沙漠研究 24-1, 231-235 (2014)
Journal of Arid Land Studies

– DT11 Refereed Paper –

Halophyte Biomass

- A Promising Source of Renewable Energy -

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Abstract: Halophytes are suggested as energy crops in arid saline lands. Anaerobic digestion of 7 halophytes collected in the Kyzylkum desert (Uzbekistan) were studied in batch-mode tests in mesophilic (35°C) and thermophilic (55°C) conditions with stirring and F/M=0.2. Obtained results showed that halophytic biomass should be considered as a valuable renewable source of biogas. Though high mineral content was detected in the biomass (*i.e.*, Na^+, K^+, Cl^- and SO_4^{2-}), total biogas yields in results of anaerobic degradation were about 200-400 mL (at 35°C) and 300-500 mL (at 55°C) from 1 gDM (with 60% of methane-gas). Total organic matter and organic carbon (OC) concentrations were determined to investigate plant biomass. Organic matter concentrations were between 736-900 mgVS/gDM. The highest organic carbon content found in biomass of *Suaeda paradoxa*, *Atriplex nitens*, *Karelinia caspia* and conventional grass *Cynodon dactylon* were 243.9, 337.6, 394 and 396 mgOC/gDM, respectively. Low OC content (about 200 mgOC/gDM) was measured in biomasses of *Salicornia*, *Halostachys* and *Climacoptera*. Results indicated that 40-60% of total organic matter in halophyte biomass can be decomposed into biogas. The highest yield of approximately 300-500 m^3 of biogas from 1 tDM could be produced from *Atriplex nitens*, *Karelinia caspia*, *Suaeda paradoxa* and *Cynodon dactylon*. After considering annual biomass yield of the studied plants, their current use, and biogas generation measured in the laboratory, *Karelinia caspia* (wild associations or cultivated plantations) is recommended as one of the most promising renewable sources for biogas production in desert salt-affected areas of Central Asia.

Key Words: Biogas, Biomass, Halophyte, *Karelinia caspia* (Pall.) Less

1. Introduction

The importance of seeking renewable sources of energy is growing steadily. Leading the way is the use of methane gas obtained from fermentation processes in biogas digesters.

The idea to use dedicated plant biomass, the so called "energy crops", for methane production (biomethanation) is not new. Early investigations on the biomethanation potential of different crops and plant materials were carried out in the 1930s by Buswell in the USA and later in the 1950s by Reinhold and Noack in Germany. In 1980, Stewart described the potential use of oats, grass and straw for energy production in New Zealand (Hendricks and Bushnell, 2008).

Numerous plants and plant materials have been tested for their methane formation potential. In principle several varieties of grass, clover, cereal and maize including whole plants, as well as, rape or sunflower have proven feasible for methane production. Even hemp, flax, nettle, miscanthus, potatoes, beets, kale, turnip, rhubarb and artichoke have been tested successfully (Hendricks and Bushnell, 2008).

Plant biomass utilization for renewable energy production is usually related to using arable lands for energy crop cultivation, which has given rise to the criticism that food crops are being diverted to energy production in developed countries even as millions in the developing world do not have adequate food to eat.

Therefore it is important to use fertile lands for food and fodder production. Alternatively, marginal resources (saline lands and mineralized / drainage / thermal water) could be used to cultivate plants for energy. Halophytes and salt-tolerant plants can be grown in salt-affected, degraded and abandoned unproductive lands.

There are a number of annual and perennial species among halophytes that are able to uptake significant amounts of salts in biomass and remove them from saline soils. Halophytic biomasses could be used in different ways because most are multipurpose plants. Some halophytes can be used for food, fodder, or forage production in marginal environments. In other words, cultivation and sustainable utilization of wild or domesticated halophytic and salt-tolerant plants could play an important role for salinity control, remediation of saline lands and improvement of livelihoods of rural communities in the

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(Received, September 15th, 2013; Accepted, January 19th, 2014)

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Central Asian region (Gintzburger, 2003; Akinshina, 2012). In addition, halophytes may be useful as sources of biogas.

