Analysis of Biogas Produced from Switchgrass by Anaerobic Digestion

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Material flow analysis (MFA) was applied to study the process of biogas production from switchgrass using a mid-temperature (35 ± 1 °C) batch anaerobic digestion process. The flow distributions of energy and material, including carbon (C) and nitrogen (N), were analyzed, as were the material and energy conversion efficiencies. The results showed that biogas and CH_4 production were 268.80 and 135.31 NmL·gVS^{-1} added, respectively, and the average CH_4 content in biogas was 50.34%. Based on the MFA of the anaerobic digestion process, 30.6%, 3.6%, and 65.8% of C was converted into biogas, biogas slurry, and biogas residue, respectively; and 11.7% and 88.3% of N was converted into biogas slurry and biogas residue, respectively. The conversion efficiencies of the material and energy from switchgrass to biogas were 36.1% and 30.1%. Because of the low conversion efficiencies of matter and energy during biogas production, it is necessary to strengthen the secondary use of the fermentation residue. This study provides a basis for the optimization of the anaerobic digestion process and efficient utilization of resources and energy of energy-grass.

Keywords: Switchgrass; Anaerobic digestion; Biogas; Methane; Material flow analysis

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INTRODUCTION

Energy crops may become a sustainable alternative to the use of fossil fuels and a more environmentally friendly energy source in the future. Various perennial grasses have been studied and identified as promising energy crops, such as *Miscanthus* (Clifton-Brown *et al.* 2004; Toma *et al.* 2011; Jurado *et al.* 2013), reed canarygrass (Massé *et al.* 2011), and switchgrass (Ahn *et al.* 2010; Massé *et al.* 2011; Jin *et al.* 2012 El-Mashad 2013). Switchgrass, a C4 grass, is considered a more promising energy crop than many other grasses because of its efficient photosynthetic pathway. Switchgrass has additional advantages, such as superior aboveground biomass yield across a wide geographical range, adaptability to marginal quality land, and low requirements for water, energy, and nutrients. Moreover, switchgrass roots can enhance the structural stability of soil (Massé *et al.* 2010; Hu and Ragauskas 2011).

Anaerobic digestion is a biological method for the conversion of organic wastes into stable products for land applications with reduced environmental impacts (Ahn *et al.* 2010). Methane produced by anaerobic digestion may be a significant energy source for the generation of heat and power. Biomethanation of switchgrass is becoming a more common practice, *e.g.*, anaerobic digestion of switchgrass harvested at different stages

(Massé *et al.* 2010) and co-digestion of animal manure–switchgrass mixture (Ahn *et al.* 2010). The use of switchgrass for biogas has several potential benefits, including greater biogas production using codigestion with animal or human waste, as well as providing an interim market for energy crops producing ethanol and supplemental "tipping fee" revenue, which could enhance the economics and widespread adoption of switchgrass anaerobic digestion.

Material flow analysis (MFA) is a systematic assessment of the flows and stocks of materials within a defined system (Brunner and Rechberger 2004). MFA connects the flows and sinks of a material, making it a useful decision-making support tool for the management of resources, waste, and the environment (Huang *et al.* 2012). In recent decades, MFA has become widely used in many fields, including process control (Chen *et al.* 2012; Fang *et al.* 2012), waste and wastewater treatment (Aparcana *et al.* 2013, Chen *et al.* 2013), and resource conservation and recovery (Cha *et al.* 2013; Arena and Di Gregorio 2014).

It has been debated in previous articles whether the production of biogas or bioethanol for a given material is the best use (Papa *et al.* 2015). Much research on the anaerobic digestion of switchgrass has been performed, but the flow distribution of material and energy in the anaerobic digestion process has not been clearly explained. In this study, MFA was used to analyze the process of using switchgrass to produce biogas *via* mid-temperature (35 ± 1 °C) batch anaerobic digestion. The flow distributions of materials, energy, carbon (C), and nitrogen (N) were presented and discussed. Based on the MFA results, some suggestions on improving efficiency of resource and biogas productivity were proposed.

