Process optimization of biogas energy production from cow dung with alkali pre-treated coffee pulp

T. Selvankumar^{1,2} · C. Sudhakar¹ · M. Govindaraju² ·
K. Selvam¹ · V. Aroulmoji³ · N. Sivakumar⁴ · M. Govarthan^{1,5}

Received: 25 April 2017 / Accepted: 11 July 2017 / Published online: 19 July 2017
© Springer-Verlag GmbH Germany 2017

Abstract Biogas production from cow dung with co-substrate agricultural waste is one of the most demanding technologies for generating energy in a sustainable approach considering eco-friendly. In the present study, coffee pulp (CP) was pre-treated with 1% NaOH and combined with various proportions of cow dung (CD) to explore its biogas producing potentiality. The optimization of the process was studied using Response surface methodology. Statistics based on 3-D plots were generated to evaluate the changes in the response surface and to understand the relationship between the biogas yield and other parameters. The highest methane production (144 mL/kg) was achieved after 90 h of incubation with 1:3 of CP and CD at 40 °C. Gas chromatography analyzes

the chemical compositions of the generated biogas and its post combustion emissions. The chemical composition of the substrates before digestion and after fermentation (biogas spent sludge) were measured in terms of fiber content and the values were noted as, total solids (0.53%), ash content (9.2%), volatile fatty acid (100 mg/L), organic carbon (46%) and a total carbohydrate (179 mg/g). The results of the optimization of biogas production presented in this work found to have significance with the process parameters. The outcome of the study has supported the fact of conventional combustion technology that has to be upgraded to prevent these hazardous emissions into the atmosphere.

Keywords Biogas · Coffee pulp · Cow dung · Response surface methodology · GC–MS

T. Selvankumar and C. Sudhakar equally contributed this work.

✉ T. Selvankumar
t_selvankumar@yahoo.com

✉ M. Govarthan
gova.muthu@gmail.com

¹ PG and Research Department of Biotechnology, Mahendra Arts and Science College (Autonomous), Kalippatti, Namakkal, Tamil Nadu 637501, India

² Department of Environmental Biotechnology, School of Environmental Sciences, Bharathidasan University, Tiruchirappalli, Tamil Nadu 620 024, India

³ Center for Research and Development, Mahendra Educational Institutions, Mallasamudram, Namakkal, Tamil Nadu 637503, India

⁴ Department of Molecular Microbiology, School of Biotechnology, Madurai Kamaraj University, Madurai, Tamil Nadu 625 021, India

⁵ Department of Energy and Environmental System Engineering, University of Seoul, Seoul, Republic of Korea

Introduction

Biogas production from a variety of agro-industrial wastes through anaerobic digestion is growing worldwide and is considered ideal in many ways due to its economic and environmental benefits (Grisel et al. 2014; Fantozzi and Buratti, 2011; Abbasi and Abbasi 2010; Fantozzi and Buratti 2009; Simpson-Holley et al. 2007; Pandey et al. 2000). Methane fermentation is the most efficient technology for energy generation from biomass in terms of energy output/input ratio (28.8 MJ/MJ) among all the technologies used for energy production through biological and thermo-chemical routes (Deublein and Steinhauser 2008).

Coffee is the second largest traded commodity in the world and generates large amounts of by-products and residues during processing (Grisel et al. 2014). Industrial processing of coffee cherries is performed to separate

coffee beans by removing its shell and mucilaginous part. In wet industrial processes a large amount (about 29% dry weight of the whole coffee berry) of coffee pulp waste is produced as the first waste product. The organic components present in coffee pulp waste include cellulose (63%), lignin (17%), proteins (11.5%), hemicelluloses (2.3%), tannins (1.80–8.56%), pectic substances (6.5%), reducing sugars (12.4%), non-reducing sugars (2.0%), caffeine (1.3%), chlorogenic acid (2.6%) and caffeic acid (1.6%) (Corro et al. 2013; Solangel et al. 2011; Franca et al. 2009). Coffee pulp waste and the by-products produced during coffee berry processing contribute a source of severe contamination and pose serious environmental problems. Therefore, disposal of coffee pulp waste has become an emerging environmental problem worldwide due to its natural degradation. Due to improper anaerobic treatment in open pulp waste storage and composting areas, an uncontrolled emission of methane (CH_4) and nitrous oxide (N_2O) cannot be excluded (Madahava Naidu et al. 2004; Boopathy et al. 1986; Adams and Dougan 1981). Hence, an effective utilization and management of coffee wastes in large-scale still remains a challenge worldwide. In addition to uncontrolled gas production, these processes are also responsible for their high contents of caffeine, free phenols, tannins, and by-products, which are reported as toxic agents for many biological processes (Fan et al. 2003).

