BIOGAS YIELD FROM ANAEROBIC BATCH CO-DIGESTION OF RICE STRAW AND ZEBU DUNG*

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The suitability of rice straw waste biomass for anaerobic digestion was tested and the energy potential of the co-digestion of rice straw with zebu dung was examined. Rice straw and zebu dung were studied under batch anaerobic conditions as separate wastes as well as mixed in various proportions. All experiments were carried out at 5% of total solids. The methane yields achieved by single substrate digestion of rice straw and zebu dung were $60.51 \ l$ CH₄ kg⁻¹ volatile solids (VS) and $96.09 \ l$ CH₄ kg⁻¹ VS, respectively. The highest energy potential was reached by co-digested mixtures 80:20 and 60:40 (rice straw: zebu dung) giving the methane yield of $163.231 \ l$ CH4 kg⁻¹ VS and $138.961 \ l$ CH4 kg⁻¹ VS, respectively. According to these results, rice straw is suitable for the energy production through the anaerobic digestion. The degradation and methane production potential of rice straw is significantly increasing when co-fermented with zebu dung. The most appropriate proportions for co-digestion were determined as 8:20 and 60:40 (rice straw: zebu dung), because it was found that with the increasing content of rice straw up to the ratio 80:20, the amount of produced biogas increases due to the optimization of pH of the mixture.

anaerobic digestion; methane yield; agricultural residues; energy

INTRODUCTION

Energy has always been the most important driving force of progress and growth over the centuries. The recent need to explore and exploit new energy sources that are both ecological and renewable is essential, especially in developing countries. The energy demand of millions of households in remote areas can be saturated using locally available small-scale technologies treating waste materials and agricultural residues (C u n d r, H a l a d o v á, 2012).

Rice is the most important staple food consumed daily by at least half of the world's population. Per each kilogram of harvested rice, some 0.41–3.96 kg of rice straw is produced (L i m et al., 2012). For this reason, rice straw is nowadays one of the most abundant agriculture residues worldwide, which can be used for the renewable energy production. The Food and Agriculture Organization of the United Nations (FAO) estimated that a total of 679 million t of rice were produced in 2009 (FAOSTAT, 2011), which equates to approximately 916 million t of rice straw available for energy production (K a d a m et al., 2000).

FAO forecast for global rice production in 2012 was 729 million t.

Common solutions for dealing with rice straw are open-field burning or tilling the straw back into the field, both contributing to increased greenhouse gas emissions (Glissmann, Conrad, 2000; Gadde et al., 2009). According to a Thai survey, 90% of the rice straw collected during the peak harvesting season is burnt in the open fields (Tipayarom, Oanh, 2007). These habitual burning activities release a large number of noxious pollutants such as CO₂, CO, unburnt carbon (with trace amount of methane), NO and trace amount of SO₂, along with other particulate matters that contain polycyclic aromatic hydrocarbon n-alkanes (Yang et al., 2006; Gadde et al., 2009) and dioxins (K orenaga et al., 2001). These pollutants can adversely affect human health and also cause the cancer. In addition, CO₂ emissions from open field burning accelerate the increase in atmospheric temperature and can cause global warming. Due to the health and environmental concerns, many countries have imposed new regulations to restrict field burning activities (Mansaray et al., 1999; Lim et al.,

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Table 1. Characteristics of biomass substrates

	Rice straw	Zebu dung	Inoculum
TS (wet, %)	91.96	18.14	7.5
pН	_	9.10	7.8
C/N	69.96	14.60	_
VS (dry, %)	79.50	86.00	_
TOC (dry, %)	35.68	5.55	_
TKN (dry, %)	0.51	0.38	_

TS = total solids, VS = volatile solids, TOC = total organic carbon, TKN = total Kjeldahl nitrogen

2012). As for straw tilling, CH_4 emissions from anoxic soils amended with rice straw are much higher than those without straw (Glissmann. Conrad, 2000; Kumaraswamy et al., 2001; Koga, Tajima, 2011).

