INT J CURR SCI 2011, 1: 98- 106

RESEARCH ARTICLE

Hydrogen production from dairy manure by dark fermentation using carbon tetrachloride

Rohit J*, Anupama S and S. Shrihari

Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore-575 025, India

**Corresponding author: biotech.rohit@gmail.com; Phone:+91-9263631797*

Abstract

Hydrogen is a clean energy carrier which has a great potential to be an alternative fuel. Abundant biomass from various industries could be a source for bio-hydrogen production where combination of waste treatment and energy production would be an advantage. Nowadays, the large amounts of livestock manure, which come from cattle feedlots, poultry, and swine buildings, are causing a major environmental issue because it has become a primary source of odours, gases, dust, and groundwater contamination. It is well known that anaerobic digestion had successfully been used for the disposal of manures to produce methane in the last two decades. Recently, an alternative strategy has been developed to convert livestock manures (e.g. dairy manures) to bio-hydrogen as a high value-added clean energy source instead of methane. The focus of this study was investigating the performance and optimal operating conditions of bio-hydrogen production from dairy manure feedstock by dairy manure compost and evaluating its feasibility for bio-hydrogen production. The results indicated that it was feasible to produce hydrogen from dairy manure by methanogenesis inhibited dark fermentation.

Keywords: dairy manure, hydrogen, fermentation, carbon tetrachloride

---

Received: 20th August; Revised: 2nd September; Accepted: 28th September;

Introduction

Global energy demand is projected to grow by 50% from present, by the year 2030 (IEA, 2007). Fossil fuels are used to meet our daily energy demands. This contributes to resource depletion, and environmental, and public health problems (climate change, acid rain, ground level ozone, inhalable particles). Atmospheric carbon di oxide concentrations (379 ppm in 2005) have increased by almost 100 ppm compared to its pre-industrial level (Rogner et al., 2007). Global warming is evident based on the observations about the increased global average air and ocean temperatures, rising global average sea level, and widespread melting of snow and ice (IPCC, 2007). Strikingly, eleven of the last twelve years (1995-2006) rank among the twelve warmest years recorded since 1850. According to Intergovernmental Panel on Climate Change (IPCC) there is a very high confidence that human activities have contributed to the climate warming. Global average surface temperatures have raised 0.74°C over the past 100 years, and depending on the emission scenarios, expected to increase from 1.8 to 4°C, by the end of the 21st century (IPCC, 2007). The temperature increase is widespread over the globe, and is greater at higher northern latitudes. The global warming is projected to result in serious impacts on ecosystems, food production, water resources, human health and the economics (IPCC, 2007). Contrasting or additional theories to anthropogenic greenhouse gas emissions on global warming include increased solar activity (Rind, 2002; Solanki et al., 2004) and cosmic rays (Svensmark, 1998; Svensmark and Friis-Christensen, 2007).

Hydrogen is a secondary energy produced from primary energy sources, and therefore, considered as energy carrier, like electricity or gasoline, to transport energy to users (Koroneos et al., 2004; Busby, 2005). Unlike electricity, hydrogen can be stored. Hydrogen is the most abundant element on the Earth. Hydrogen has the highest energy content per mass unit of all compounds, about three times higher than that of liquid hydrocarbons (Schlapbach and Züttel, 2001). The sources of hydrogen are versatile (biomass, organic wastes, water, fossil fuels) and globally distributed. In fuel cells (fcs), hydrogen can be converted to electricity efficiently and without air emissions (Schlapbach and Züttel, 2001; Dincer, 2002). The potential uses of hydrogen are many: as a fuel in traffic (vehicles, busses, airplanes etc.), as in stationary applications for generation of electric power and heat and in portable applications in electronic equipment.