Cow dung (CD) contains a considerable amount of methanogenic bacteria but low amounts of cellulose, lignocelluloses, lignin and other organic components which are essential for bacterial growth and for biogas production. On the other hand, though coffee pulp contains cellulose, hemicelluloses, and proteins in large amount, but it lacks considerable bacterial population to degrade the toxic components (such as tannins and phenols) to produce biogas. These facts suggested us to employ a mixture of CP/CD that would hopefully result in a synergetic effect towards high biogas production.

Optimization of fermentation processes involves a number of interactive process controlling parameters. At industrial level, even a small improvement in the process leading to a better yield is considered to be highly beneficial in terms of commercial prospective. Therefore, studies on intense process optimization has already become a major area of research in the field of industrial biotechnology as reported by various researchers (Reddy et al. 2008; Selvam et al. 2014, 2016a, b; Govarthan et al. 2014). This signifies the need of the present study in which, the process optimization for biogas production is discussed.

Hence, the main objective of the present study is to comprehensively analyze the use of CP and CD additives in a right ratio to increase the aerobic stability towards biogas production at laboratory scale. This can be achieved by the following steps, (i) Optimization of CP/CD for

biogas production from CP and CD using RSM; (ii) Estimating the biogas production by water displacement method; and (iii) analyzing the produced biogas using GC-MS.

Materials and methods

Collection and preparation of substrates

The coffee pulp waste was collected from the coffee seed processing industry in Yercaud hill station, Salem, Tamil Nadu, India. Cow dung was collected from a dairy farm. The cow dung inoculum was scraped off the feed lanes and collected in a bucket. The inoculum was transported immediately to our laboratory and placed in the digesters.

Pre-treatment and characterization of coffee pulp waste

The CP was grounded in blender to prepare particles with mean size of 10 mm. The alkali pre-treatment of CP was conducted with 1:10 ratio using 1% (w/v) NaOH (1 g of substrate in 10 mL of 1% NaOH solution) (Selvam et al. 2014, 2016a, b; Wang and Huang, 2005). Alkali pre-treated CP were then washed with distilled water and neutralized to around pH 7 and base followed by drying (Bansal et al. 2011). Scanning electron microscope (Jeol JSM 6390 model) was used to examine the morphological modifications of CP before and after the alkaline pre-treatment according to Amiri and karimi (2015), Diaz-Malvaez et al. (2013). Samples were dehydrated and mounted on stubs and sputter-coated with gold for 300 s using high vacuum and a voltage acceleration of 10 kV.

Anaerobic digestion assembly

The anaerobic digestion process was studied in batch reactors to develop an appropriate technology for the production of biogas from the alkali pre-treated mixed substrate of CP and CD. The different ratio of coffee pulp and CD slurry was prepared in 1L of anaerobic digester. Control of CP slurry and CD was prepared in separate 1L anaerobic digester and incubates at 37 °C for 40 days, wide mouth glass bottle. All of the bottles were sealed with air tight rubber stoppers, and another bottle was filled with water to collect gas and was equipped with glass tubes for gas removal.

Optimization of biogas production

Design of experiment (DOE) is a well-accepted statistical technique able to design and optimize the experimental

process that involves choosing the optimal experimental design and estimate the effect of the several variables independently and also the interactions simultaneously. Response surface methodology combined with BBD was established using Design Expert software (9.0.6.2 trial version). Four factors, namely, CP, CD, incubation time, and temperature were optimized for biogas production. Based on BBD, the factors were analyzed at two levels: -1 , for the low level, and $+1$, for high level. A total of 29 runs were performed to optimize the process parameters, and experiments were carried out in accordance with the experimental design matrix. The results were assessed by applying the coefficient of determination (R^2), analysis of variance (ANOVA) and response plots. Employing RSM, the most widely used second-order polynomial equation developed to fit the experimental results and identify the relevant model terms

$$Y = \beta_0 \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum X_i X_j, \quad (1)$$

where Y is the predicted response; β_0 , β_i , and β_{ij} are constant regression coefficients of the model; and X_i and X_j represent independent variables.

