

Use Alfalfa Grown On Contaminated Land as an Energy Crop For Biogas Production

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ABSTRACT: Crops grown for energy could be produced in large quantities, just as food crops are. While maize is currently the most widely used energy crop, native trees and grasses are likely to become the most popular in the future. The primary purpose of growing Lucerne (*Medicago sativa*) is certainly animal nutrition, but with the help of plant high protein content and the favorable ratio of macronutrients, relatively high moisture content, it can be used as an energy crop for biofuels. Furthermore, country of Bosnia and Herzegovina has the misfortune to have beautiful landscapes and areas that are weighted with various pollutants. That being said and considering the fact that the production of plant crops for food purposes on these areas is not allowed, an opportunity came across to go deeper into the matter and look through aforementioned specie as a raw material for biogas production in laboratory conditions through a series of experimental measurements. The aim of this paper was to investigate and determine the energy potential of the blue clover (*Medicago sativa*) grown on contaminated soil, through implementation of anaerobic digestion in mesophilic conditions with different ratios of Lucerne, sludge from the municipal wastewater treatment plant and manure from the farm. The obtained results will be based on the assessment of the possibility of applying energy crops grown on polluted or recultivated areas.

KEYWORDS: energy crops, Lucerne, biogas, contaminated soil, bioremediation, recultivated areas.

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I. INTRODUCTION

Population growth, urbanization and industrialization have caused a significant pollution of the human environment and impairment of land quality, water and air. Among large number and types of pollutants that are released into biosphere, heavy metals pose a great danger to the environment and the living world [1]. Releasing heavy metals into the soil has serious consequences regarding human activities and life in general [2]. Plants have the ability to accumulate heavy metals from the soil, which are essential for their growth and development (Fe, Mn, Zn, Cu, Mg, Mo, Ni). Given the toxicity of heavy metals, excessive accumulation in plants can be harmful to the environment. Plants that have the ability to accumulate heavy metals are: potatoes, beans, maize, barley and sativa that has the ability to accumulate As, B, Cr, Cs, Se, Mo, Ni. Lucerne is a perennial legume, mainly used for the production of quality animal feed and can be used fresh and canned as hay, silage, flour, pellets etc [3]. The main problem is what to do with plants that have accumulated heavy metals from the soil. Good and effective solution is that energy crops have the possibility to bear anaerobic digestion which has become a popular technology for producing energy from renewable sources [4].

In recent decades, the process of anaerobic digestion has become widespread across Europe with the help of legislation aimed at increasing biogas production in various economic sectors. The importance of this technology is reflected not only in environmental benefits but also as an additional source of income.

Crops with significant biomass yields and degradable substances are particularly suitable for anaerobic digestion and are also capable to give high methane yields. Crops that can be stored for a long time with minimal losses are also recommended for biogas production, e.g. crops that can be easily ensiled [5].

II. MATERIALS AND METHODS

Lucerne cultivated on contaminated land of slag and ash landfills in Tuzla together with waste sludge from Živinice municipal wastewater treatment plant and cattle manure from Spreča farm has been used in process. For the purposes of this paper, a laboratory reactor system for anaerobic digestion of organic matter with glass eudiometric pipes (manufacturer's Šurlan-Medulin), mounted on glass bottles (usable volume of 500 ml) has been used. Provision of anaerobic conditions was performed by sparging of nitrogen in order to displace the air from the reactor, while providing the required constant temperature of the reactor system at $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ has been carried out by heating in a water bath with circulating water (Fig. 1). Using the eudiometric pipes, the production of biogas is simple to read off, because produced gas pushes the liquid level down, while the fluid goes back into the storage bottle.



Fig. 1. Laboratory reactor system

The pressure and temperature of the ambient air were measured on the set pressure hydrometers or eudiometric tubes, whose values are used to convert the volume of the resulting biogas to normal conditions. Mixing of the substrate is realized mechanically using a magnetic stirrer. Measuring the volume of biogas produced in the reactor has been performed in accordance with DIN 38 414 [6], and gas composition analysis has been performed on a gas chromatograph "PERKIN ELMER", equipped with the software package "Arnel". Because of the inhibition of anaerobic substrate degradation due to a sudden increase in the concentration of volatile fatty acids at the beginning of the process, which was reflected in a decrease of pH below 4, it was necessary to buffer the substrate by combining two bicarbonate buffers. By adding 150 mg of NaHCO_3 and 170 mg of KHCO_3 in relation to 1 g of total organic volatile matter [7] in the substrate, the optimum pH range is obtained.