The process of the conversion of biomass residues into a renewable energy using anaerobic digestion has been known for centuries. During the digestion, microorganisms convert biomass into biogas, a mixture of methane and carbon dioxide with trace amount of other gases, which can be used for various purposes. However, the rice straw as a substrate with high lignin content, inappropriate C/N ratio, and high total solids content can be easily anaerobically digested only when it is pretreated.

Various pretreatment methods, increasing the digestibility of rice straw, include alkali pretreatment, heat pretreatment, size reduction, and seeding (Ward et al., 2008, Teghamaretal., 2012). Nowadays, the application of a small scale anaerobic digestion can be found in many developing countries (Limetal., 2012). However, using these pretreatment methods in small scale digesters can be problematic due to the lack of available materials and technical complexity. For this reason, additional methods to increase the digestibility of rice straw are studied, such as the inoculation with appropriate inoculum or the co-digestion with other available waste materials.

The main objective of this work was to examine the suitability of rice straw for anaerobic digestion and to analyze the energy potential of the co-digestion of rice straw with zebu dung as well as to determine the most appropriate substrate co-digestion mixture.

MATERIAL AND METHODS

All experiments were conducted under controlled laboratory conditions, in the laboratories of the Faculty of Tropical AgriSciences of the Czech University of Life Sciences Prague.

The rice (*Oryza sativa*) straw used during the experiments was obtained in a rice mill of Ranobe village (southwestern Madagascar) in August 2011. Zebu (*Bos indicus*) dung was obtained from the Zoological garden in Vyškov, Czech Republic. The inocula to inoculate the substrate during laboratory experiments were obtained from a mesophilic farm digester in Krásná Hora at the biogas plant Agricultural station Krásná Hůrka, Czech Republic. This biogas plant is fed with cow manure, corn and grass silage as substrate. All materials were stored at 4°C until used.

The characteristics of the rice straw and zebu dung such as total solids (TS), volatile solids (VS), total organic carbon (TOC), and total Kjeldahl nitrogen (TKN) content were measured according to the Standard methods (Clescerl et al., 1999). The C/N ratio was calculated using the TOC and TKN measured. The pH of zebu dung and inoculum was measured. All measured and calculated characteristics of substrates are presented in Table 1. Prior to the experiments, rice straw was physically pretreated (chopped to 10–15 mm pieces by a hand mixer).

The samples of the biomass were mixed in specific ratios of TS to constitute six different mixtures of rice straw and zebu dung (0:100, 20:80, 40:60, 60:40, 80:20, 100:0). The biogas production of all mixtures was measured simultaneously during each run of the experiments (Table 2). All experiments were run at 5% of total solids (TS), and always 10% of the total volume of inoculum was added to inoculate the substrate. The biogas production from 100% inoculum was also monitored to show its stability. All the experiments were triplicated to prevent the errors which could possibly occur during the testing.

The pH of the co-fermented mixtures was measured at the beginning and at the end of each experimental run with Voltcraft PH 100 ATC (Voltcraft, Czech Republic) and C/N ratio was calculated. The results are presented in Table 2. At the beginning of the ex-

Table 2. Experimental substrates mixtures and their parameters

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Rice straw: zebu dung (%)	Rice straw TS (g)	Zebu dung TS (g)	C/N	pH initial	pH final		
20:80	5	20	28.51	8.08	7.4		
40 : 60	10	15	40.74	7.85	7.38		
60 : 40	15	10	51.59	7.76	7.44		
80:20	20	5	61.27	7.5	7.47		
0:100	0	25	14.60	9.1	7.44		
100:0	25	0	69.96	-	7.41		

TS = total solids

Table 3. Results of anaerobic co-fermentation of rice straw and zebu dung

Rice straw : zebu dung (%)	Cumulative biogas production (ml)	CH ₄ (%)	CH ₄ (l CH ₄ kg ⁻¹ VS)
20:80	3475.67	56	89.29
40:60	3954.00	49	87.68
60 : 40	5186.33	60	138.96
80:20	6386.33	58	163.23
0:100	3501.67	59	96.09
100:0	3091.33	45	60.51

VS = volatile solids

periments, any methods of modification of the pH to optimal range for anaerobic digestion were not used.

