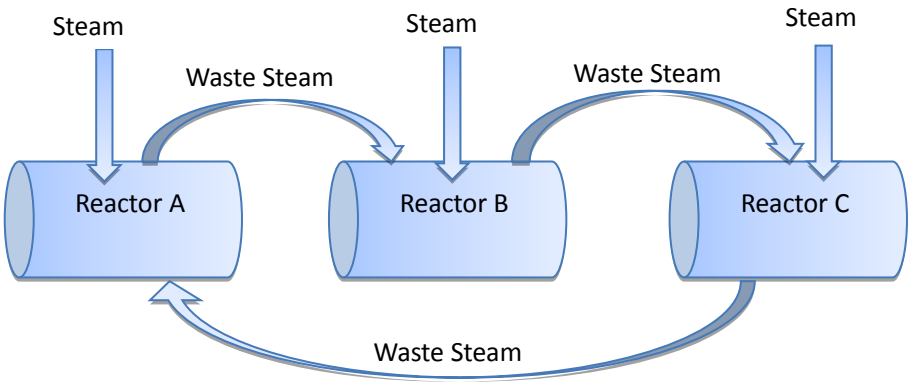

Fig. 4.4 Concept map of energy-saving for sludge hydrothermal system

We take the hydrothermal reactors A, B, and C as examples. The optimized technological operation process is as follows:

- The handling capacity of a reactor for each batch is 4.2 t, according to the model selection of the sludge pump, and the sludge feed time to a reactor is set as 15 min.

- For the first group of reactions, after finishing the sludge supply, steam injection into the reactor A will be started. The stirring is set at 15 rpm, and the jacket temperature is set at < 180 °C. When the sludge feed ends, the feedstock valve is closed, and steam enters the reactor A. The three reactors have three saturated steam inlets at the top, bottom left side, and bottom right side. When the sludge temperature reaches 190 °C and is maintained for 30 min, this group of reactions is completed, and steam entry is stopped to begin depressurization. The residual steam in the reactor A is discharged into the reactor B where the sludge feed is finished.

- In the depressurization stage, spent steam enters the condenser directly and is

then discharged after the deodorization treatment under the original design. In the energy-saving process, the residual steam in the reactor A is discharged into the reactor B directly. After 15 min, the pressure in the reactor A levels off with that in the reactor B, and the valve is closed. At this time, the pressure reached approximately 0.8 MPa–1.0 MPa. The remainder of the spent steam from the reactor A is discharged into the subordinate cooling tower. Stirring and depressurization are stopped when the pressure inside steam the reactor A is < 0.4 MPa. The reactor A begins to discharge sludge into the subordinate buffer storage. This process takes 3 min–5 min to complete. A part of spent steam enters the cooling tower and is condensed into water. A part of non-condensable gas is discharged after the deodorization treatment. This group of reactions in the reactor A is then completed.

- The temperature in the reactor B is expected to reach 70 °C–90 °C within 15 min. At this time, the steam supply valve is opened. The saturated steam inflow is the same as that in the reactor A, and the temperature is expected to reach 190 °C within 30 min. The gas supply is then stopped, and depressurization is initiated after the temperature is maintained for 30 min. The spent steam is discharged into the reactor C. When the pressure balance is achieved, the sludge is unloaded to the reactor B, and similar to the case of the reactor A, this group of reactions is completed.

- The same group of reactions is conducted in the reactor C. The spent steam from the reactors A, B, and C is used alternately to complete the hydrothermal treatment. The reaction for each batch is expected to be completed in 2 h.

4.4.2 Evaluation of the reaction time of each batch in the energy-saving sludge hydrothermal system

The reaction time of each batch under the design conditions for the energy-saving sludge hydrothermal system is shown in Fig. 4.5. The designed feed-in time for sludge is 15 min, the heating time is 40 min, the holding time is 30 min, the depressurization time is 15 min, and the sludge discharging time is 5 min for a total of 105 min. The reaction is completed in 2 h, which is close to the previously presented design conditions.

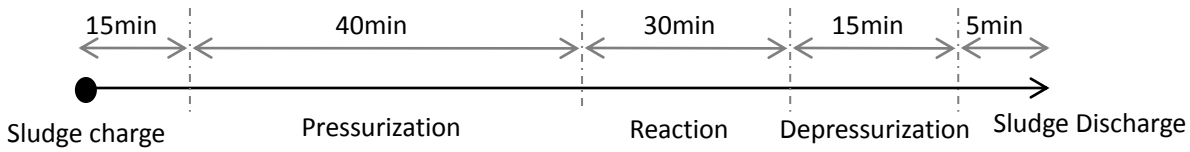

Fig. 4.5 One cycle time of the batch reactor for the optimization process

Eight groups of reaction time results of the energy-saving sludge hydrothermal treatment under the designed operation conditions are shown in Table 4.4. Under the actual operation conditions of the energy-saving system, 105 min of one batch time is required to obtain the optimum reaction parameters of each batch. The average time required for each reaction stage of the sludge hydrothermal treatment comprises the feed-in time for sludge of 15 min, the heating and pressurizing time of 40 min, the holding time of 30 min, the depressurization time of 15 min, and the sludge discharging time of 5 min.

