Redox flow batteries instead of biogas plants

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***Abstract*— In this paper, the conversion of an old biogas plant into a redox flow battery is investigated. The technical potential is determined and a utilisation concept for the redox flow battery and the resulting waste heat is presented.**

***Keywords*— redox flow battery, biogas plant, energy storage, automatic frequency restauration reserve**

I. Introduction

With the rapid expansion of renewable energies and an increasing demand for electricity due to new consumers caused by sector coupling, security of supply must nevertheless be guaranteed [1, p. 10]. Energy storage systems are used to achieve a temporal decoupling of generation and consumption. In Germany, the Renewable Energies Act (EEG) subsidies for the first biogas plants have already expired and more plants will follow in the next few years. Since some of these plants do not stand a chance of being put out to tender again and can therefore no longer be operated economically, a way should be found to continue using the plants [2, pp. 82-88]. Therefore, it is to be investigated to what extent the conversion of a biogas plant into a redox flow battery (RFB) is technically and economically feasible.

II. Analysis of the System Components

In the following, the basic components of a biogas plant and a RFB are described. Based on this, it is examined which system components of the biogas plant can be used for a RFB system in the future.

A. *System components of a biogas plant*

There are many different types of biogas plants, which are composed of different system components. Depending on the substrate used, different technical processes are used for biogas production [3, p. 1614] and multiple fermenters can be connected in series [3, p. 1624]. In Germany, manure and renewable raw materials represent the largest substrate share for biogas plants [4, p. 46]. The biogas produced can be used to generate heat, electricity, or fuel [3, p. 1725]. The use of biogas in a combined heat and power (CHP) plant for the combined generation of heat and electricity is the most common use in Europe [3, pp. 1727-1728]. In the following, the system components of an agricultural biogas plant for manure fermentation with subsequent use of the biogas in a CHP plant are examined.

Fig. 1 shows the schematic structure of such a biogas plant. In the manure pit, the manure produced on the farm is first collected and in the next step mixed with other organic materials, the co-substrate, in the pre-pit [3, p. 1716]. Anaerobic fermentation of the substrate takes place in a fermenter with a foil roof. Fermenters in the agricultural sector are usually made of steel-reinforced concrete, but can also be made of steel or synthetic material [3, p. 1662]. Concrete fermenters are built in all size ranges, up to 8,000 m³[3, p. 1662]. Due to the chemical impact of the substrate, the concrete tanks of a biogas plant should be additionally protected [5, p. 953]. Coatings made from epoxy resin, or a particularly thick sacrificial concrete layer can be used for this purpose [5, pp. 953-954]. Biogas fermenters are insulated against heat loss [3, p. 1662] and are equipped with fermenter-internal or external heating systems [3, pp. 1668-1669]. For this purpose, the heat generated in the CHP plant is usually transferred to the substrate via heat exchangers [3, pp. 1668-1669]. In the fermenter, an agitator ensures that the substrate is mixed [3, p. 1716]. The biogas produced in the fermenter is stored between the substrate surface and the gas-tight foil roof [3, p. 1716]. The fermented substrate is temporarily stored in a fermentation residue store for up to 6 months before it is spread on fields as fertilizer [3, p. 1704]. The fermentation residue storage also has a gas-tight foil roof to collect biogas produced there [3, p. 1716].

The biogas produced in the fermenter and fermentation residue storage is extracted at the top of the reactor and, after cleaning and drying, is fed to the CHP plant [3, p. 1716]. The CHP plant is located in the immediate vicinity of the biogas plant [3, p. 1716] and is housed in a sound-absorbing enclosure, such as a shipping container [3, p. 1729]. Here, the biogas is converted into electricity and heat using a combustion engine [3, p. 1727]. The electricity is usually fed into the public grid [3, p. 1727]. The engine and exhaust gas heat is dissipated through heat exchangers to provide process heat or to heat nearby buildings [3, p. 1727]. Alternatively, excess heat is released into the atmosphere [3, p. 1716]. A CHP plant for the conversion of biogas into electricity can have an electrical output of 20 kW_{el} to over 3,000 kW_{el} [3, p. 1728]. Most plants in Germany have an electrical output between 75 kW_{el} and 500 kW_{el} [6, p. 3]. Smaller plants were also installed in the early 2000s and larger plants from 2004 onwards [6, p. 3].