This paper presents original work regarding biogas potential of some halophytes in Central Asia, including an assessment and identification of the most promising species as energy crops.

2. Materials and Methods

Biomasses of widespread wild halophytes were sampled for the study on desert salt-affected sand-loamy soils in the Karakata saline depression, 80-100 m above sea level, Central Kyzylkum, Uzbekistan in 2012-2013. The predominant soil salinity was sulfate-chloride. Ground water mineralization was 2.0-8.2 g/L. Sodium and magnesium were the dominant cations. The ground water table fluctuated from 0.8-2.5 m. Thermal water from artesian wells (EC about 4 mS/cm) was the single water source in the area.

Halostachys belangeriana, *Salicornia europaea*, *Climacoptera lanata*, *Climacoptera brachiata*, *Suaeda paradoxa*, *Atriplex nitens* and *Karelinia caspia* were investigated. Conventional grass, *Cynodon dactylon*, was taken for comparison with halophytes. Plant biomass was air-dried and well-milled before the study.

Chemical compositions of the plant biomass were identified. Total mineral compounds (ash) and organic fractions (VS, volatile solids) in biomasses were measured by the gravimetric method after burning of dried biomass in melt pots was complete (at 605°C, 1 hour) (Vorobyova and Makarenko, 2005). Concentrations of main mineral ions (Na^+, K^+, Mg^{2+}, Cl^-, SO_4^{2-}) were determined in water extracts of the biomass (0.2gDM in 100 mL deionized water, shaken 1 hour and filtered). Sodium, potassium and chloride ions were measured using a pH/ion meter ("Expert-001.3" (Russia)) in accordance with standard electrometric methods of measurement for ion-selective electrodes (Elit-031 (K^+); Elit-261 (Cl^-), Elis-112Na (Na^+)). Sulfate-ion concentrations were measured in the same water extracts using UV/VIS Spectrophotometer V-530 ("Jasco"). Organic carbon (OC) was also measured by a spectrophotometric method with preliminary wet process of biomass by 0,4 M chrome mixture ($K_2Cr_2O_7$+H_2SO_4) (Vorobyova and Makarenko, 2005).

Anaerobic degradation of plant biomass for biogas production was studied in lab-scale batch-mode experiments. Anaerobic sludge was taken from Salar Waste Water Treatment Station in Tashkent City and Institute of Microbiology of Academy of Science of Uzbekistan. Reactors (1 L glass vessels) were operated in mesophilic (35°C) and thermophilic (55°C) conditions with stirring with an F/M ratio of 0.2.

OriginPro7.5 was used for statistical analysis of the data.

Table 1. Mineral matter (Ash), Volatile solids (VS) and Organic carbon (OC) in plant biomass.

Name	mg/g DM		
	Ash	VS	OC
Halostachys belangeriana (Hal)	447.91± 70.41	552.09±40.44	178.75±27.22
Salicornia europaea (Sal)	485.52± 10.11	514.48±10.13	168.31±18.04
Climacoptera lanata (Cli l.)	428.02±13.94	572.03±13.87	207.98±19.50
Climacoptera brachiata (Cli b.)	372.51±30.42	624.84±30.37	213.04±24.73
Suaeda paradoxa (Sua)	264.04±41.24	735.95±51.25	243.96±44.15
Atriplex nitens (Atr)	172.31±19.83	827.73± 19.80	337.58±45.43
Karelinia caspia (Kar)	137.61±5.51	862.41±5.48	394.02±17.20
Cynodon dactylon (Cyn)	101.22±0.32	898.91±0.34	395.64±79.20

3. Results and Discussion

3.1. Study of chemical composition of halophytes

Chemical composition of substrate for anaerobic digestion is essential for successful operation with anaerobic reactors. Any plant biomass contains organic matter which can be converted into biogas (CH_4 + CO_2) by anaerobic bacterial communities. Meanwhile it is known that several organic and inorganic compounds can be toxic or inhibit microbial activity (de Lemos Chernicharo, 2007). Many halophytes are able to accumulate significant amounts of salts in their biomass. Therefore total organic matter and mineral content of the biomass were investigated. Some results are presented in the Figures and Tables below.