Table 4.4 One cycle time of the batch reactor of the energy-saving system under the designed operational conditions

No.	Sludge charge Time [min]	Pressurization [min]	Reaction [min]	Depressurization [min]	Sludge Discharge [min]
1#	14	11+29	30	10+5	5
2#	16	10+29	30	13+4	5
3#	15	12+28	30	10+4	5
4#	16	10+30	30	11+4	4
5#	15	10+31	30	12+5	4
6#	15	11+27	30	11+5	6
7#	15	10+30	30	10+3	6
8#	14	13+28	30	10+3	5
AVR.	15	40	30	15	5

Results revealed that 15 min was a suitable feeding time for the sludge feed-in stage. As regards the heating and pressurizing time, the shortest actual operation condition needed by the energy-saving system was approximately 40 min. The reaction time was 30 min, which is the same as the holding time under the optimum technological conditions.

At the sludge discharging and unloading stage, the unloading time was greatly reduced compared with the original process under the designed conditions because the pressure release was conducted in the optimized process. Meanwhile, the depressurization time was shortened by 5 min compared with that before the optimization because the spent steam in the reactor had to be discharged after the heat transfer by the condenser in the original process. By contrast, the gas could be directly

discharged to the next reactor without a condensate in the optimized process, thus resulting in a shortened depressurization time. The energy-saving process operation conditions could save 15 min for each batch reaction when compared with the original process.

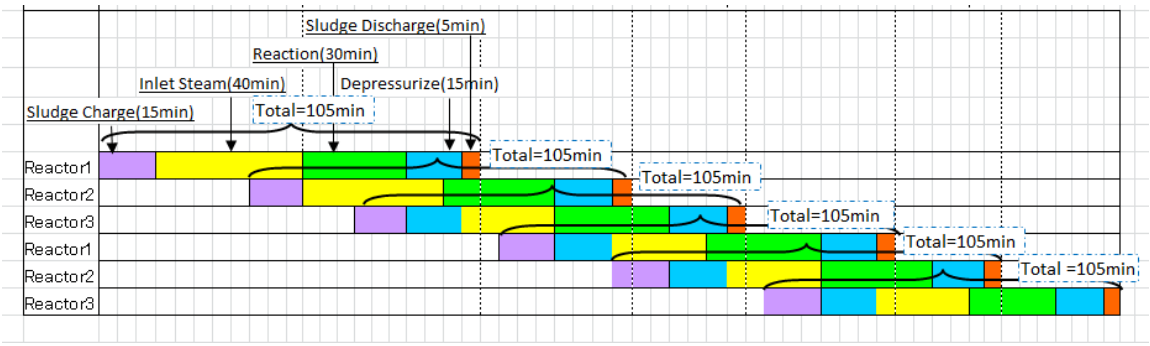

Fig. 4.6 Sequencing of three reactors working time in the energy-saving process

Fig. 4.6 shows the sequencing of the working time of the three reactors under the energy-saving process. After a normal startup, the Reactor1 receives spent steam from a previous reactor after adding sludge for preheating. The saturated steam then enters the inlet for heating. Each reactor follows this order to complete the process. In the original process operation conditions, a single reactor running for 24 h can process only 12 batches with a processing capacity of 50.4 t/d. Under the energy-saving process operation conditions, a single reactor running continuously for 24h can process 13 batches with a processing capacity of 54.6 t/d, which improves the process capability of 9%.

4.4.3 Material and energy balance calculation of the energy-saving system

(1)Material balance

The energy-efficient system operation conditions included the reaction temperature of 190 °C maintained for 30 min and the supply of the saturated steam at 200 °C. Table 4.5 shows the data in the energy-saving system operation conditions.

Table 4.5 Data in the energy-saving system operation conditions

Serial number	Single batch sludge quantity [t]	Reaction temperature [°C]	Single batch reaction time [min]	Determination of steam consumption [t]	Moisture content of dewatered sludge [%]	Dewatered sludge H.H.V. [MJ/Kg]
1#	4.2	190	105	1774	37.2	14.7
2#	4.3	190	107	1756	35.9	14.5

3#	4.2	191	103	1764	34.0	13.9
4#	4.2	190	104	1742	34.8	14.1
5#	4.1	189	106	1754	36.6	13.8
Average	4.2	190	105	1758	35.7	14.2

Table 4.6 shows the data in the energy-saving system operation conditions. Tables 4.5 and 4.6 show that the processing of 100 t/d of wet sludge consumed 20.95 t of saturated steam, where the single batch time was 105 min, and the sludge moisture decreased to 35.7% after the mechanical dewatering to meet the design requirements. The dissolution rate was 11.8%.