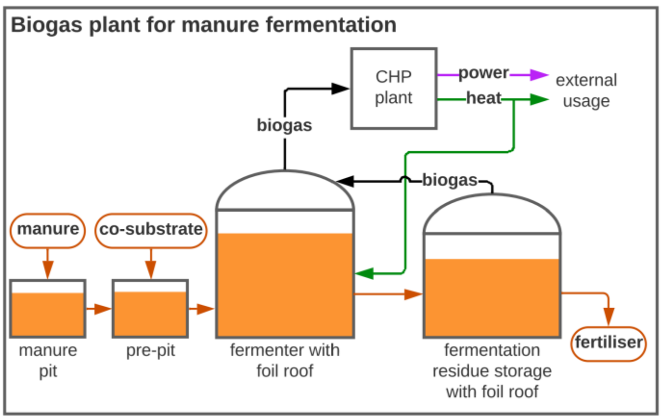

Fig. 1: Schematic layout of a biogas plant for manure fermentation according to [3, p. 1717]

B. *System components of a RFB*

A RFB uses the redox reaction to store energy in redox pairs [7, p. 315]. Fig. 2 shows the schematic layout of a RFB. This essentially consists of two electrolyte tanks and a galvanic cell [7, p. 315]. These are supplemented by the system periphery consisting of pumps, pipes, valves, heat exchangers and control electronics [7, p. 316].

The liquid energy-storing electrolytes are stored outside the cell in two electrolyte tanks. From there, the electrolytes are pumped through the cell in two separate circuits. A membrane separates the galvanic cell into two half cells, each with one electrode. The reactions take place at the electrodes, and the membrane allows the exchange of ions. [7, p. 315]

The electrolytes consist of redox-active material dissolved in a liquid solvent [8, p. 704]. Metal-based redox partners are often used as active materials, although the use of organic materials is also possible [8, p. 706]. Currently, mainly the pure vanadium cell and the zinc-bromine cell are commercially available [7, p. 324]. However, most metal-based RFBs entail ecological and socio-political problems [8, p. 709]. Intensive research into the use of organic redox partners is expected to result in a cheaper and more sustainable RFB [8, p. 710].

Some redox partners are water-soluble, others require the use of a solvent [8, p. 706]. Organic or inorganic acids can be used as solvents [7, p. 316]. A conducting salt is added to the electrolyte for ion transport across the cell membrane [8, p. 704]. Metal-based redox partners, such as vanadium, are usually dissolved in a watery medium [8, p. 706]. Components that are in contact with the electrolyte must be resistant to sulphuric acid or have an acid-resistant coating in order to prevent electrolyte loss through leakage and the resulting malfunctions [7, p. 316].

The cell is charged by applying an external voltage. Several cells can be connected in series to form a stack [7, p. 316]. A battery management system monitors the temperature, voltage and current to keep the cells at an optimal operating point [7, p. 320].

Standard components are used for most of the system components [7, p. 316]. Manufacturers of RFBs, such as VoltStorage GmbH [9], offer complete systems consisting of stacks, tanks and the other system peripherals, which are usually housed together in a container. Some of these systems are also modularly expandable, such as the CellCube from Enerox GmbH [10]. Jenabatteries GmbH offers an organic RFB [11].

C. *Conversion of a biogas plant into a RFB*

In the following, an analysis is made of how the biogas plant for manure fermentation shown in Fig. 1 could be converted into a RFB. Fig. 3 shows schematically how this RFB can be structured.

The two largest tanks of the biogas plant are used for the two electrolyte tanks: the fermenter and the fermentation residue storage. Since the two electrolyte tanks must have the same volume, the second largest tank, in this case the fermentation residue storage, limits the maximum volume. The agitator in the fermenter must be removed. Existing openings in the tanks for the substrate feed and discharge, the heating system and the agitator drive can be used for the feed and discharge of the electrolyte tanks if the size and positioning are suitable.