EXPERIMENTAL

Materials

Switchgrass preparation

Switchgrass provided by the Beijing University of Chemical Technology was dried, crushed, and sieved (20 mesh, < 0.85 mm). The inoculum was trained long-term in a mesophilic anaerobic fermentation tank in Biomass Bio-chemical Conversion Laboratory of GuangZhou Institute of Energy Conversion, Chinese Academy of Sciences (short for GIEC-BBC, CAS).

Digester setup and operation

Lab-scale digesters were arranged, as shown in Fig. 1. Briefly, 2500-mL Büchner flasks (BA) with one sampling opening were filled with inoculum and switchgrass mix (12:1 m/m, 8% TS), while nitrogen was used to remove the air in the flasks. Water baths were controlled at 35 ± 1 °C, and the digesters were stirred manually twice a day. The experiments were stopped after 44 d when the daily biogas productions were less than 1.5 $mL \cdot gVS^{-1}$ added$\cdot d^{-1}$ for a period of more than 5 d. The fermentation residues in BA were filtered and the solid residues were dried at 60 °C, while the filtrate (biogas slurry) was stored at -20 °C.

Biogas generated from bottle A was collected in bottle B and measured with saturated NaCl solution displace method. Biogas production was measured daily by measuring the volume of the solution in Bottle C with a graduated cylinder. All tests were run in duplicate.

Fig. 1. Lab-scale setup for anaerobic digestion. Bottle A: anaerobic reactor; Bottle B: biogas collector; Bottle C: solution collector; Tube A: biogas-guide tube; Tube B: solution-guide tube; Valve A was used for biogas sampling; Valve B for biogas metering.

Methods of Analysis

Composition analyses

Composition analyses of switchgrass and biogas residue were performed in triplicate. Total solids (TS) and volatile solids (VS) were assessed at 105 and 550 °C, respectively. Cellulose (CL), hemicellulose (HCL), and lignin (LG) were measured according to the National Renewable Energy Laboratory's (NREL) laboratory analytical procedures (LAPs). The carbon (C) and nitrogen (N) contents of switchgrass and biogas residue were measured using a Vario EL cube analyzer (Elementar, Germany), while the total inorganic carbon (TIC), total carbon (TC), and total nitrogen (TN) of the inoculum and biogas slurry were measured using a Vario TOC analyzer (Elementar, Germany).

Gross heat of combustion (GHC)

The GHCs of switchgrass and biogas residue were determined using an oxygen bomb calorimeter (C 2000, IKA, Germany), with an initial oxygen pressure of 5.0 MPa (50 atm) and a final temperature of 20 to 25 °C. Benzoic acid was used for calibration.

Biogas analysis

Biogas analysis was conducted at 120 °C using a GC-2014 gas chromatograph (Shimadzu, Japan) equipped with a TCD detector. A Porapak Q column, maintained at 50 °C, was used with an argon gas flow rate of 30 $mL \cdot min^{-1}$ and a retention time of 5 min. Calibration of the instrument to a standard biogas (5% N_2, 60% CH_4, 35% CO_2) was conducted weekly.

Gas production

Gas production was calculated as the ratio of the total gas yield over the mass of the volatile solids added to the reactor (VS_{added}, assuming that $VS_{added} = VS_{switchgrass}$ in this experiment), and expressed as $mL \cdot gVS^{-1}$ added. Gas production was normalized and reported (273 K, 1 atm) as mL per g of the added volatile solids ($NmL \cdot gVS^{-1}$ added). Daily gas production (DGP) and cumulative gas production (CGP) were expressed as $NmL \cdot gVS^{-1}$ added$\cdot d^{-1}$ and $NmL \cdot gVS^{-1}$ added, respectively.

Material flow analysis (MFA)

The MFA was performed as described by Brunner and Rechberger (2004). In the current study, the systematic assessment object was the experimental anaerobic fermentation process of biogas produced with switchgrass. Substance flow analysis software (STAN 2.5) was applied to establish the MFA system model, and an algorithm

(IAL-IMPL 2013) was created to optimize the experimental data to ensure the conservation of matter (Smith and Tan 2013; Rechberger *et al.* 2014). Graphical renderings of MFA results were prepared using the e!Sankey 3.2 flow chart designer.