To determine the necessary parameters in the substrates, the methods described below are used. Determination of dry and volatile organic matter has been performed according to Method 2540-B and 2540 Solid-Solid E. Standard Methods for the Examination of Water and Wastewater [8]. Electrometric measurement of pH was carried out by direct measurement, with the pH meter METTLER TOLEDO FE 20/EL 20. Prior to each measurement, internal control was performed with certified reference materials of pH- value 4.1; 7.01; 10.01. The nitrogen content by Kjeldahl has been determined according to Method 4500- N_{org} B. Standard Methods for the Examination of Water and Wastewater 20nd edition. APHA, Washington, DC [9]. The method consists of three stages: digestion at a temperature of 340°C (boiling point of H_2SO_4) in the presence of concentrated sulfuric acid and selenium Kjeldahl catalyst; distillation in the presence of NaOH where distillate accepts in the solution of boric acid, and titration with 0.1 M HCl in the presence of indicator bromocresol green. Determination has been made on Kjeldahl apparatus Gerhardt. To determine the chemical oxygen demand, the standard method is used according to the ISO 6060:2000 [10].

III. RESULTS AND DISCUSSION

Mixtures from the supstrate are showing (using ratios) in Table I.

Table I. Substrate composition

Mixtures	Unit	Lucerne	Sludge	Manure
1	g	150	250	200
2	g	100	300	200
3	g	50	350	200

Formed mixtures from Table I, before the start of the process had the values showing in Table II.

Table II. Physico-chemical characteristics of the substrate mixtures used in the experiment

Parameter	Unit	1	2	3
pH	-	7.84	8.07	8.08
TS	%	9.33	7.68	5.96
VS	%	7.35	5.81	4.22
COD	g/kg	59.24	54.83	43.15
TKN	g/kg	4.49	4.43	4.42
TP	g/kg	0.45	0.47	0.45
COD:TKN:TP		130:10:1	116:10:1	96:10:1

The parameter that is directly related to biogas production is VOC, so the theoretical biogas yield ranges from 0.25 to 0.65 liters per gram of VS with a methane content of 70%. As the VS/TS ratio in all three samples is approx. 0.7 the condition for the presence of sufficient amount of organic matter in the reactors is satisfied.

The previous statement can be confirmed if the COD value is analyzed, which has a relatively high value that decreases with increasing share of Lucerne. TKN and TP have approximately the same values in all three substrates which is associated with a manure content that is equal in all three substrates because manure is the majority source of nitrogen and phosphorus.

The most favorable C:N ratio is 30:1 which is needed since methane bacteria consumes carbon 30 times faster than nitrogen. Since the parameters representing organic matter and nitrogen in this experiment are expressed through the parameters COD and TKN, the COD:TKN:TP ratio shows a sufficient presence of macronutrients, but still deviates from the literature recommended 600:7:1 [11].

Diagrams (Fig. 2 and Fig. 3) are showing daily biogas production and biogas cumulative yield in cosubstrate 1, 2 and 3.

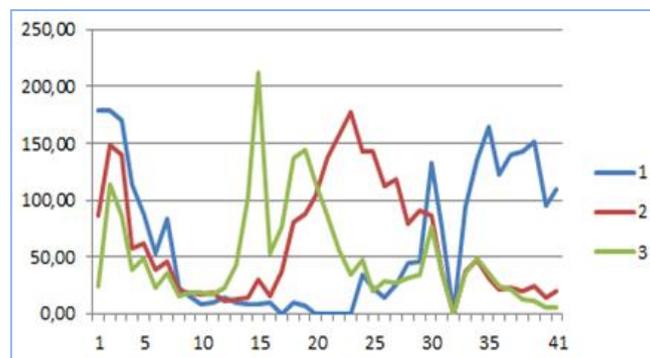


Fig. 2. Diagram of daily biogas production per ml

Diagram of daily biogas production shows a discontinuous biogas production that cannot be stated with any kind of proportionality, however a visible increase in production can be distinguished (15 days for cosubstrate 3, 24 days for cosubstrate 2 and 30 days for cosubstrate 1). That can be seen as a period where the final decomposition of Lucerne in samples occurred. Have in mind that with less Lucerne content, the process time is shorter and vice versa.