Quantification of biogas by water displacement method

The total biogas production was measured by water displacement method according to Bagi et al. (2007). The volume of water displaced in the container is equal to that of the volume of the gas. One end of the gassing gadget was connected to the biogas plant and other end connected to invert measuring cylinder which contained water. The amount of gas was calculated is equal to the mL of water displaced. The biogas was allowed to collect in the inverted measuring cylinder by displacing water.

Chemical analysis of substrates

The substrates were subjected to analysis of the chemical parameter such as total solids, ash content, volatile solids; volatile fatty acid was estimated according to APHA (1995). Organic carbon was determined by Walkley and Black (1934) and a total carbohydrate was estimated by Anthrone Method (Trevelyan and Harrison 1952) from the substrates in before and after treatment.

Analysis of biogas

The methane content in the biogas was measured with gas chromatograph according to Westerholm et al. (2012) (Varian Saturn 2200, Shimadzu). The methane gas was collected in gas bottle by water displacement method and properly sealed. The bottles were subjected to determine

the methane gas analysis using Porapack Q (180 to 100 mesh) column, helium is the carrier gas at 30 mL/min and thermal conductivity detector. Temperature of the detector and oven were 110 and 35 °C, respectively.

Results and Discussion

Effect of alkali pre-treatment and its characterization

Alkali pre-treatment method was applied to coffee pulp waste before anaerobic digestion. Scanning electron microscopy micrographs showed modified out layer of before and after pre-treated CP (Fig. 1a, b). The alkali pre-treatment method has been reported to enhance the biodegradability and enhance the yield (Selvam et al. 2016a, b; Govarthanan et al. 2015; Chandra et al. 2012). However, the most suitable pre-treatment method was based greatly upon the type of lignocelluloses waste (Shaochuan et al. 2013). The effect of pre-treatment on anaerobic biodegradation of CP waste to enhance the digestion process. The alkali-treated substrate to enhance the carbohydrate and proteins (Table 1).

Optimization of the biogas production

The experimental design and the actual response values paired with the biogas production rate are presented from Table 2. ANOVA of the quadratic regression model (Table 3) exhibits that it was a highly significant model as was evident from the Fisher's F test with a very low probability value (F value = 7.21). Values of 'Prob >F' (0.0001) indicate that the term of the model was significant. The Model F value of 7.21 implies that the model was significant. There was only a 0.01% chance that a model F value could occur due to noise. The predicted R^2 (0.2219) and adjusted R^2 (0.7271) values for optimal conditions were in reasonable agreement with the value of R^2 (0.8636), which is closer to 1.0, indicating the better fit of the model in the experimental data. The model for optimal conditions for biogas production, three different tests, namely, sequential model sum of squares, lack of fit tests and model summary statistics was carried out in the present study.

3D graphical a representation was generated (Fig. 2). The results demonstrate that there was a significant relation of CP (g), CD (g), incubation time (h), temperature (°C), were optimized for methane production. The optimum levels of the variables were obtained by utilizing BBD. The model predicted a maximum methane production recovery of 144 mL/kg appearing after CP (750 g), CD (250 g), incubation time (96 h), temperature (40 °C), were

Fig. 1 Scanning electron microscope images of CP. **a** Raw CP without treatment; **b** CP after pretreatment with 1% NaOH

Table 1 Effect of alkali-treated CP waste

	Untreated CPW	Alkali treatment CPW
TS (g/L)	170.3 ± 14.2	182.4 ± 11.4
VS (g/L)	152.1 ± 11.2	161.8 ± 12.1
Carbohydrates (g/L)	9 ± 2.6	16 ± 7.4
Proteins (g/L)	14 ± 2.5	20 ± 1.6

optimized for methane production. Predicted model was validated and experiments were conducted using these optimal conditions. The predicted model values were in good agreement with the values measured in these experiments, thus mitigating the validity of the response model and the necessity for optimal conditions. Graphs highlighted the roles played by the variables for the production of methane.