Table 4.6 Material balance diagram under the energy-saving system operation conditions

Input			
	Weight [Kg]	Water [Kg]	Dry Weight [Kg]
Raw Sludge	4200	3457	743
Steam	1017	1017	
Waste steam	741	741	
Sum	5958	5215	743

Output			
	Weight [Kg]	Water [Kg]	Dry Weight [Kg]
Dehydrated Solid product	1041	372	669
Waste Steam	1482	1482	0
Liquid	3435	3361	74
Sum	5958	5215	743

(2)Energy balance

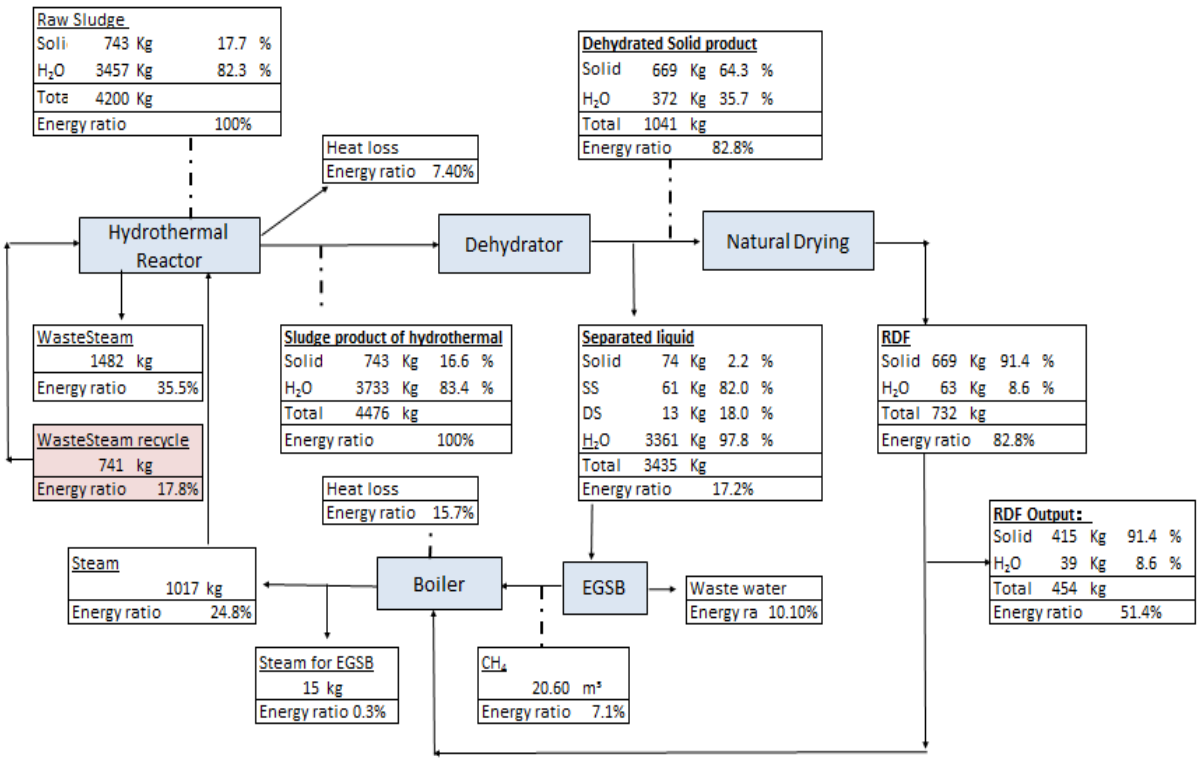

Fig. 4.7 Mass and energy balances with RDF, waste steam and CH_4 recycles

Fig.4.7 shows the energy balance data under the reaction temperature of 190℃ and the reaction time of 30 minutes. Here, the total energy content in the raw sludge is assumed to be 100%, and the energy content of each substance is shown by relative %.

The sludge is usually composed of 80% of water and 20% of solid material. Sludge Energy ： Energy content in sludge (=dry sludge weight × dry base heating value of the solid material)

Steam Energy ： Energy content in steam (=consumed steam weight × enthalpy of steam)

According to the relationship between the energy input and output, the consumed energy was used to heat up sludge. Table 4.7 shows that the energy input was the energy consumption for sludge heating during the hydrothermal treatment process. According to the data obtained from the operation conditions, with the processing capacity of the single batch of 4200 kg, the heating process to the target temperature of 190°C requires 1017kg of saturated steam and 741kg of the waste steam.