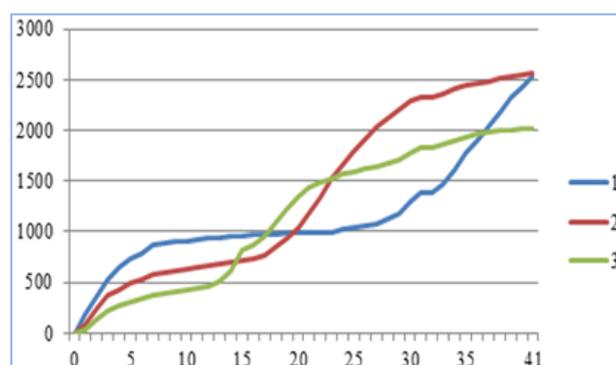


Fig. 3. Cumulative biogas yield (day/ml)

Diagram of cumulative biogas yield (Fig. 3) confirms phases off adaptation and the beginning of hydrolysis during first days of the process. The diagram is showing insignificant difference in production in all three cosubstrates. That being said, it can be concluded that Lucerne does not have impact on the amount of gas, yet by adding larger quantity of Lucerne in sludge and manure mixture, the duration of the process is longer, however it does not effect the amount of biogas which is produced.

Based on the share of methane in biogas and the production of biogas, calculation of daily and cumulative production of methane has been performed as well.

There is an increase in gas production in the case of methane at identical intervals as in the diagram of daily biogas production.

As in the case of cumulative biogas production, methane production from all of three cosubstrates is quite uniform. That being said, it can be concluded that Lucerne has no effect on the amount of biomethane that is produced.

Table III. Final anaerobic digestion results after concluded experiment

Parameter	Unit	1	2	3
pH	-	7.33	7.40	7.49
TS	%	7.12	5.45	4.37
VS	%	5.15	3.58	2.61
COD	g/kg	51.78	39.78	29.56
TKN	g/kg	5.01	4.56	3.80
TP	g/kg	0.76	0.49	0.46
V biogas	ml	2536.38	2565.8	2019.08
V methane	ml	1094.11	970.41	1067.95
Wmax methane	%	66.80	65.00	67.02
Biogas yield	mlCH ₄ /gVSi*	26.05	26.95	44.49

*VSi – Volatile solids input

After the experiment, the results shown in Table III, Fig. 2 and Fig. 3 indicate a uniform production of biogas (the same case is with biomethane), obtained by mixing different ratios of Lucerne, waste sludge and manure. Based on the different ratios, the addition of a smaller amount of Lucerne to the substrate shortens the duration of the process without a noticeable difference when it comes to the production of biogas and biomethane.

After anaerobic treatment, digestate can be used in agriculture for soil conditioning. The pH value in the digestate ranged in one narrow range from 7.33 to 7.49, meaning a positive effect when it comes to soil acidity. Taken into account the fact that agricultural areas with low pH values are dominant in Bosnia and Herzegovina, use of digestate can improve soil properties. That being said, it can be stated that by adding different ratios of Lucerne to waste sludge and manure does not affect biogas or biomethane production.

With the results of research based on biogas and biomethane yield in relation to organic load, this paper represents valuable contribution to development of anaerobic treatments of waste sludge and manure in a mixture with Lucerne grown on contaminated soil.

IV. CONCLUSION

As a plant culture, Lucerne can be used for bioremediation contaminated areas that contain heavy metals. The presence of metal in soil also causes its presence in Lucerne while the distribution of the metal itself in plant organs depends on the type of element. Disposal problem of Lucerne grown in this way can be solved by anaerobic digestion, which besides biogas production presents efficient and ecologically acceptable technology of producing energy from biodegradable organic waste. Biogas is renewable energy source which production reduces greenhouse gas emissions and enables the disposal of organic waste. A slight difference in the amount of biogas and biomethane that were produced, has been recorded. By comparing the contents of TS, VS, COD, TKN and TP before and after the process of anaerobic digestion, a certain amount of organic matter was transformed into gaseous products. Impact of Lucerne content does not affect biogas yield and quality. However, there is an impact on the duration of process. With higher content of Lucerne, the duration of the process itself is longer and vice versa.

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