The coefficients of the regression equation were calculated and the following regression equation was achieved,

$$\begin{aligned}
 \text{Methane yield (mL/kg)} = & 110.60 - 13.42A + 12.08B \\
 & + 11.83C - 5.17D \\
 & + 1.50AB + 0.50AC \\
 & + 5.50BC + 0.75BD \\
 & - 9.50CD - 4.26A^2 \\
 & - 16.26B^2 - 3.13C^2 \\
 & - 28.88D^2,
 \end{aligned}
 \quad (2)$$

where Y stands for methane production, A is CP, B is CD, C is incubation time, D is temperature, respectively. A high degree of similarity of experimental values were observed, thus reflecting the precision and applicability of RSM to optimize the methane production. The biogas yield results indicated that the processes of biogas generation from a mixture of CP with CD substrate proceeds agreement with that reported by Osman et al. (2006), Fujita et al. (1980), as

Table 2 Responses of variables and experimental observed on Box–Behnken design

Run	Coffee pulp (g)	Cow dung (g)	Incubation time (h)	Temperature (°C)	Methane yield (mL/kg)
1	3	5	60	40	94
2	2	1	96	40	78
3	1	3	60	50	70
4	2	5	60	30	82
5	2	1	60	30	74
6	2	3	24	30	62
7	1	1	60	40	80
8	2	5	24	40	80
9	2	3	96	50	73
10	2	3	60	40	110
11	2	5	96	40	115
12	3	1	60	40	60
13	3	3	60	50	62
14	2	3	60	40	110
15	2	3	60	40	110
16	2	1	24	40	65
17	2	3	60	40	110
18	1	5	60	40	120
19	3	3	96	40	102
20	1	3	24	40	122
21	2	3	60	40	113
22	3	3	60	30	65
23	1	3	60	30	86
24	2	3	24	50	68
25	3	3	24	40	78
26	1	3	96	40	144
27	2	3	96	30	105
28	2	1	60	50	64
29	2	5	60	50	75

Table 3 ANOVA for the response surface quadratic model

Source	Sum of squares	df	Mean square	F value	P value prob >F
Model	12797.00	14	914.07	7.27	<0.0001
A-coffee pulp	2160.08	1	2160.08	17.18	0.0010
B-cow dung	1752.08	1	1752.08	13.93	0.0022
C-incubation time	1680.33	1	1680.33	13.36	0.0026
D-temperature	320.33	1	320.33	2.55	0.1328
AB	9.00	1	9.00	0.072	0.7930
AC	1.00	1	1.00	7.953E – 003	0.9302
AD	42.25	1	42.25	0.34	0.5714
BC	121.00	1	121.00	0.96	0.3433
BD	2.25	1	2.25	0.018	0.8955
CD	361.00	1	361.00	2.87	0.1123
A ²	117.62	1	117.62	0.94	0.3499
B ²	1714.60	1	1714.60	13.64	0.0024
C ²	63.68	1	63.68	0.51	0.4884
D ²	5411.33	1	5411.33	43.03	<0.0001
Residual	1760.45	14	125.75	–	–
Lack of fit	1753.25	10	175.33	97.40	<0.0002
Pure error	7.20	4	1.80	–	–
Cor total	14557.45	28	–	–	–

Significance values are in bold

biogas production from swine manure supplemented with corn stalks was enhanced in excess 50% than non supplemented manure.

Chemical analysis of substrate

The biogas released from the digester was analyzed by water displacement method. The maximum biogas yield 144 ml/kg appearing after 96 h in 1:3 of CP and CD. The gas production results suggested that the CP alone has 92 percent biogas production potential to conventional CD. Similarly, Borja et al. (2002) applied a dilution of 1:2.5 ratio of olive pulp and animal manure showed maximum yield of 81 L/g at HRT of 10–25 days under anaerobic digestion. However, the maximum yield was obtained within 2–5 days of the study (Leaneza Coalla et al. 2009). The gas yield was obtained maximum in most of the anaerobic system after 3–4 days of HRT (Hydraulic Retention Time) (Francese et al. 2000) and the biogas released from the reactor system was recovered by water displacement method. This method of gas collection by water displacement is to avoid pressure build up during the gas evolves from the digester. This similar work was also adopted in the laboratory scale production by Zoltan Bagi et al. (2007). After fermentation the substrate content such total solids (0.53%), ash content (9.2%), volatile fatty acid (100 mg/L), organic carbon (46%) and a total carbohydrate (179 mg/g).

Analysis of biogas

The biogas was analyzed through GC–MS. it contained 70% methane, 18% CO₂, 3% nitrogen, less than 0.5 and 1% of hydrogen sulphide and carbon monoxide. The methane fraction in the biogas was analyzed using the in-built NIST library of GC–MS systems and the experimental report of mass spectrogram was reported in Fig. 3. The gas chromatogram peak was obtained in 6.3 min and the mass spectrogram of methane peak of 281 mass separations. The similar methodology was adopted by Niemann et al. (2005) for analysis of methane content in the mines and the methane in biogas also analyzed by GC in CD digester system Wang et al. (2010).