RESULTS AND DISCUSSION

Anaerobic Digestion of Switchgrass

The physicochemical properties of the inoculum, switchgrass, biogas slurry, and biogas residue are shown in Table 1. The TIC, TC, and TOC (TC-TIC) in the inoculum (0.750, 1.055, and 0.305 g/L, respectively) were slightly lower than those recovered from the biogas slurry (0.894, 1.399, and 0.505 g/L, respectively), while the TN content in the inoculum (0.71 g/L) was higher than that of biogas slurry (0.12 g/L). Some of the degraded organic matters in the biogas slurry were not converted into biogas because of their low concentrations. The majority of N in the inoculum was recovered from the biogas slurry. The biogas slurry with high content of N element not only could be used as inoculum to adjust C/N rate of anaerobic digestive substrates, but also applied as plant nutrient solution to realize the recycling of resources. The GHC, VS, and the relative contents of CL, HCL, and C in the biogas residue were lower than those in switchgrass, while the relative contents of LG and N were greater than those in switchgrass.

Table 1. Component Analysis of Inoculum, Switchgrass, Biogas Slurry, and Biogas Residue

		Inoculum*	Switchgrass§	Biogas slurry*	Biogas residue§
TM (g)		1854	154.03	1802.5	92.79
GHC (J/g_{TS})		17.48	18.37	17.48	17.48
Component Analysis (%)	TS	1.18	92.9	1.01	100
	VS	54.39	95.8	52.12	80.7
	CL_{TS}	/	36.98	/	27.9
	HCL_{TS}	/	25.07	/	19.65
	LG_{TS}	/	21.62	/	30.87
	C_{TS}	0.102	46.26	0.136	44.33
	N_{TS}	0.069	0.46	0.012	1.53

*C(N) = TC(TN)/ρ_{liquid}, ρ_{liquid} =1.03 g/mL, §Assume $GHC_{Inoculum}$ = $GHC_{Biogas\ slurry}$ = $GHC_{Biogas\ residue}$.

Some components of switchgrass, such as cellulose, hemicellulose, and other organic matters, were efficiently degraded and transformed into biogas, while LG and N were degraded less efficiently, which resulted in a relative increase in the content of these elements. In the biogas residue, the concentration of LG was higher than CL and HCL, indicating the formation of biogas. The majority of N in the biogas residue originated from the inoculum. During the anaerobic fermentation process, the removal rates of TS, VS, CL, HCL, LG, C, and N elements were 43.75%, 49.74%, 51.08%, 49.17%, 7.41%, 36.00%, and 15.83%, respectively. Degradation rate of CL and HCL had important effects on biogas production in anaerobic digestion (Surendra 2015).

Biogas Production from Switchgrass

In the anaerobic digestion process (during which switchgrass produced biogas), the CH_4 volume in biogas reached up to 62.32% on day 9 (denoted as d), and then decreased and stabilized between 53% and 56%. The production of biogas and CH_4 are shown in Fig. 2. The highest peak of daily gas production appeared on d 4, where daily gas productions of biogas and CH_4 were 20.25 and 10.29 NmL·gVS^{-1} added·d^{-1}. The CGP of biogas and CH_4 were 268.80 and 135.31 NmL·gVS^{-1} added, respectively, and the average CH_4 content was 50.34%; 80% of the cumulative gas production was reached within the first 22 to 23 days. Barbanti *et al.* (2014) reported that the highest CH_4 DGP was 7.0 NmL·gVS^{-1} added·d^{-1} at d 10, but the CGP was 216 NmL·gVS^{-1} added at d 58. Jin *et al.* (2014) reported the results of batch digestion studies for ammonia-pretreated switchgrass, where the CH_4 DGP was approximately 160 mL·gVS^{-1} for 21 days. The main reason for the differences in gas production was the composition of the raw material, especially the lignocellulose content, which can change at different localities and stages of growth.