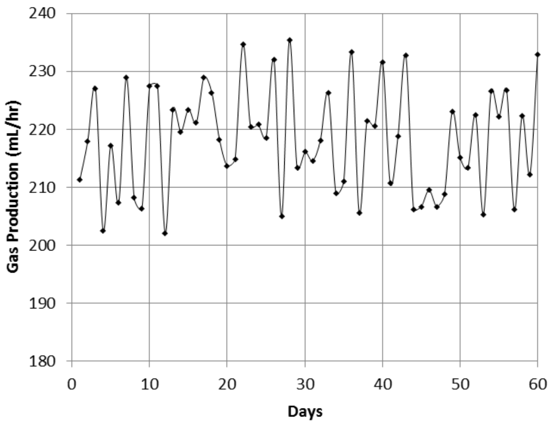
Hydrogen can be produced from a variety of feedstock including fossil fuels, biomass and water. Even though hydrogen conversion to energy in fcs is emission less, the sustainability of hydrogen energy depends on the production method. Presently, hydrogen is produced mainly from fossil fuels, which is not sustainable (Turner, 2004). Microbial fermentations offer an attractive alternative to produce sustainable energy. Fermentations can use various kinds of biomass or organic waste to produce energy carriers such as ethanol, butanol, methane or hydrogen (Claassen et al., 1999; Antoni et al., 2007). However, little information is available on the bio-hydrogen production using dairy manures as feedstock via the mixed anaerobic microbe. As far as we know, the hydrogen production is habitually accompanied with production of volatile fatty acids (vfas), such as acetate, butyrate, and propionate, which are also an optimal feedstock for production of methane by anaerobic digestion. Provided that the bio-hydrogen production from dairy manure is further combined with the anaerobic digestion of the effluent from the producing hydrogen reactor that would be a one-stone two-bird paradigm, it not only produces a clean and readily usable biologic energy but also cleans up simultaneously the environment in a sustainable fashion. For the above reasons, the focus of this study was investigating the performance and optimal operating conditions of bio-hydrogen production from dairy manure feedstock by dairy manure compost and evaluating its feasibility for bio-hydrogen production.

Results and discussion

Stabilization of the seed reactor: *Gas production*

The amount of gas collected from the seed reactor was measured using water displacement method. Gas production was measured 4 times every day, 0, 3, 6 and 24 hrs, respectively. The various time intervals were chosen to investigate the variation in gas production with room temperature fluctuations and kinetics after feeding and the total gas production for every cycle of feeding is calculated. The gas production data collected over a period of 60 days (29/09/2010 – 27/11/2010) was found to be consistent every day. Fig.1 shows the variation of daily average gas production over the course of experiment (29/09/2010 – 27/11/2010). The mean daily gas production is about 5.236 Litres.

Fig. 1. Mean daily gas production rate



COD Mass balance

A theoretical amount of gas produced can be arrived by the approximate analysis of COD and TVS of the reactor. A volume of 0.382 litre of methane at 25 C and I atm is equivalent to I g COD assuming digester gas contains 60% methane.

Table 1 gives the Gas / COD ratio (ratio of gas volume measured to the gas equivalent to the COD reduction) is found as 0.90, which shows the stabilization of the reactor.

Volatile Fatty Acid (VFA) concentration

Maintenance of VFA under limit is also an important factor of steady state of the reactor. VFA concentration was measured by taking samples from reactor every Monday and Friday.

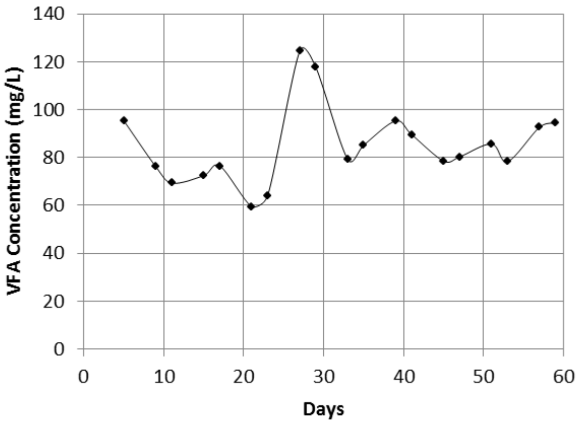
It was evident from figure 2 that the VFA concentration was maintained well below the limit of digester instability, 250 mg/L (Speece, 1983). In this study, the pH was 6.9±0.5 throughout. Moreover, effluent alkalinity was about 50% higher than influent alkalinity, a further indication that the digestion was stable and that there were no incipient pH problems.

Table 1. Substrate degradation and COD mass balance

	TVS (g/L)	TVS reduction %	COD (g/L)	COD reduction %	Gas equivalent to COD reduction (Litre)	Actual gas production (Litre)	Gas / COD ratio
Influent	34.4 (1.7)[28]*		38.9 (2.2) [19]				
Effluent	22.9 (0.4) [28]	33.43	23.6 (1.3) [19]	39.33	5.8446	5.2360 (0.22) [60]	0.8996

*Numbers in parentheses are standard deviations. In brackets are the numbers of observations