The energy output included the usage of the anaerobically produced biogas from the separated liquid and the dewatered sludge as fuel for RDF in two parts. According to the EGSB operation result shown in Chapter 3, 4200kg sludge could produce 20.06 m^3 biogas

from the separated liquid with methane purity of 60%. The sludge product with the moisture content of 35.7% was 1041kg, whose heating value was 14.19×10^3 kJ/kg.

According to the energy-saving system operation conditions, 4200kg sewage sludge with the moisture content of 82.7%, about 278kg of RDF fuel energy by way of recycling and methane can be prepared saturated steam 1032Kg of 200 ℃, where about 1017kg for heating sludge and about 15kg for EGSB. There are still about the rest of 454Kg RDF can be output can create additional value.

4.5 ERR calculation and effect contrast

Based on the above experimental results, the mass and energy balances under different reaction conditions are calculated to clarify the optimum operation conditions of the system in view of maximizing the ERR associated with RDF production from sewage sludge.

(1) ERR calculation in this system

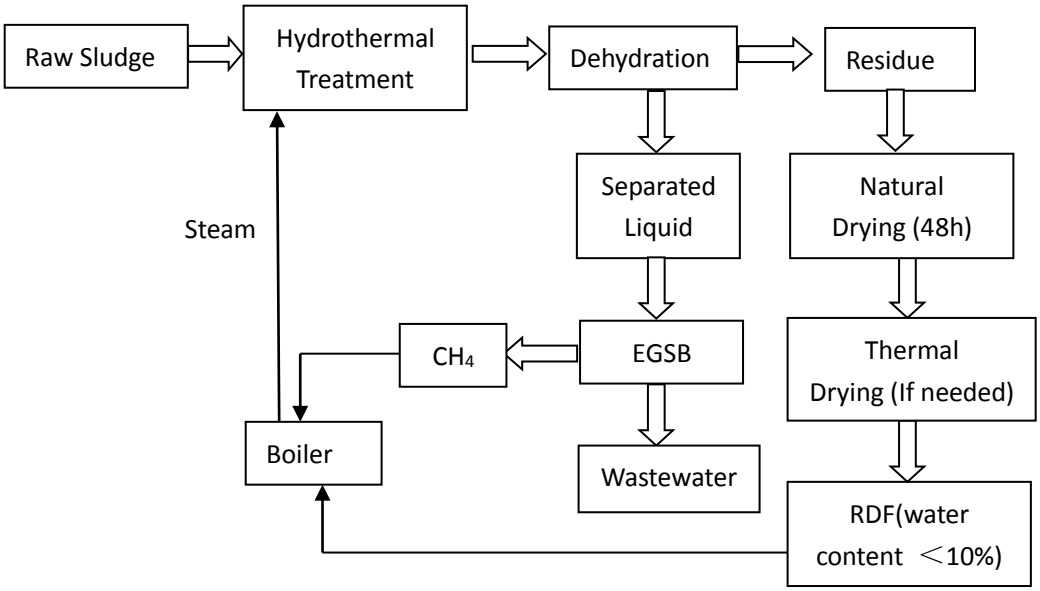

Figure 4.8 Flow Chart of the hydrothermal treatment System

The main purpose of this study is to produce RDF from sewage sludge and to produce CH_4 from the separated liquid, which can be used to fuel in boilers. From the previous investigation [4-1–4-2], the moisture content of RDF should be less than 10% for fuel in most coal-fired boilers. Therefore, the target moisture content of RDF is set to be 10% in this study. The moisture content of the dehydrated residue of the hydrothermal products can reach 10% after the natural drying. Fig. 4.8 shows the flow chart of the total system to

produce RDF from sewage sludge and to produce CH_4 from the separated liquid. Based on the flow chart, the ERR is defined as

ERR = (Energy content in RDF + Energy content in separated liquid (this energy content in the produced biogas) − Energy requirement of steam generation − Energy requirement of drying) / Energy content in sludge

By evaluating the ERR value under different operation conditions, we could identify the optimal operation conditions to maximize the ERR value.

Table 4.7 Energy balance of the commercial plant system

Temperature	Energy Content in RDF	Energy Requirement for Steam Generation	Energy Content in Raw Sludge	Energy Requirement of Dryer	Energy Content in Separated liquid (this produced by biogas)
°C	kJ	kJ	kJ	kJ	kJ
190	2261.17	1171.43	2731.11	0	194.16

The energy balance of the commercial plant system is shown in Table 4.7. A larger ERR makes more energy recoverable from sludge. From the previous investigation and the characteristics of sludge drying, the ERR value, the system investment, and the operational costs, we can confirm that the optimal hydrothermal reaction temperature is 190 °C, and the hydrothermal reaction time is 30 min, at which the ERR value is approximately 40%. In accordance with results shown in Chapter 3, with CH_4 production by EGSB, the ERR value was 47%, the increase of 7% when compared with the non-anaerobic process.