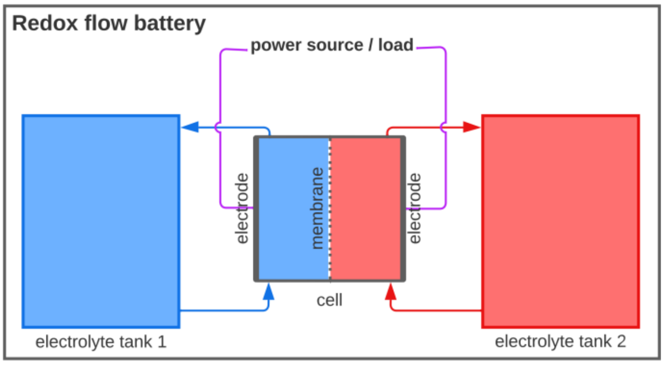

Fig. 2: Schematic layout of a RFB according to [7, p. 316]

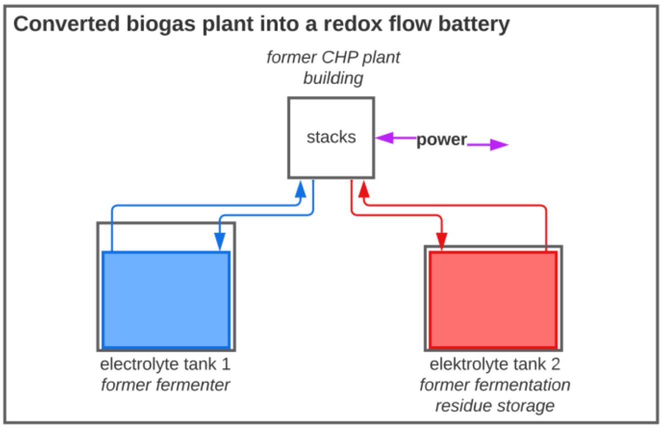

Fig. 3: Schematic layout of the biogas plant converted into a RFB [own illustration]

Any excess or unsuitable openings must be sealed. The foil roofs of the fermenter and fermentation residue storage must be replaced with solid building roofs. In addition, it is necessary to evaluate whether the existing fermenter and fermentation residue storage can provide sufficient stability and impermeability over the lifetime of the RFB. The sulphuric acid used in RFBs has a dissolving and driving attack on cement stone [12]. If the two tanks are assumed to be made of steel-reinforced concrete, they do not provide sufficient acid resistance for the safe storage of electrolytes. Two options are available to ensure acid resistance. The tank surfaces could be coated with an acid-resistant material, which must be regularly inspected for leakage. Alternatively, prefabricated plastic tanks can be placed in the containers. In this case, the fermenter and the fermentation residue storage only serve as external weather protection.

The already existing heating system of the fermenter can also be used for the electrolyte tank. Since the fermentation residue storage is not heated, a heating system must be installed for the second electrolyte tank. It should be examined whether the heating system in the fermenter could also be replaced at the same time.

The pipes and pumps between the electrolyte tanks and the stacks must be newly installed. The stacks of the RFB can be installed in the former building of the CHP plant. This building is already in the immediate vicinity of the tanks and provides protection from the weather. The existing grid connection to the public electricity grid can still be used and extended if necessary.

III. Calculation of the technical potential

The dimensioning of power and capacity is independent of each other for RFBs [7, p. 315]. The storage capacity is dependent on the energy density of the electrolyte and the volume of the electrolyte tanks [7, p. 316]. The energy density of the electrolyte depends on the selected redox pairs and the concentration of these in the solvent [13, pp. 6-11]. Modern vanadium electrolytes based on a sulphuric and hydrochloric acid mixture have an energy density of 51 Wh/l [13, p. 6]. Organic solvents can theoretically achieve higher energy densities, but this has not yet been sufficiently researched to be able to name concrete energy densities [13, pp. 7-10]. For the following calculations, an energy density of 51 Wh/l is assumed. The volume of the former biogas plant that can be used as electrolyte tanks can vary greatly depending on the plant configuration. In the following calculations, a total volume of the electrolyte tanks of 1,000 m³ is assumed. This results in a storage capacity of 51 MWh for the investigated model plant.