The experimental set-up consisted of 7 anaerobic batch digesters, using wide-mouth 1.25 l Erlenmeyer flasks with a working volume of 0.9 l. Each digester was connected to 10 l plastic flasks (gasholder) where the biogas was collected. This gasholder was filled with a solution of distilled water with added $\rm H_2SO_4$ (0.06 ml $\rm l^{-1}$) and NaCl (10.2 g $\rm l^{-1}$) in order to prevent that $\rm CO_2$, one of the main constituents of biogas, dissolves in water (A d e y e m o , A d e y a n j u , 2008). The accumulated biogas was then measured by the amount of water displaced from the gasholder to a graduated cylinder.

The experiments lasted for 34 days (800 h) and the substrates were tested in mesophilic conditions (30°C). In order to keep the constant temperature, the digesters were placed in the heated water bath (accuracy ± 1 °C). The content of the digesters was manually stirred twice a day for 1 min. The amount of biogas was measured at least once a day. Methane content in biogas was measured at the end of each experimental run with a gas detector OLDHAM EX 2000C (Oldham, France). The cumulative biogas production and the methane yield were calculated using experimental values.

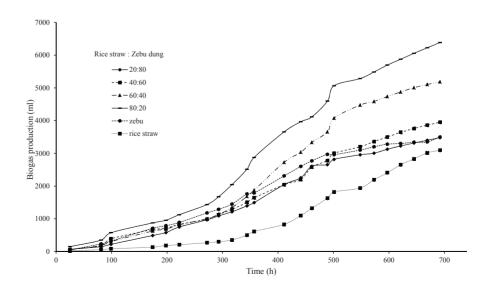
RESULTS AND DISCUSSION

During the laboratory experiments, three monofermentations (zebu dung, rice straw, and inoculum) and four zebu dung and rice straw co-digestions were tested. The inoculum used in the experiments showed very low degradable potential with the average values of the cumulative biogas production being 250 ml and of methane content in biogas 26%. The biogas production of the inoculum was subtracted from the total biogas production of each tested mixture. The values of pH measured before and after the testing indicated the decrease of pH during the digestion, however, the final pH was always slightly alkaline (Table 2), close to neutral.

The results of the fermentation experiments such as the cumulative biogas production, the methane content in biogas, and the methane yield, are summarized in Table 3.

The digestion process is demonstrated in Figs. 1 and 2 where the daily and cumulative biogas productions of six different ratios of rice straw and zebu dung (0:100,20:80,40:60,60:40,80:20,100:0) are presented. The curves indicate the early begging of the biogas production for most of the mixtures due to the easily degradable part of zebu dung. The daily produc-

Fig. 1. Cumulative biogas production



tion of biogas (Fig. 2) was low at the beginning with the stagnation on day 8, but since day 12 until day 18 the production increased. Then the production lowered again, however it continued until the end of the experiment. The stagnation could be due to the acidification caused by accumulation of fatty acids in the digester.

Rice straw single substrate showed the lowest digestibility. The biogas produced, the methane yield and the average $\mathrm{CH_4}$ content in biogas produced by anaerobic digestion of rice straw were 3.09 l, 60.51 l $\mathrm{CH_4}$ kg⁻¹ VS, and 45%, respectively. The low digestibility of rice husk was due to high lignin content and the presence of other hardly digestible polymers in the substrate or could be caused by a high C/N ratio which was 69.96.

The C/N ratios of the co-digested substrates ranged 28.51–61.27 and mostly were not within the optimal C/N ratio required for stable biological conversions of organic wastes. K a y h a n i a n, H a r d y (1994) reported C/N ratios between 25 and 30 as being optimal. However, N y n s (1986) or K i v a i s i, M t i l a (1998) reported the optimal C/N ratio 16–19 for methanogenic performance when poorly degradable compounds such as lignin are taken into account (M s h a n d e t e et al., 2004).