Fig. 2. VFA Concentration profile in the reactor



Hence, the reactor was stabilized under a steady state with

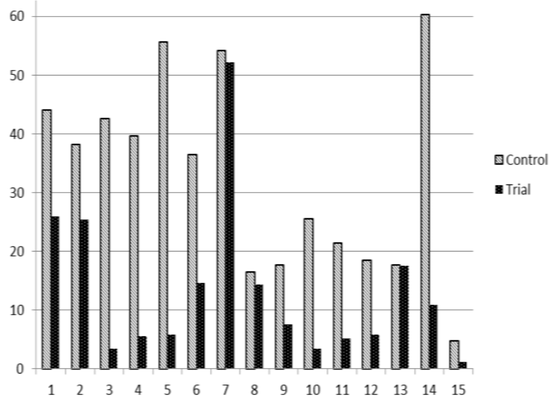
- Mean gas production, 5.2360 L/day,
- Mean COD removal efficiency, 39.33%,
- Gas/COD ratio, 0.90,
- VFA concentration, 85.02 mg/L
- pH, 6.9±0.5

Having established that the digestion process is reproducible and stable, further batch experiments to investigate bio-hydrogen production and the methanogenesis inhibition were performed.

Batch experiments: Gas concentration

The gaseous content of each trial in batch experiment is analysed using gas chromatography and the concentration of hydrogen and methane was observed to study the methanogenesis inhibition. The following figure 3 shows the methanogenesis inhibition of various trials by comparison with a control of that trial without adding the inhibitor (CCl_4). From the Fig, it was observed that the methanogenesis was inhibited in all the trials except for trial no 7 (pH 7, Substrate concentration [S] 70 gVs/L, Inhibitor concentration [I] 0.2 mM), which was due to the low concentration of inhibitor added. Hence, the inhibition is due to the addition of CCl_4 only since methane is found in high concentration in the controls.

Figure 3. Study of methanogenesis inhibition of each trial of the batch experiments



Kinetics of hydrogen production

The cumulative hydrogen production curves were generated for each trial by fitting the trial data to the Gompertz model using Systat^{TM} 8.0 and the parameters of interest (Rm, Hmax, and l) were calculated. The cumulative hydrogen production data for trial one (pH 7, [S] 60 gVS/L, [I] 0.6 mM) is shown in Table 2.

Table 2. Kinetics of hydrogen production for trial 1

Time (t) hrs.	Cumulative hydrogen production (H) (mL/g VS)
0	0
6	0
12	1.525
18	4.578
24	7.475
30	9.605
36	11.524
42	12.975
48	13.045
54	13.045

Fitting data to modified gompertz equation:

$$H = Hmax \times exp\left\{-exp\left[\frac{Rm \times e}{Hmax}(\lambda - t) + 1\right]\right\}$$

Where,

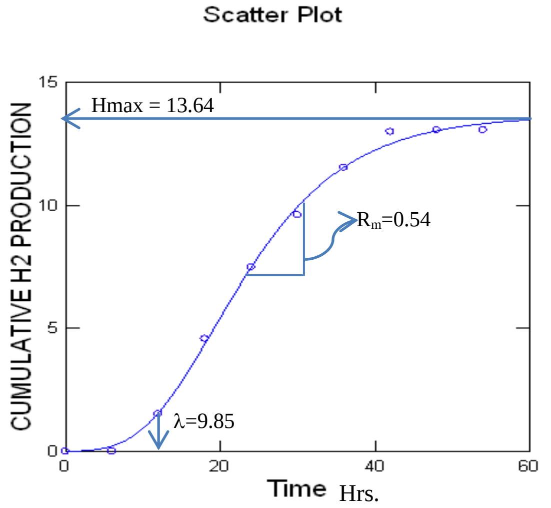
H – Cumulative Hydrogen Production (mL/gVS)

$Hmax$ – Hydrogen Production Potential (mL/gVS)

Rm – Maximum Hydrogen Production Rate (mL/hr.gVS)

λ – Lag Time

Fig. 4. Plot of the modified gompertz model for trial 1



It can be seen from the figure 4 that all data fit the model well (R^2 = 0.997) and the variation between the replicates was small. Similarly the data for the cumulative hydrogen production data for the other trials were also fitted to the model and the results were shown in the table 3. In general, all the experiments showed good reproducibility.