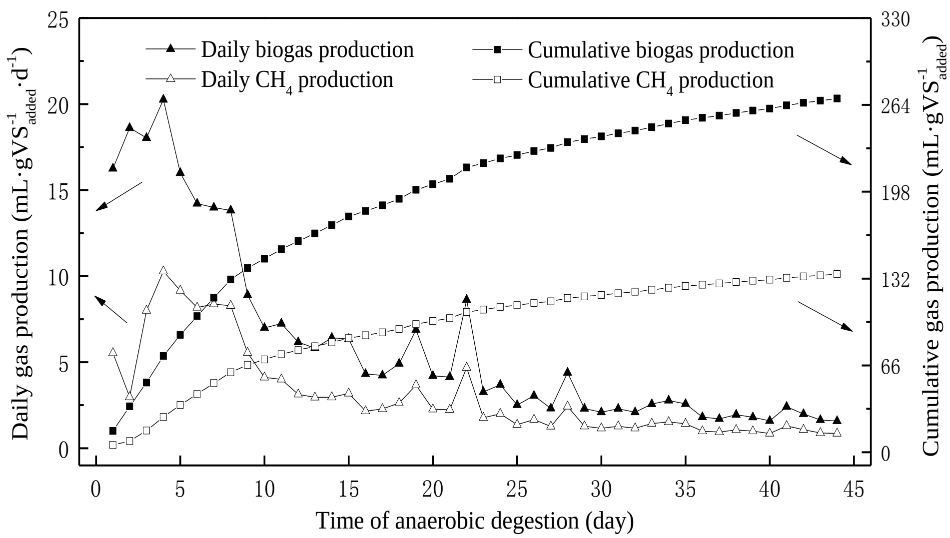

Fig. 2. Production of biogas and CH_4 during anaerobic digestion

MFA model of the anaerobic digestion process

Based on the lab-scale anaerobic digestion process of biogas produced from switchgrass, a model of an open MFA system was established, as shown in Fig. 3. An experimental cycle (EC) was defined as the system time boundary, while the system space boundary was simplified to include only the anaerobic digestion process. With the aid of the model, the flow distribution of materials for different levels were analyzed. The levels of inoculum, switchgrass, biogas, biogas slurry, and biogas residue, the amounts of C and N (substance flow analysis, SFA) and the level of chemical energy fixed in goods (energy flow analysis, EFA) were tracked and analyzed.

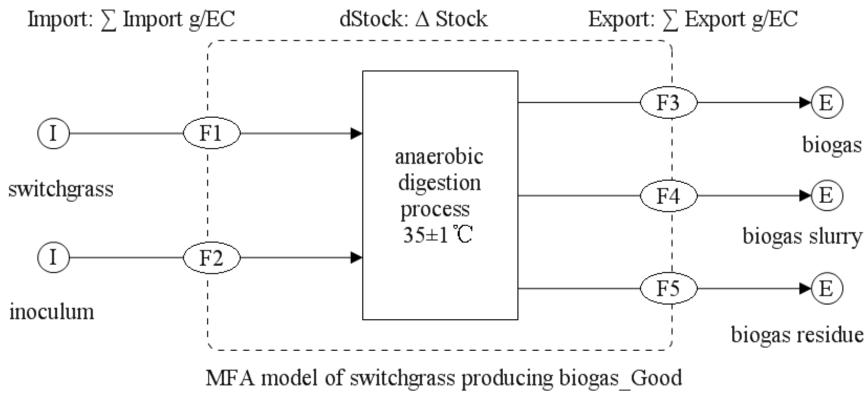

Fig. 3. Material flow analysis system model for switchgrass producing biogas

SFA of Anaerobic Digestion Process

The objects subjected to SFA (shown in Table 2) were the flow distributions of C and N. The densities of both the inoculum and biogas residues (ρ_{liquid}) were approximately 1.03 g·mL^{-1}, while the biogas density (ρ_{biogas}) was approximately 1.34 g·L^{-1}, calculated at CO_2 49.7% and CH_4 50.3%. The SFA data were logged and optimized in the MFA model, and the results were shown as a Sankey diagram in Fig. 4.