Investigated plants contained between 10 to 49% mineral salts in dry matter (**Table 1**). Large amounts of mineral compounds were measured in biomass of *Salicornia europaea* (48.6%), and the least salt accumulation among studied halophytes was demonstrated by *Karilinia caspia* (about 14% DM).

The plants in this study can be ranged in ascending order of mineral content: Cyn<Kar<Atr<Sua<Cli b.<Cli l.<Hal<Sal. Such high salt accumulation by plant biomass like *Salicornia*, *Halostachys* or *Climacoptera* is typical for euhalophytes, because selective uptake of sodium (and chloride) ions is one of the important mechanisms of adaptation to living in a saline environment.

Organic biomass is food for anaerobic bacteria, and it is decomposed by anaerobic digestion to simple inorganic substances as CO_2 and CH_4 (and H_2, H_2O, H_2S) which are considered as biogas. The highest organic fractions were

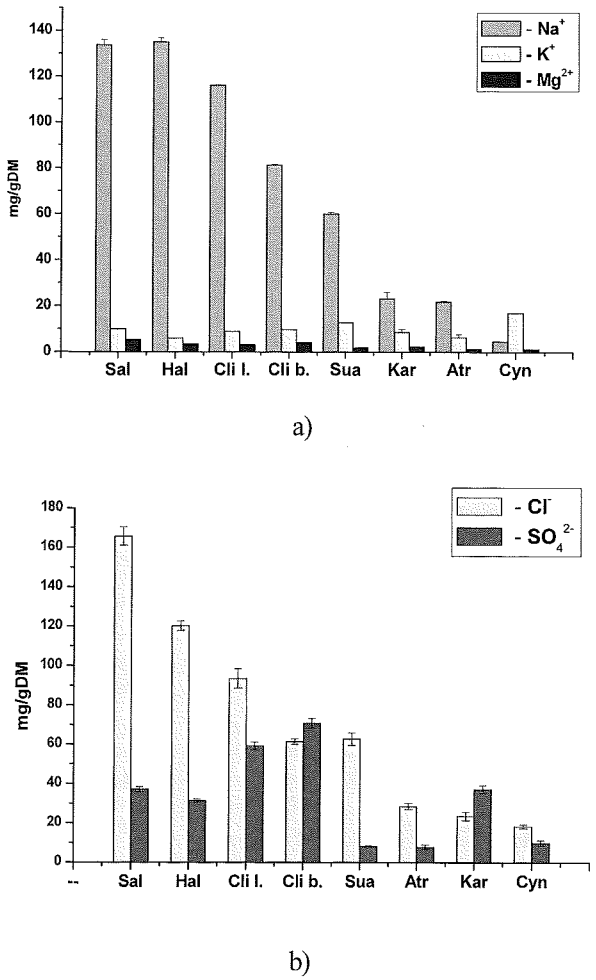

Fig. 1. Content of mineral compounds in plant biomass. a) Soluble Na^+, K^+ and Mg^{2+}; b) Chlorides and sulfates. See Table 1 for plant abbreviations.

observed in biomass of *Suaeda paradoxa*, *Atriplex nitens*, *Karelinia caspia* and *Cynodon dactilon* and ranged from about 736-900 mgVS/gDM. Organic carbon concentrations were 243.9, 337.6, 394 and 396 mgOC/gDM in these species, respectively. Low organic carbon content (about 200 mgOC/gDM) was measured in biomasses of *Salicornia*, *Halostachys* and *Climacoptera*.

Measurement of certain cations and anions in plant biomass has shown that halophytes accumulated a fair amount of Na^+, Cl^- and SO_4^{2-} ions (**Fig. 1**). It would be interesting to analyze cation/anion content of different halophytes during several years and by season. The results thus far show that halophytes have much higher ion composition in comparison with ordinary grass *Cynodon dactylon* which contained about 5 mg Na^+/gDM. *Salicornia*,, *Halostachys* and *Climacoptera* accumulated enormous amounts of Na-ions; in June 2012 it was about 134, 135 and 116 mg/gDM, respectively. In April 2013, *Salicornia* accumulated 110-130 mg Na^+ mg/gDM (in top part of plant) and *Climacoptera* accumulated 80-150 mg/gDM.