The energy balance of the energy-saving sludge hydrothermal treatment system with recycling of waste steam, the ERR was as high as 64.8%. Through the recovery of biogas and spent steam, the ERR in the energy-saving system increased by 24.9% over the cases without recycling.

(2) ERR calculation of other process systems

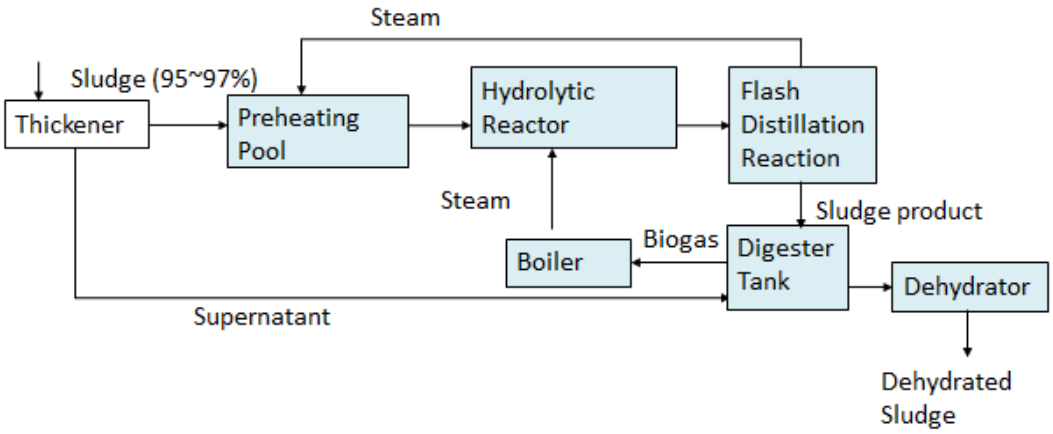

Fig. 4.9 Process of sludge hydrothermal treatment technology 1

Fig.4.9 shows the process of sludge hydrothermal treatment for the technology 1. Compared with the proposed hydrothermal treatment technology in this article, the mechanism of the destruction of the sludge water-holding structure was same, but the raw sludge characteristics are different. The raw sludge used in this paper had a water content of 80% after the mechanical dehydration, but in the technology 1, the raw sludge did not undergo the mechanical dewatering and its water content was approximately 95%–97%. Meanwhile, the proposed process involved the recycling of the separated liquid after the hydrothermal treatment and the mechanical dewatering, but in the technology 1, the hydrothermally treated sludge was directly used for the anaerobic digestion to produce biogas.

In the technology 1, ERR = (Energy content in biogas + Energy content in dehydrated sludge − Energy requirement of steam generation) / Energy content in raw sludge. According to Table 4.8, the calculated ERR under this condition is 38%.

Table 4.8 Energy balance of the technology 1

Temperature	Energy Content in biogas	Energy Requirement for Steam Generation	Energy Content in Raw Sludge	Energy Content in dehydrated sludge
℃	kJ	kJ	kJ	kJ
170	3381.5	3146.8	617.52	0

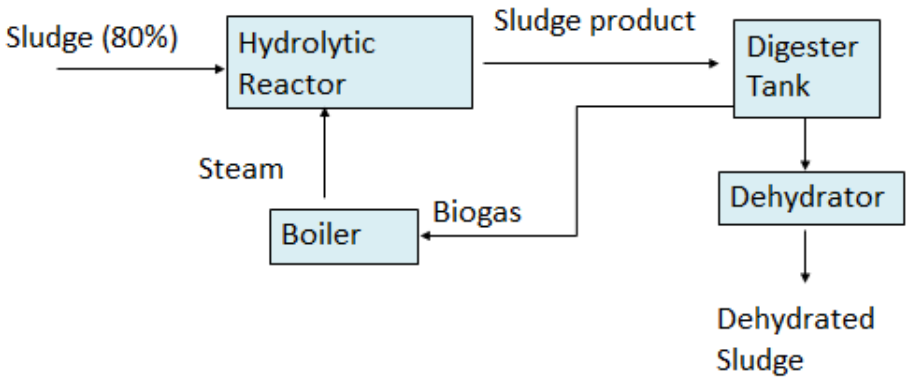

Fig. 4.10 Process sludge hydrothermal treatment technology 2

Fig 4.10 shows the technology 2 of the sludge hydrothermal treatment. Compared with the proposed hydrothermal treatment technology, sludge with moisture content of approximately 80% was subjected to the hydrothermal treatment at the reaction temperature of 150 °C and the reaction time of 30 min. The sludge product was then directly subjected to the anaerobic digestion to recycle methane, and biogas residue was used for mechanical dewatering.