Conclusion

Coffee pulp with an optimum proportion of cow dung was found to be a substrate with a high potential for biogas generation by anaerobic digestion. The coffee pulp and cow dung co-digestion at 1:3 ratios of mixture had showed maximum biogas yield 144 mL/kg water displaced after 96 h. The biodegradability percentage of CP: CD (1:3) = 15.30. The maximum yield of biogas was obtained at pH 8.0 and also at the temperature of 40 °C. Furthermore, the other parameters such as total solids (0.53%), ash content (9.2%), volatile fatty acids (100 mg/L), organic

Fig. 2 3-D plots of the combined effects of two variables on methane production

Fig. 3 GC–MS chromatogram of methane

carbon (46%), total carbohydrates (179 mg/g) and protein content (88 mg/g) showed the significant value in all parameters.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Abbasi T, Abbasi SA (2010) Biomass energy and the environmental impacts associated with its utilization. *Renew Sustain Energy Rev* 14:919–937
- Adams MR, Dougan J (1981) Biological management of coffee processing wastes. *Trop Sci* 23(3):177–195
- Amiri H, Karimi K (2015) Improvement of acetone butanol and ethanol production from woody biomass by using organosolv pretreatment. *Bioprocess Biosyst Eng* 38:1959–1972
- APHA (1995) Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, Washington
- Bagi Z, Norbat AC, Balint B, Horvath L, Dobo K, Katalin R, Rakhely G, Kovacs K (2007) Biotechnological intoxicification of biogas production. *Appl Microbiol Biotechnol* 76:473–482
- Bansal N, Tewari R, Gupta JK, Soni SK, Soni R (2011) A novel strain of *Aspergillus niger* producing a cocktail of industrial depolymerising enzymes for the production of second generation biofuels. *Bio Res* 6:552–569
- Boopathy R, Mariappan M, Sunderasan BB (1986) The carbon to nitrogen ratio and methane production of coffee pulp. *J Coffee Res* 16:47–50
- Borja R, Rincon B, Alba J, Martin A (2002) A study of anaerobic digestibility of two phase olive mill solid waste (OMSW) at mesophilic temperature. *Process Biochem* 38:733–742
- Chandra R, Takeuchi H, Hasegawa T, Kumar R (2012) Improving biodegradability and biogas production of wheat straw substrates using sodium hydroxide and hydrothermal pretreatments. *Energy* 43:273–282
- Corro G, Paniagua L, Pal U, Banuelos F, Rosas M (2013) Generation of biogas from coffee-pulp and cow dung co-digestion: infrared