The power is dependent on the type of interconnection of the stacks and the resulting size of the active electrode area [7, pp. 316-322]. To determine the power of the RFB, the grid connection and economic aspects can act as limiting factors. In addition, depending on the utilisation concept, an appropriate power-to-capacity ratio should be chosen. A discharge time of 4 to 10 hours is commonly used [14]. The power output of the model plant should accordingly range between 5.1 MW and 12.75 MW.

At the end of 2023, 150 biogas plants throughout Germany will no longer be eligible for EEG support [15]. By 2028, the subsidies will expire for a total of 2,141 more plants [15]. A peak of between 1,100 and 1,500 biogas plants per year will follow in the years 2029 to 2031 [15]. If it is assumed that half of the biogas plants that will lose EEG subsidies in the next five years will be converted to RFBs and that these will have the same storage capacity and power as the example plant described, a total of 53.8 GWh of storage capacity and 9.4 GW of power can be provided. This corresponds to almost the entire installed power of all German pumped storage power plants with 9.7 GW [16].

IV. Potential Utilisation concept of the System

Currently, RFBs are mainly used for peak load balancing. The use for the provision of control and compensation energy, emergency power supply and the supply of island grids also suit RFBs [7, p. 324]. In this paper the focus is on the control energy used to keep the grid frequency stable at a target value of 50 Hz. If the frequency drops below 50 Hz, positive control energy is required. If the frequency rises above the target value, negative control energy is required. A distinction is made between frequency containment reserve (FCR), automatic frequency restauration reserve (aFRR) and manual frequency restauration reserve (mFRR) [17, pp. 98-99]. The aFRR is economically very attractive [18], since, as with the mFRR, there is a power and working price. In contrast to FCR, aFFR is very rarely called [17, p. 104]. The aFRR is used to relieve the FCR and is activated after about 30 seconds and must provide control power in full within 5 minutes. The call-up is fully automatic via the transmission system operator [17, p. 99]. The provisioning period is limited to 15 minutes and can be reactivated at the earliest after a period of 25 minutes. The requirements for provisioning speed, as well as the minimum requirement of 1 MW, are no problem for RFBs.

The generated waste heat has a low temperature level, which makes it difficult to use it effectively. At most, it is possible to use a cold local heating network. However, the temperature level at the consumers must then be raised by using heat pumps [19, p. 21]. Alternatively, the waste heat can be used directly on the farm. On the one hand, it can be used in breeding by keeping the breeding facilities at an ideal temperature level all year round [19, p. 6]. On the other hand, it can also be used in agriculture to keep greenhouses or foil tunnels at a suitable temperature level [19, p. 6].

There are various utilisation concepts for biogas plants that are no longer eligible. However, these options also incur new investment costs. Probably the most economical option is to participate in another tender for 10 years [20, pp. 24-29]. Other concepts such as the provision of fuel, the construction of a new liquid manure plant, own consumption and direct delivery or the merger of plant operators and the continued operation of a joint plant for example are also possible for an old plant [20, p. 6].

V. Profitability analysis

The following profitability analysis will examine whether or to what extent such a system can be operated economically. Since RFBs are not yet a mature technology [7], there is a wide range of acquisition costs. Table 1 lists the price ranges from various sources. These values refer exclusively to the vanadium RFB, as this is the most common variant and no prices are yet available for organic RFBs. From these values, the economic evaluation is calculated for three cases. The result is only intended to provide a rough estimate of the profitability, as the prices vary greatly depending on the size of the system and the compensation.

The calculation is based on the utilisation concept of the provision of aFFR, as the additional revenues from the balancing power market and the expectation of high price peaks in shortage situations make economic investments possible [1, pp. 12-14]. It is assumed that negative balancing energy with an energy price of 5 €/MWh and positive balancing energy with 50 €/MWh is provided for 1.5 hours per day. Current prices for aFRR are used for the payment [18]. According to [21, p. 6], operating and maintenance costs of 40 €/kW are assumed. The profitability is calculated for the model plant described above with a storage capacity of 51 MWh. Since a higher capacity has a better effect on the remuneration in the aFRR and no long discharge times are required, a capacity of 12.5 MW is assumed. The result of the calculation is shown in Fig. 4.