For the technology 2, ERR = (Energy content in biogas + Energy content in dehydrated sludge − Energy requirement of steam generation) / Energy content in raw sludge. According to Table 4.9, the calculated ERR under this condition is 35%.

Table 4.9 Energy balance of the technology 2

Temperature	Energy Content in biogas	Energy Requirement for Steam Generation	Energy Content in Raw Sludge	Energy Content in dehydrated sludge
°C	kJ	kJ	kJ	kJ
150	1893	937.2	2731.11	0

(3) ERR comparison

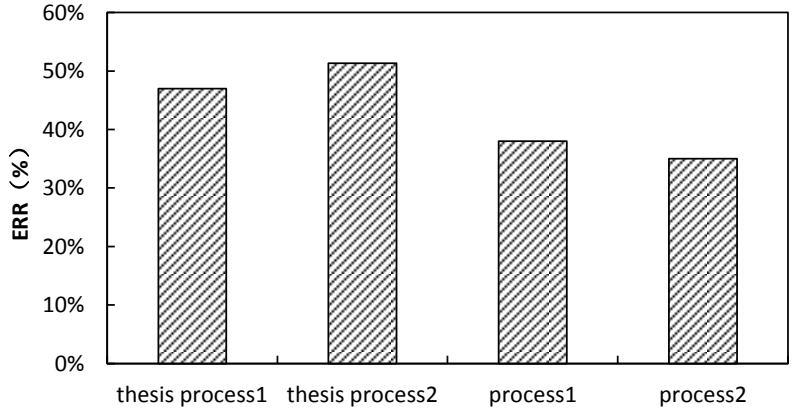

Fig. 4.11 ERR comparison of different treatment processes (process1→technology 1, process2→technology2)

Fig. 4.11 shows the ERR comparison of four different treatment processes. In this paper, the process1 was based on the biogas energy recovery by the EGSB reactor, whereas the process 2 was based on the energy recovery by the EGSB reactor and the spent stream. According to the results, the proposed hydrothermal process used dehydrated sludge as RDF fuel for recycling; whereas the separated liquid was adopted to produce biogas, thus acquiring a higher ERR of 47%. The ERR by employing the spent steam recycling was 51.3%.

In the technology 1, sludge with high water content was subjected to the hydrothermal treatment at 170 °C for 30 min, and the sludge product was used for the anaerobic digestion to obtain energy through the reuse of methane recovery resulting in the ERR of 38%. In the technology 2, sludge with 80% water content was subjected to the hydrothermal treatment at 150 °C for 30 min, and the sludge product was directly used for the anaerobic digestion to obtain energy through the reuse of methane recovery resulting in the ERR of 35%. Higher ERR values indicate higher energy recovery from sludge. A comparison of the results of the four main processes indicated that the proposed process maximizes the energy recovery from sewage sludge and is thus the best process.

4.6 Conclusion

(1) For a single batch reaction, compared with the original process operation conditions, the energy-saving process operation condition saved 15 min of one batch time. Under the original process operation conditions, a single reactor is continuously running for 24 h and could only process 12 batches with a processing capacity of 50.4 t/d. Under the energy-saving process, a single reactor is continuously running for 24 h and can

process 13 batches with a processing capacity of 54.6 t/d, which is a processing capacity improvement of 9%.

(2) The original design was optimized to form a new energy-saving hydrothermal treatment system. The steam line of the original designed process was optimized and transformed. The hydrothermal reactor still adopted a batch intermittent reaction, but the system was changed to fully utilize the spent steam. One part of the spent steam from a reactor was recycled and used by another. Before discharging, another part was directly discharged into the subordinate cooling tower after the deodorization treatment. Three reactors conducted an intermittent alternant type of reaction.

(3) According to the energy-saving system operation conditions, 4200kg sewage sludge with the moisture content of 82.7%, about 278kg of RDF fuel energy by way of recycling and methane can be prepared saturated steam 1032Kg of 200 ℃, where about 1017kg for heating sludge and about 15kg for EGSB. There are still about the rest of 454Kg RDF can be output can create additional value.

(4) The CH_4 digested from the separated liquid by EGSB was recycled to obtain the ERR value of 46.6%. The ERR after recovering the spent steam was 64.8%, an increase of 24.9% compared with the case without recycling. In the technology 1, where sludge with high water content was subjected to the hydrothermal treatment at 170 °C for 30 min, and the sludge product was used for the anaerobic digestion to obtain energy through the reuse of methane recovery to obtain the ERR of 38%. In the technology 2, sludge with 80% water content was subjected to the hydrothermal treatment at 150 °C for 30 min, and the sludge product was directly used for the anaerobic digestion to obtain energy through the reuse of methane recovery to obtain the ERR of 35%. Higher ERR values indicated higher energy recovery from sludge. A comparison of the results of the four main processes indicated that the proposed process maximized the energy recovery and thus is the best process.