When treated alone, the zebu dung produced only 3.51 of biogas, however the average $\mathrm{CH_4}$ content in biogas was higher (59%) than in the case of rice straw and for this reason the methane yield was $96.091\,\mathrm{CH_4}\,\mathrm{kg^{-1}}\,\mathrm{VS}$. According to Moller et al. (2004), methane yield of the cattle manure was $1481\,\mathrm{CH_4}\,\mathrm{kg^{-1}}\,\mathrm{VS}$. This can be explained by the fact that the degradability of animal waste varies according to the animal feedstock. According to Lam, ter Heegde (2010), the methane yield in $1\,\mathrm{CH_4}\,\mathrm{kg^{-1}}\,\mathrm{VS}$ for non-dairy cattle was 170 in Europe and North America, while in Africa, Latin America, and Asia it was only 100.

Results of the single substrate digestion of zebu dung were comparable to the co-fermentation mixtures 20: 80 and 40: 60 (rice straw: zebu dung) yielding 89.29 l $\rm CH_4~kg^{-1}~VS$ and 87.68 l $\rm CH_4~kg^{-1}~VS$, respectively.

In this study, the best results of all experimental testing were obtained for mixtures with a higher percentage of rice straw (60 : 40 and 80 : 20) (Table 3) where the mixture 80 : 20 produced 6.38 l of biogas with the average $\mathrm{CH_4}$ content of 58%. The methane yield for this mixture was 163.23 l $\mathrm{CH_4}$ kg⁻¹ VS. Surprisingly, this highest methane yield was obtained for the mixture with nonoptimal C/N ratio (61.27). That was due to the pH of the mixtures.

The pH measured at the beginning of the experiments ranged 7.5–9.1 (Table 2). Due to the alkalinity of zebu dung, when increasing the proportion of rice straw, the pH was closer to the optimal pH for anaerobic digestion which is between 6.5 and 7.5 (Werner, 2005). The mixture of 20: 80 (rice straw: zebu dung) had the pH of 8.08 before the experiment and with increased content of rice straw, the initial pH also decreased to 7.5 for the mixture of 80: 20 (rice straw: zebu dung). Therefore the best degradation results were most probably caused by the almost optimal pH for anaerobic digestion in the mixture 80: 20.

According to the results of the study, the co-digestion of rice straw with zebu dung in different ratios improved biogas production, methane yield, and methane content in biogas in comparison with the results of the single-substrate fermentation. These results were in accordance with Jingura, Matengaifa (2009) who reported that the co-digestion helps keeping the degradation stable and increases the biogas yield. Kalra, Panwar (1986) stated that co-fermentation of rice straw with cow manure in the ratio of 1:1 (dry

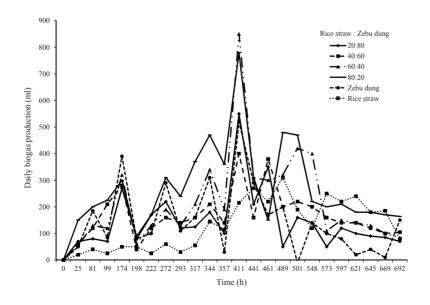


Fig. 2. Daily biogas production

weight) increased biogas production by 9.1% compared to fermentation of rice straw alone.

CONCLUSION

The present study has shown that anaerobic codigestion of rice straw and zebu dung is a feasible process. Furthermore, the anaerobic co-digestion of rice straw and zebu dung is a viable alternative for recovering energy in the form of biogas with 49-60% methane content and at the same time, for abating environmental pollution. The experiments showed that co-digestion of rice straw and zebu dung enhances anaerobic digestion and improves the biogas yield. The highest methane yield (163.23 l CH₄ kg⁻¹ of VS) was produced by the substrate mixture of 80: 20 (rice straw: zebu dung) with a high average content of methane in the biogas produced (58% of CH₄). The rice industry produces globally over 685.24 million t of rice straw that can be used for biogas production, particularly in Asia, where 618.24 million t of rice straw are produced every year (Lim et al., 2012). The strategy of anaerobic co-digestion could help to improve the economy of small rice producers and reduce ecological and disposal problems related to rice straw. Moreover, the simple batch anaerobic codigestion has been proved to be applicable also in developing countries or remote areas where inexpensive and low-technology alternatives to produce energy are generally missing.

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