Table 1. Acquisition costs for RFBs

	Costs	
	Power [€/kW]	***Capacity [€/kWh]***
M. Zapf [22]	1,000 - 1,150	150 - 300
M. Sterner et al. [7]	710 - 1,790	250 - 700
Y. Xu et al. [21]	2,220 - 2,460	315 - 440
Best Case	**710**	**150**
Worst Case	**2,460**	**700**
Average	**1,550**	**359**

Fig. 4: Results of the profitability analysis over 20 years [own illustration]

The remuneration for aFRR is made up of a working price and a power price. Due to the limited call-off time of 15 minutes, however, the working price is many times smaller than the power price. Even assuming a much smaller or larger called-up work output, the impact on the overall result is small. Therefore, a higher output leads to a better payment and thus for a better economic efficiency of the plant. With an even smaller power-to-capacity ratio, the investment costs would increase enormously, but the plant would pay for itself more quickly. With an increase in capacity, on the other hand, the payback point occurs later. In addition, it would not make sense to increase the capacity so much because of the limited call-up time. In the utilisation concept of aFRR, the power is therefore the decisive factor for economic efficiency.

VI. Conclusion

The analyses show that it is possible to convert old biogas plants into RFBs. However, it is only the fermenters and fermentation residue storages that are useful for further applications and require additional costly processing and conversion. Since most manufacturers of RFBs offer all-in-one systems, a complete deconstruction of the biogas plant would be the most appropriate, leaving space as the only resource used from the biogas plant. In addition, RFBs are associated with high acquisition costs. Although the profitability analysis shows correspondingly high revenues for the provision of aFFR, the calculations are made up of many assumptions. As a result, investments in other utilisation concepts for the old biogas plants may be more attractive at this point of time.

References

[1] Bundesnetzagentur für Elektrizität, Gas, Telekommunikation, Post und Eisenbahnen, Ed., "Bericht zu Stand und Entwicklung der Versorgungssicherheit im Bereich der Versorgung mit Elektrizität," Accessed: Sep. 4, 2023. [Online]. Available: https://www.bmwk.de/Redaktion/DE/Downloads/V/versorgungssicherheitsbericht-strom.pdf?__blob=publicationFile&v=4

[2] Umweltbundesamt, Ed., "Optionen für Biogas-Bestandsanlagen bis 2030 aus ökonomischer und energiewirtschaftlicher Sicht: Abschlussbericht," Accessed: Nov. 13, 2022. [Online]. Available: https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2020-01-30_texte_24-2020_biogas2030.pdf

[3] M. Kaltschmitt, H. Hartmann, and H. Hofbauer, Eds. *Energie aus Biomasse: Grundlagen, Techniken und Verfahren,* 3rd ed. Berlin Heidelberg, Germany: Springer Vieweg, 2016.

[4] Fachagentur Nachwachsende Rohstoffe e. V. (FNR), Ed., "Basisdaten Bioenergie Deutschland 2022: Grafiken Tabellen Kennwerte," Accessed: Apr. 16, 2023. [Online]. Available: https://www.fnr.de/fileadmin/Projekte/2022/Mediathek/broschuere_basisdaten_bioenergie_2022_06_web.pdf

[5] H. Tebbe, J. Gerlach, and B. Siebert, "Landwirtschaftliches Bauen – Chemischer Angriff auf Betonbauwerke," *Beton-Kalender*, vol. 2016, pp. 939–973, Jan. 2016, doi: 10.1002/9783433603413.ch10.

[6] J. Daniel-Gromke, N. Rensberg, and V. Denysenko, "Biogas – Status quo und Anlagenentwicklung," in *Biogasfachgespräche Leipzig „Neues für Biogas- und Biomethananlagen – Was bringt das Jahr 2021?"*. Accessed: Aug. 27, 2023. [Online]. Available: https://www.dbfz.de/fileadmin/user_upload/Fachgespraeche/Biogas-Fachgespraeche/Vortraege/2021-02_BGFG_Vortraege.pdf

[7] M. Sterner and I. Stadler, Eds. *Energiespeicher: Bedarf, Technologien, Integration,* 2nd ed. Berlin, Germany: Springer Vieweg, 2017.