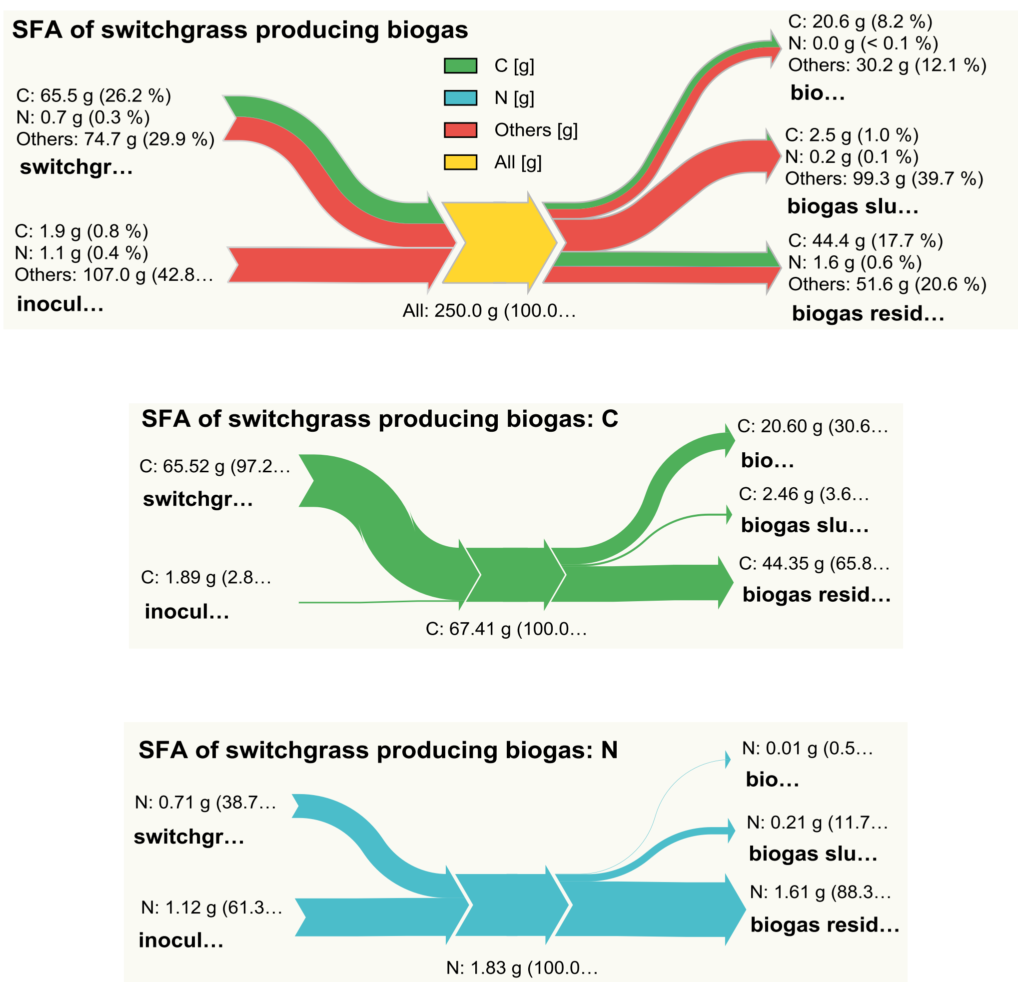

Fig. 4. Substance flow analysis of switchgrass producing biogas

Table 2. Substance Flow Analysis of the Anaerobic Digestion Process

		Mass Flow	Substance Concentration		Substance Flow¶	
		g·EC^{-1}	C, mg·g^{-1}	N,mg·g^{-1}	C, g·EC^{-1}	N, g·EC^{-1}
Import flow	Inoculum*	1854	1.024	0.6893	1.898	1.278
	Switchgrass	154.03	498.0	4.952	76.707	0.763
Export flow	Biogas§	49.49	401.1	/	19.850	/
	Biogas slurry*	1802.5	1.358	0.1165	2.448	0.210
	Biogas residue	92.79	443.3	15.30	41.134	1.420

* $C(N)_{conc}$= $TC(TN)/\rho_{liquid}$; § m_{biogas}= $TV_{biogas} \times \rho_{biogas}$, C_{conc}= $Mc/V_m/\rho_{biogas}$, V_m=22.4 L/mol, M_C= 12 g/mol, N_{biogas} was ignored; ¶ Substance Flow = Mass Flow × Substance Concentration.