Potassium and magnesium ions play important roles in plant physiology. K^+-ion contents in summer biomasses of investigated plants varied from 6 to 13 mg/gDM and Mg^{2+} -varied from 1.3 to 5.4 mg/gDM.

Salicornia, *Halostachys* and *Climacoptera* accumulated approximately 90-170 mg-Cl^-/gDM, and large amounts of sulfate-ions were measured in biomass of *Climacoptera*, *Salicornia*, *Halostachys* and *Karelinia* (59.24, 37.25, 31.4 and 37.2 mg/gDM, respectively). Presence of sulfate causes a change in the metabolic pathways in an anaerobic digester (AD) because of a competition for substrate established between the sulfate-reducing bacteria and fermentative, acetogenic and methanogenic microorganisms. Hence, two final products are formed: methane (by methanogenesis) and sulfide (by sulfate reduction). The production of sulfides may cause serious problems during anaerobic digestion, reduce activity of methanogens and capacity of the anaerobic reactor for conversion of biomass into CH_4. Our previous investigations (Akinshina, 2012) have demonstrated that it is possible to avoid or mitigate negative effects of sulfates/sulfides on anaerobic digestion by Fe^{2+} or Fe^{3+} (10 ppm).

It should be noted that content of mineral salts in plant biomass corresponds to the soil salinity level in the root zone under the plants. For instance, *Climacoptera lanata* from the farm trial plot in Central Kyzylkum with moderate salinity contained fewer amounts of Na^+, Cl^- and SO_4^{2-} in comparison with the same plant species grown in a solonchak area. In solonchak lands, *Climacoptera lanata* had Na^+ content of 133-146 mg/gDM, Cl^- content of 100-129 mg/gDM, and SO_4^{2-} content of 40-60 mg/gDM. In contrast, the same plant had Na^+ content of 84 mg/gDM, Cl^- content of 55 mg/gDM, and SO_4^{2-} content of 11 mg/gDM in the cultivated area of the farm plot. The same tendency was observed for wild *Karelinia caspia* grown in areas with different levels of soil salinity (**Fig. 2**).

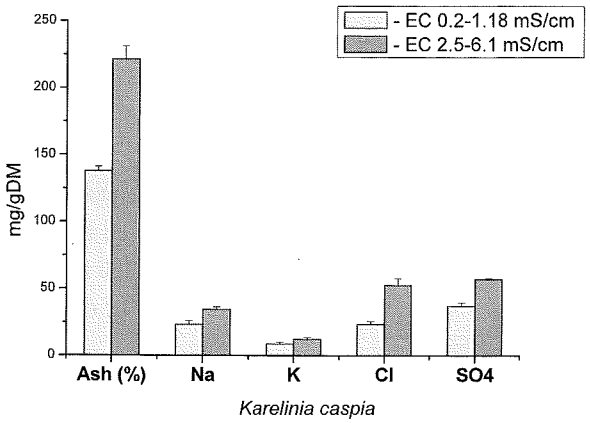

Fig. 2. Mineral content of plant biomass from tested areas with different soil salinity.

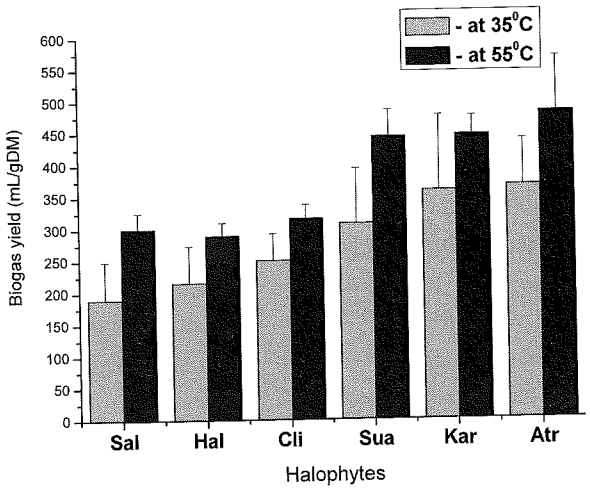

Fig. 3. Biogas yield at anaerobic digestion of halophytes biomass.