Reference

[4-1] Jiang Zili, Process Optimization of Hydrothermal Treatment of Sewage Sludge for Solid Fuel Production, Tokyo Institute of technology, 2010.

[4-2] Jang ZiLi.et al. Study on the hydrothermal drying technology of sewage sludge. SCIENCE CHINA, 2010, 53(1):160-163.

Chapter 5

Conclusion

Sewage sludge production has increased year after year in China. Sewage treatment is developing at an unprecedented rate. However, a large portion of sludge is still disposed in landfills or simply discarded. If we do not find reasonable solutions for sludge disposal and treatment, land resources for stacking, discarding, and landfill purposes will continuously decrease. At present, the disposal methods are: agricultural use, landfills, incineration, etc. Due to financial and technical reasons, the difference between China and developed countries in terms of existing sludge treatment facilities is quite large.

At present, the key issue of sludge treatment is its running cost in developing countries, such as China. Development of cheap and effective technologies to treat sludge is urgently needed. So, it is very important to find cheap and effective technologies to produce alternative fuel not only to improve the dehydration ability of the sludge but also to utilize the RDF (Refuse Derived Fuel). So we have developed the hydrothermal treatment system for sewage sludge to produce solid fuel (RDF) by taking into consideration of sludge properties in China.

In this thesis, I aimed at investigating the energy production technology for the separated liquid from sewage sludge by the hydrothermal treatment and subsequent dehydration. Also the energy efficiency of the commercial-scale hydrothermal treatment system was investigated. Previous works on the hydrothermal treatment were discussed for improving the dehydration ability of sewage sludge and drying of sewage sludge to produce solid fuel. But the potential usage of the liquid product associated with the hydrothermal process has not been well investigated. Actually, during the hydrothermal process, a certain amount of nutrient in the biomass waste can move into the liquid product, which shows a new possibility of the hydrothermal treatment. This study focuses on the possibility of the biochemical methane production from the separated liquid produced from sewage sludge by the hydrothermal treatment. Optimum operational parameters of the hydrothermal

treatment for maximizing the energy efficiency of the commercial-scale hydrothermal sewage sludge treatment plant are also investigated.

Chapter 2. Study on Potential of Biochemical Methane Production from Separated Liquid Produced from Sewage Sludge by Different Operating Conditions of the Hydrothermal Treatment

This chapter investigates the impact of the different operating conditions of the hydrothermal treatment on the characteristics of the separated liquid. The methane-producing potential of the separated liquid with different reaction conditions of the hydrothermal treatment is evaluated. The characteristics of the separated liquid is discussed in view of COD, VFA (Volatile Fatty Acid), TOC (Total Organic Carbon), NH_4^+-N,TN and C/N. The results of the component analysis show that the separated liquid produced from sewage sludge by the hydrothermal treatment contained large amounts of organic matter, which could be digested by anaerobic microorganisms to produce biogas. The conclusion of STR (Stirred Tank Reactor) test shows that the optimum hydrothermal reaction temperature was 190℃, when the digestion time was the shortest and the biogas yield was the highest among all the reaction conditions. The unit methane yield was 210mL/gCOD and the methane content was approximately 62.2%. The separated liquid obtained from the hydrothermal treatment at 190 °C was diluted with water in the ratio of 1:0, 1:1, 1:3, and 1:7, respectively, and added into STR tanks named #1, #2, #3, and #4, respectively. The results of the separated liquid with different dilution gradients show that the dilution multiples of #3 was confirmed as the optimal one. The final cumulative gas production, the unit gas production, the methane conversion, and the COD removal efficiency of #3 were 13607.8 mL, 388 mL/gCOD, 98.2%, and 86%, respectively. The biogas produced from the anaerobic digestion could be used as an energy source for the production of steam.

Chapter 3. Study on Performance of Anaerobic Digestion of Separated Liquid Produced from Sewage Sludge by Hydrothermal Treatment

In Chapter 2, the STR experiments verified the feasibility of the anaerobic treatment and evaluated the performance of biogas production. In this chapter, according to the conclusion of Chapter 2, EGSB (Expanded Granular Sludge Bed) was designed for the commercial-scale plant. The performance of the commercial-scale reactor was investigated by focusing on the comparison with the small-scale reactor to confirm the optimum operating parameters clarified in Chapter 2. The results of the COD removal ratio were almost the same between the small-scale reactor and the commercial-scale reactor. The monitoring and recording of the variation tendency of COD, NH_4^+-N, VFA of the EGSB reactor

were carried out to study the effects of these values on the anaerobic digestion biogas production. Based on the small-scale reactor achievements, this chapter analyzes the efficiency of the EGSB reactor.