- studies of post combustion emissions. *Energy Convers Manage* 74:471–481
- Deublein D, Steinhauser A (2008) Biogas from waste and renewable sources: an introduction. Wiley-VCH, Weinheim
- Diaz-Malvaez BE, Garcia-Almendarez A, Hernandez-Arana A, Amaro-Reyes C, Regalado-Gonzalez C (2013) Isolation and properties of β -xylosidase from *Aspergillus niger* GS1 using corn pericarp upon solid state fermentation. *Process Biochem* 48:1018–1024
- Fan L, Soccol AT, Pandey A, Soccol CR (2003) Cultivation of pleurotus mushroom on Brazilian coffee husk and its effect on caffeine and tannic acid. *Micol Aplicada Int* 15:15–21
- Fantozzi F, Buratti C (2009) Biogas production from different substrates in an experimental continuously stirred tank reactor anaerobic digester. *Bioresour Technol* 100:5783–5789
- Fantozzi F, Buratti C (2011) Anaerobic digestion of mechanically treated OFMSW: experimental data on biogas/methane production and residues characterization. *Bioresour Technol* 102:8885–8892
- Franca AS, Oliveira IS, Ferreira ME (2009) Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. *Desalination* 249:267–272
- Francese AP, Aboagye-mathiesen G, Olesen T, Cordoba PR, Sinerz F (2000) Feeding approaches for biogas production from animal wastes and industrial effluents. *World J Microbiol Biotechnol* 10:147–150
- Fujita M, Scharo JM, Moo-Yeng M (1980) Effect of corn straw addition on the anaerobic digestion of swine manure. *Agri Wastes* 2:177–184
- Govarthanan M, Park SH, Kim JW, Lee KJ, Cho M, Kamala-Kannan S, Oh BT (2014) Statistical optimization of alkaline protease production from brackish environment *Bacillus* sp. SKK11 by SSF using horse gram husk. *Prep Biochem Biotechnol* 44:119–131
- Govarthanan M, Selvankumar T, Selvam K, Sudhakar C, Vincent Aroulmoji, Kamala-Kannan S (2015) Response surface methodology based optimization of keratinase production from alkali-treated feather waste and horn waste using *Bacillus* sp. MGMASC-BT. *J Ind Eng Chem* 27:25–30
- Grisel C, Umapada P, Surinam C (2014) Enhanced biogas production from coffee pulp through deligninocellulosic photocatalytic pretreatment. *Energy Sci Eng* 2:177–187
- Leaneza Coalla H, Blanco JM, Fernandez MA, Moran M, Lopez Bobo MR (2009) Biogas generation apple pulp. *Bioresour Technol* 100:3843–3847
- Madahava Naidu M, Vijayanada P, Usha Devi A, Vijayalakshmi MR, Ramalakshmi K (2004) Utilization of coffee by-products in food industry, preparation of jam using coffee pulp as raw material. In: *Plantation crops research and development in the new millennium*, Placrosym XIV, pp 201–203
- Niemann HB, Atreya SK, Bauer SJ, Carignan GR, Demick JE, Frost RL, Gautier D, Haberman JA (2005) The abundance of constituents of Titan's atmosphere from the GC-MS instrument on the Huggens probe. *Nature* 438:779–784
- Osman GA, Eitnay AH, Mohamed EF (2006) Biogas production from agricultural wastes. *J Food Technol* 4:37–39
- Pandey A, Soccol CR, Nigam P, Brand D, Mohan R, Roussos S (2000) Biotechnological potential of coffee pulp and coffee husk for bioprocesses. *J Biochem Eng* 6:153–158
- Reddy LV, Wee YJ, Yun JS, Ryu HW (2008) Optimization of alkaline protease production by batch culture of *Bacillus* sp. RKY3 through Plackett–Burman and response surface methodological approaches. *Bioresour Technol* 99:2242–2249
- Selvam K, Govarthanan M, Kamala-Kannan S, Govindharaju M, Senthilkumar B, Selvankumar T, Sengottaiyan A (2014) Process optimization of cellulase production from alkali-treated coffee pulp and pineapple waste using *Acinetobacter* sp. TSK272 MASC. *RSC Adv* 4:13045–13051
- Selvam K, Selvankumar T, Rajiniganth R, Srinivasan P, Sudhakar C, Senthilkumar B, Govarthanan M (2016a) Enhanced production of amylase from *Bacillus* sp. using groundnut shell and cassava waste as a substrate under process optimization: waste to wealth approach. *Biocatal Agric Biotechnol* 7:250–256
- Selvam K, Govarthanan M, Senthilkumar B, Senbagam D, Selvankumar T, Kamala-Kannan S, Sudhakar C (2016b) Optimization of protease production from surface-modified coffee pulp waste and corncobs using *Bacillus* sp. by SSF. *3 Biotech* 6:167
- Shaochuan S, Nges IA, Yun J, Liu J (2013) Pre-treatments for enhanced bio-chemical methane potential of bamboo waste. *Chem Eng J* 240:253–259
- Simpson-Holley M, Higson A, Evans G (2007) Bring on the biorefinery. *J Chem Eng* 163:46–59
- Solangel IM, Ercilia MSM, Silvia M, Jose AT (2011) Production composition and application of coffee and its industrial residues. *Food Bioprocess Technol* 4:661–672
- Trevelyan WE, Harrison JS (1952) Studies on yeast metabolism yeast carbohydrate fractions, separation from nucleic acid analysis and behaviour during anaerobic fermentation. *Biochem J* 50:298
- Walkley A, Black IA (1934) An examination of Degtjareff method for determining organic carbon in soils: effect of variations in digestion conditions and of inorganic soil constituents. *Soil Sci* 63:251–263
- Wang SH, Huang DJ (2005) Assessment of greenhouse gas emissions from poultry enteric fermentation. *Asian-Aust J Anim Sci* 18:873–878
- Wang J, Duan C, Ji Y, Sun Y (2010) Methane emissions during storage of different treatments from cattle manure in Tianjin. *J Environ sci* 22:1564–1569
- Westerholm M, Hansson M, Schnurer A (2012) Improved biogas production from whole stillage by co-digestion with cattle manure. *Bioresour Technol* 114:314–319