Table 3. Kinetic co-efficients of modified Gompertz model (T-Trial; A-Substrate concentration (gVS/L); B-Inhibitor concentration (mM))

T	pH	A	B	Kinetic Coefficients			R^2
				H_{max}	λ	R_m	
1	6	7	0.6	13.6	9.8	0.5	0.998
2	8	8	0.4	5.4	18.9	0.2	0.993
3	6	7	1	13.9	9.8	0.5	0.999
4	8	6	0.8	12.2	9.6	0.4	0.998
5	2	7	0.6	3.5	24.5	0.3	0.997
6	4	8	0.4	3.8	23.1	0.3	0.997
7	6	7	0.2	3.6	18.3	0.2	0.995
8	8	6	0.4	4.8	16.3	0.2	0.998
9	4	6	0.8	12.0	11.7	0.4	0.996
10	8	8	0.8	7.2	7.6	0.2	0.996
11	4	8	0.8	10.8	11.3	0.4	0.997
12	6	9	0.6	13.2	9.6	0.5	0.994
13	4	6	0.4	8.8	8.9	0.3	0.997
14	10	7	0.6	2.7	12.6	0.09	0.997
15	6	5	0.6	17.3	10.7	0.7	0.997

Optimizing key parameters for hydrogen production

The optimum levels of the three key factors (Substrate concentration, initial pH and inhibitor concentration) were further explored by CCD. Yields of Hydrogen were obtained with the design matrix of the three- variables, representing different fermentative conditions (15 runs) (Table 4).

By applying multiple regression analysis, the following second-order polynomial equation was established to explain the hydrogen yield,

$$\text{Cumulative hydrogen production} = 12.41 - 0.3 (X_1) - 1.2 (X_2) + 2.34 (X_3) + 0.17 (X_1X_2) - 0.26 (X_1X_3) + 0.059(X_2X_3) - 2.79 (X_1)^2 - 0.11(X_2)^2 - 1.59(X_3)^2$$

The predicted values of hydrogen yield were obtained using the above equation. Analysis of variance (ANOVA) was conducted to test the significance of the fit to the second-order polynomial equation for the experimental data (Table 5).

Table 4. Actual cumulative hydrogen production (A – Substrate concentration; Ac – Actual; B – Inhibitor concentration; C – Coded; T- Trail)

T	A(X_1) (gVS/L)		pH(X_2)		B(X_3) (mM)		Actual cumulative hydrogen production (mL/gVS)
	Ac	C	Ac	C	Ac	C	
1	60	0	7	0	2	0	13.045
2	80	1	8	1	2.5	-1	4.758
3	60	0	7	0	3	2	13.257
4	80	1	6	-1	2.5	1	11.68
5	20	-2	7	0	2	0	3.41
6	40	-1	8	1	1.5	-1	3.78
7	60	0	7	0	1	-2	3.39
8	80	1	6	-1	1.5	-1	4.651
9	40	-1	6	-1	2.5	1	11.23
10	80	1	8	1	2.5	1	6.719
11	40	-1	8	1	2.5	1	10.321
12	60	0	9	2	2	0	12.492
13	40	-1	6	-1	1.5	-1	8.25
14	100	2	7	0	2	0	2.493
15	60	0	5	-2	2	0	16.706

Table 5. Anova of the co-efficients of the model

Term	Coefficient	F value	Prob P>F
Model		13.75	<0.0002
Intercept	12.41	-	-
X_1	-0.3	0.52	0.4893
X_2	-1.2	8.19	0.0169
X_3	2.34	31.22	0.0002
X_1X_2	0.17	0.081	0.7819
X_1X_3	-0.26	0.2	0.6661
X_2X_3	-0.059	0.010	0.9222
X_1^2	-2.79	70.11	<0.0001
X_2^2	-0.11	0.11	0.7423
X_3^2	-1.59	22.57	0.0008

The computed F-value of 18.27 implied that the model was significant. There is only a 0.01% chance that a 'Model F-value' could occur due to noise. The P-values were used to verify the significance of each variable, which also indicated the intensity of the interaction between each independent variable (Liu et al., 2003). Given a P-value of 0.0206 (<0.0500), the model terms were considered significant, whereas P-values > 0.1000 were not significant. The coded values X_2, X_3, X_1^2, X_3^2 were considered significant model terms. The R^2 value of 0.9252 indicated a close relationship between the experimental and predicted values, which suggests that this is a very reliable mathematical model for hydrogen production.

Interaction between the parameters

The response surface and contour plots depict the interactions between two variables for hydrogen yield, while maintaining the other variables at base line (zero level) (Figs. 5-7). The shapes of the contour plots, elliptical or circular, indicate whether the mutual interactions between the variables are significant or not.