SFA results showed that (1) 36.1% of the raw material of switchgrass was degraded to be transformed into biogas; (2) 30.6% C of switchgrass was degraded to be transformed into biogas in the form of CH_4 and CO_2, while approximately 3.6% and 65.8% flowed into biogas slurry and biogas residue, respectively; and (3) very little N from the switchgrass was degraded to be transformed into biogas, while 11.7% and 88.3% flowed into biogas slurry and biogas residue, respectively. It is clear that the switchgrass-producing biogas had lower material conversion efficiency after batch anaerobic fermentation. Over 60% of the C and 80% of the N in switchgrass were still stored in fermentation residue, especially within the biogas residue. The rational development of fermentation residues for solid and liquid organic fertilizers may improve the material conversion efficiency of resources, and it also can decrease environmental pollution.

EFA of Anaerobic Digestion Process

EFA data are shown in Table 3. It was assumed that energy contained within the liquid parts of the inoculum and biogas slurry could be ignored, while the GHC of the solid parts were same and equal to the biogas residue. The EFA data were logged and optimized in the MFA model, and the results are shown as a Sankey diagram in Fig. 5.

Table 3. Energy Flow Analysis of the Anaerobic Digestion Process

		Mass Flow	Energy Density¶	Energy Flow♯
		g·EC^{-1}	kJ·g^{-1}	kJ·EC^{-1}
Import flow	Inoculum*	1854	0.206	381.924
	Switchgrass	154.03	17.066	2628.67598
Export flow	Biogas§	49.49	16.754	829.15546
	Biogas slurry*	1802.5	0.177	319.0425
	Biogas residue	92.79	17.48	1621.9692

* Assume: $GHC_{Inoculum(TS)}$ = $GHC_{biogas\ slurry\ (TS)}$ = $GHC_{biogas\ residue}$; § GHC_{biogas} = 20~25 kJ/L, average = 22.5 kJ/L, Energy $Density_{biogas}$= $GHC_{biogas}/\rho_{biogas}$; ¶ Energy density = TS × GHC; ♯ Energy flow = Mass flow × Energy Density.

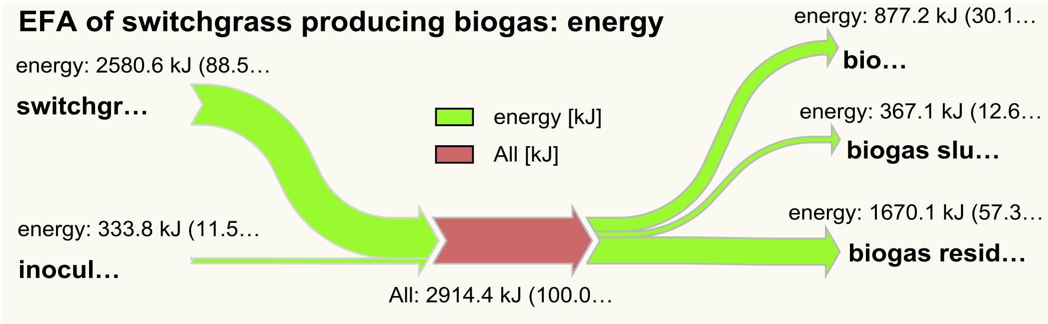

Fig. 5. Energy flow analysis of switchgrass producing biogas

EFA results showed that the energy in raw material was transformed into biogas, biogas slurry, and biogas residue. Only about 30.1% energy in switchgrass was transformed into biogas, and about 57.3% energy still was stored in biogas residue. It is also clear that the switchgrass-producing biogas had lower energy conversion efficiency by anaerobic fermentation. It is important to pay attention to the energy recycling of biogas residues.

CONCLUSIONS

1. Switchgrass producing biogas had a lower material and energy conversion efficiency. More than half of C, N, and energy were still stored in the fermentation residue, especially in the biogas residue.
2. In the batch anaerobic fermentation process for biogas produced from switchgrass, cumulative gas productions of biogas and CH_4 were 268.80 and 135.31 NmL·gVS^{-1} added, and the average CH_4 content was 50.34%.
3. The MFA revealed that the rates of C flowing into biogas, biogas slurry, and biogas residue were 30.6%, 3.6%, and 65.8%, respectively; while the rates of N that separately flowed into the biogas slurry and biogas residue were 11.7% and 88.3%.
4. When the amount of N in the biogas was ignored, the material and energy conversion efficiency of the fermentation process were 36.05% and 30.1%, respectively.

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