Thus, taking into consideration that some chemical substances in plant biomasses can reduce biogas production and damage microbial communities of AD-reactors, it is necessary to identify detailed chemical composition of plant substrates before digestion, which is especially important for halophytes.

3.2. Biogas production under anaerobic digestion of halophyte biomass

Anaerobic digestion of halophyte biomasses in batch-test mode experiments was investigated. Some findings are presented in the Figures below.

Experimental results indicated that approximately 190-366 mL biogas (with 60% CH_4) can be produced from anaerobic digestion of 1 gDM of halophytic biomass under mesophilic conditions (**Fig. 3**). It should be noted that anaerobic digestion of the plant biomass at thermophilic conditions was faster and about 30% more productive in comparison with the same process at mesophilic conditions. Anaerobic decomposition of the biomass (at F/M = 0.2) at 55°C took about 12-14 days, and at 35°C, it took 21-26 days; and mean cumulative biogas yield of AD of halophytes at 55°C varied from 289 mL/gDM (*Halostachys*) to 481 mL/gDM (*Atriplex*).

Suaeda paradoxa, *Atriplex nitens* and *Karelinia caspia* were recognized as the most productive halophytes among investigated plants in terms of biogas yield. With anaerobic decomposition of the above mentioned plant biomasses, 190 mL, 366 mL, and 358 mL biogas was produced from 1 gDM at 35°C, respectively, from these species, and 300 mL, 481 mL, and 445 mL biogas was produced from 1 g of dry matter at 55°C, respectively.

Correlation between organic matter content (measured as VS) and cumulative biogas production at AD was very strong (**Fig. 4**). Thus, the experimental data on biogas production indicate that organic fractions in halophyte biomass had quite

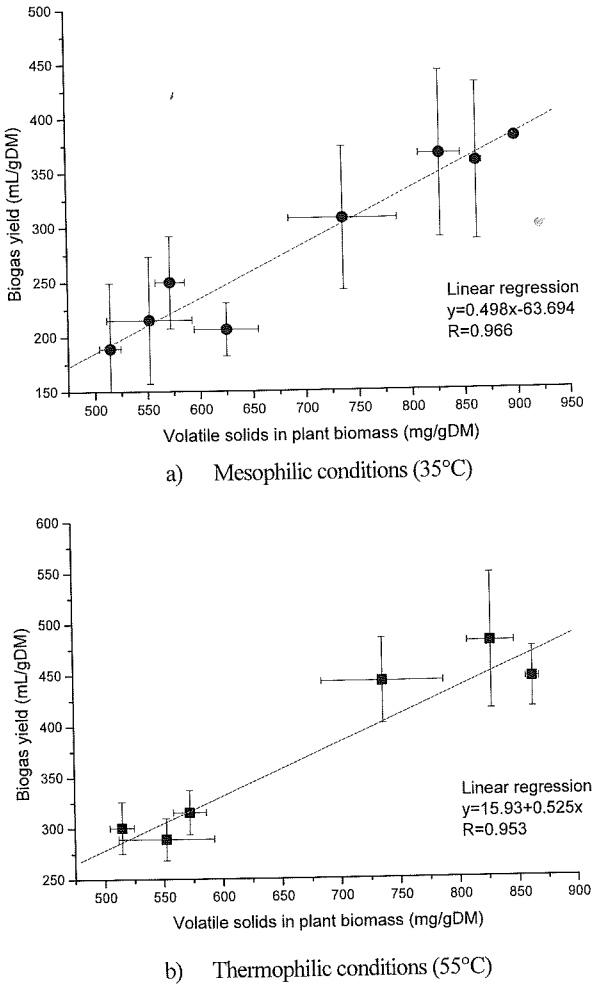

Fig. 4. Correlation between organic matter content in plant biomasses and biogas yield from them at anaerobic digestion.

high biodegradability under anaerobic digestion; this was about 40-60% at mesophilic temperature and 50-75% at thermophilic conditions.