The research results indicate that the optimal digestion time of the separated liquid treated by EGSB reactor was 8 d, the COD removal efficiency was about 79%, the removal efficiency of NH_4^+-N was 44%, VFA was less than 300 mg/L, the methanogenic process was not too constrained, and the reactor maintained normal gas production and removal rate. The results show that when the influent COD concentration is 18 gCOD/L, the unit of methane gas production was the maximum 345 ml/gCOD, the methane conversion rate was 87.3%, and methane purity was 60% after the stable operation of EGSB. The unit gas production, the conversion of methane, the methane purity, and the COD removal efficiency in this chapter were similar to the test results in Chapter 2. The data from the study can provide data support for practical application of this technology and have certain significance.

Chapter 4. Energy and Mass Balance Analysis of Commercial-scale Hydrothermal Plant

On the basis of test results described in Chapter 2 and Chapter3, in this chapter, by the energy and mass balance calculations, the energy efficiency of the commercial-scale hydrothermal treatment system was investigated. The system includes the hydrothermal system, the dehydration system and the anaerobic digestion treatment system. The Energy Recovery Ratio (ERR) is the most important parameter to evaluate the energy efficiency of the hydrothermal treatment system. The Energy Recovery Ratio (ERR) was defined as follows: Energy Recovery Ratio (ERR) = (Energy content in RDF + Energy content in separated liquid (biogas) -Energy requirement of steam generation-Energy requirement of drying)/ Energy content in the raw sludge. In order to increase the ERR value, the biogas produced from the separated liquid was recycled and the discharged steam from one reactor was recovered into another reactor to reduce the exhaust loss. By comparing the ERR value of this system with that of other sludge treatment processes, the feasibility and advantages of the present system was analyzed.

The research results indicate that under the original process operation conditions, a single reactor continuously running for 24 h could only process 12 batches with a processing capacity of 50.4 t/d. Under the energy-saving process, a single reactor continuously running for 24 h can process 13 batches with a processing capacity of 54.6 t/d, a processing capacity

improvement of 9%. According to the energy-saving system operation conditions, 4200kg sewage sludge with the moisture content of 82.7%, about 278kg of RDF fuel energy by way of recycling and methane can be prepared saturated steam 1032Kg of 200 ℃, where about 1017kg for heating sludge and about 15kg for EGSB. There are still about the rest of 454Kg RDF can be output can create additional value; system without added external energy, is the energy net output process, even taking into account the thermal efficiency of heating and insulation and heat loss, the system is still plenty of surplus energy.

The CH_4 digested from the separated liquid by EGSB was recycled to obtain the ERR value of 47%. The ERR after the exhaust steam recovery was 64.8%, an increase of 24.9% compared with the case without recycling. In the technology 1, sludge with high water content was subjected to the hydrothermal treatment at 170 °C for 30 min, and the sludge product was used for the anaerobic digestion to obtain energy through the reuse of methane recovery resulting in the ERR of 38%. In the technology 2, sludge with 80% water content was subjected to the hydrothermal treatment at 150 °C for 30 min, and the sludge product was directly used for the anaerobic digestion to obtain energy through the reuse of methane recovery resulting in the ERR of 35%. Higher ERR values indicated higher energy recovery from sludge. A comparison of the results of the four main processes indicated that the proposed process maximized the energy recovery from sewage sludge and was thus the best process.

In summary, the hydrothermal treatment is an effective sewage sludge treatment technology in China. The product of sewage sludge after the hydrothermal treatment can be used as solid fuel for resource recycling. The separated liquid associated with the hydrothermal process can be used for biogas production for resource recycling. The biogas produced from the anaerobic digestion could be used as an energy source for the production of steam. The main new findings in this research are as follows:

A. The results of the component analysis show that the separated liquid produced from sewage sludge by the hydrothermal treatment contained large amounts of organic matter, which could be digested by anaerobic microorganisms to produce biogas.

B. We have established a commercial system (100T/D) to verify the laboratory results, the optimal digestion time of the separated liquid treated by EGSB reactor was 8d, the COD removal efficiency was about 79%, the removal efficiency of NH_4^+-N was 44%, VFA was less than 300 mg/L, the methanogenic process was not too constrained, and the reactor maintained normal gas production and removal rate.

The results shows that when the influent COD concentration is 18 gCOD/L, the unit of methane gas production was the maximum 345 ml/gCOD, the methane conversion rate was 87.3%, and the methane purity was 60% after the stable operation of EGSB.

C. Based on the calculation of the mass and energy balances for the commercial-scale reactor, we got 24.9% higher ERR value than before researches.

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