[8] J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager, and U. S. Schubert, "Redox-Flow-Batterien: von metallbasierten zu organischen Aktivmaterialien," *Angewandte Chemie*, vol. 129, no. 3, pp. 702–729, Jan. 2017, doi: 10.1002/ange.201604925.

[9] VoltStorage GmbH. "Produkte." VoltStorage. https://voltstorage.com/produkte (accessed Sep. 18, 2023).

[10] Enerox GmbH. "Der CellCube." CellCube. https://www.cellcube.com/de/der-cellcube/ (accessed Sep. 18, 2023).

[11] Jenabatteries GmbH. "Unsere Stromspeicher: So nachhaltig, wie die Energie, die sie speichern." CERQ. https://www.cerq.com/technologie (accessed Sep. 20, 2023).

[12] A. Taffe, M. Pohl, W. Roeser, and B. Schwamborn, "Betonkorrosion durch Schwefelsäure an Abwasserbauwerken: Innovative Schadensdiagnose," *Beton- und Stahlbetonbau*, vol. 102, no. 10, pp. 691–698, Oct. 2007, doi: 10.1002/best.200700574.

[13] C. Modrzynski, "Redoxaktive ionische Flüssigkeiten auf der Basis von Eisen-Schwefel-Clustern als neue Elektrolyte für Redox-Flow-Batterien," Dissertation, Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Hamburg, Germany, 2018.

[14] Volterion GmbH & Co. KG (T. Seipp), private communication, Apr. 2023.

[15] Fachverband Biogas e.V., Ed., "Branchenzahlen 2021 und Prognose der Branchenentwicklung 2022," Accessed: Aug. 30, 2023. [Online]. Available: https://www.biogas.org/edcom/webfvb.nsf/id/DE_Branchenzahlen/$file/22-10-06_Biogas_Branchenzahlen-2021_Prognose-2022.pdf

[16] Bundesnetzagentur für Elektrizität, Gas, Telekommunikation, Post und Eisenbahnen. "Kraftwerksliste." Bundesnetzagentur. https://www.bundesnetzagentur.de/DE/Sachgebiete/ElektrizitaetundGas/Unternehmen_Institutionen/Versorgungssicherheit/Erzeugungskapazitaeten/Kraftwerksliste/start.html (accessed Aug. 30, 2023).

[17] T. Wawer, *Elektrizitätswirtschaft: Eine praxisorientierte Einführung in Strommärkte und Stromhandel*. Wiesbaden, Germany: Springer Gabler, 2022.

[18] C. Schäfer. "Leistungspreise." Regelleistung Online. https://www.regelleistung-online.de/srl/leistungspreise/ (accessed Aug. 21, 2023).

[19] G. Pertiller, "Nutzungsmöglichkeiten für Niedertemeratur-Abwärme der energieintensiven Industrie, am Beispiel einer Garnelenfarm," M.S. thesis, Lehrstuhl Wirtschafts- und Betriebswissenschaften, Montanuniversität Leoben, Loeben, Austria, 2018.

[20] N. Grösch *et al.,* "Biogas nach dem EEG - (wie) kann´s weitergehen?: Handlungsmöglichkeiten für Anlagenbetreiber," Accessed: Sep. 11, 2023. [Online]. Available: https://www.fh-muenster.de/egu/downloads/biogas/Leitfaden_-_Handlungsmoeglichkeiten_fuer_Biogasanlagenbetreiber.pdf

[21] Y. Xu, J. Pei, L. Cui, P. Liu, and T. Ma, "The Levelized Cost of Storage of Electrochemical Energy Storage Technologies in China," *Frontiers in Energy Research*, vol. 10, Jun. 2022, doi: 10.3389/fenrg.2022.873800.

[22] M. Zapf, *Stromspeicher und Power-to-Gas im deutschen Energiesystem: Rahmenbedingungen, Bedarf und Einsatzmöglichkeiten,* 2nd ed. Wiesbaden, Germany: Springer Vieweg, 2022.