4. Conclusion

Biogas potential of halophyte biomasses (m^3/ha/year) were assessed taking into consideration information about their biomass yield in Central Asia and biogas production measured in the study (**Table 2**). Analysis of the data showed some unexpected findings. For instance, field data for *Salicornia europaea* indicates it has very high biogas potential, but it had the lowest biogas yield from a unit of biomass in laboratory conditions. On the other hand, it was revealed that *Karelinia caspia* has a very high biogas yield from a unit of dry biomass in laboratory experiments, but at the same time it might have a very small potential biogas production in current conditions because of low yield of biomass.

Available information concerning utilization of halophytes in Central Asia is presented in **Table 3**. Most of the investigated halophytes have nutritional value as forage and are

Table 2. Biogas potential of some halophytes in Central Asia.

	Biogas yield in lab-tests (m^3/t DM)		Biomass production (tDM/ha/year)	Estimated biogas production** (m^3/ha/year)
	35°C	55°C		
Salicornia europaea	190	330	(15-20)*	(2850-3800)
Halostachys belangeriana	215	289	1-2	215-430
Climacoptera sp.	250	315	1-1.5 (20)	250 – (5000)
Suaeda paradoxa	308	443	4 (13)	1232-(4004)
Karelinia caspia	358	445	0.1-1.2	35.8-429.6
Atriplex nitens	366	481	6 (21)	2196-(7686)

*Actual data from plants under cultivation/irrigation is given in parentheses.
**Calculated for mesophilic conditions (35°C).

Table 3. Current usage of some halophytes (Gintzburger, 2003).

	Current use
Salicornia europaea	**Forage value**. Limited consumption due to high salt content. It is used for **soda-based** glassmaking and soapmaking.
Halostachys belangeriana	Poor value as forage. Fuelwood. **Source of potassium**. Alkaloid **"halostachyn"** is present.
Climacoptera brachiata; Climacoptera lanata	**Valuable food** for sheep, goats and camels; well consumed in autumn-winter. **Rehabilitation** of sandy and saline waterlogged areas. **Antioxidants** (flavonoids) and **glycosids** are present.
Suaeda paradoxa	**Forage value. Edible** for sheep, goats and camels. Land **biomelioration**. It is processed as a **source for sodium carbonate** for use in glass-making. **Alkaloids** are present.
Karelinia caspia	Poor forage, consumed a little by sheep, goats and camel in winter. Honey plant.
Atriplex nitens	**Forage value. Edible** for sheep, goats and camels.

consumed by sheep, goats and camels. In addition, they can be used as sources of valuable medicinal or some chemical compounds. Thus, using biomass of such halophytes for energy may be unreasonable since they could be useful in other ways and criticisms about diverting useful plant production for biogas use would apply.

Of the studied halophytes, only *Karelinia caspia* is not currently used for food or forage because biomass of this halophyte has very poor forage value and is recognized as useless by local people. For this reason, it has never been cultivated before. However wild plantations of *Karelinia caspia* are widespread in Central Asia, it grows to moderate heights (1.5 m), and this unpretentious perennial plant has very high salinity resistance. Moreover, *Karelinia* is noted as good honey plant; 20-22 kg/ha of honey could be produced (Sabirov, 1972).

Thus, it is concluded that biomass of *Karelinia caspia* (Pall.) Less is one of the most promising sources for biogas production in Central Asia. Wild associations of the halophyte can be used as renewable source of alternative energy, and it can be planted in abandoned saline arid lands for improving and increasing their productivity. The only drawback for this halophyte in terms of biogas production is the high sodium and sulfate content in biomass which can reduce the capacity of anaerobic digesters. However, this can be remedied with the addition of Fe^{2+} or Fe^{3+} and further research could improve the efficiency of biogas production from this halophyte.

Acknowledgements

Work was supported by USAID-National Science Fund (NSF) in the framework of joint project with International Center for Biosaline Agriculture (ICBA) and University of Nevada - Partnerships for Enhanced Engagement in Research (PEER) "Utilization of low quality water for halophytic forage and renewable energy production", AID-OAA-A-11-00012.

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