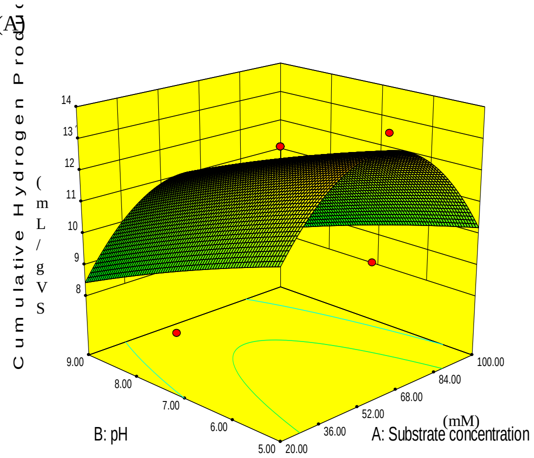
Effect of substrate concentration and pH

The elliptical plot indicates the significance between the interactions between the parameters. Understanding the dependence of substrate concentration on fermentative hydrogen production is usually a critical step toward optimal control and operation of a bioreactor. Herein, the effect of the substrate concentration on hydrogen yield was presented in Fig. 5 for dairy manure feedstock ranging from 20 to 100 g-TVS/L at the variation of initial pH from 5 to 9. As can be seen from figure 5, hydrogen yield increased remarkably with the increase of substrate concentration in the range of 20-60 g-TVS/L at any pH value. Thereafter, the cumulative hydrogen yield decreased gradually as the concentration of substrate further increased. For instance, while the substrate concentration increased from 20 to 50 and 70 g-TVS/L, the corresponding hydrogen yield increased from minimum to the maximum value of 15.934 mL/g-TVS. The maximum hydrogen yield of 15.934 mL/g-TVS occurred at the substrate concentration of 60 g-TVS/L. Then, the cumulative hydrogen yield rapidly declined from 15.934 to minimum with the increase of substrate concentration from 60 to 100 g-TVS/L.

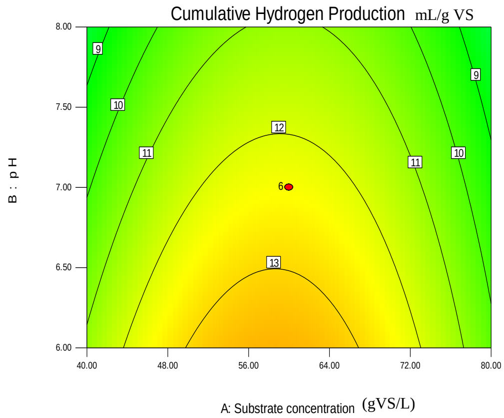
The results could be expected because excessive substrate concentration would result in the acidification of system, accumulation of VFAs, and a fall of pH value in the batch reactor. In this case, the activity of hydrogen producing microbes would be inhibited. In addition, the partial pressure of hydrogen in the batch reactor rose with the increases in substrate concentration. While the partial pressure of hydrogen increased to a certain level in the headspace of reactor, the microorganisms would switch to alcohol production, thus inhibiting hydrogen production (Lay et al., 1999).

Fig. 5. Response surface (A) and Contour plots (B) between pH and substrate concentration

(A)



(B)

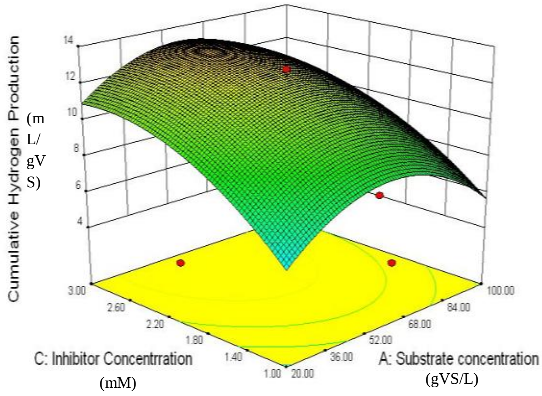


Effect of substrate concentration and inhibitor concentration

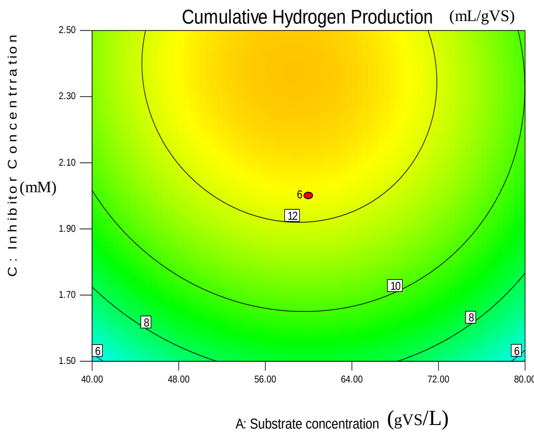
The elliptical plot indicates the significance between the interactions between the parameters. The cumulative hydrogen production increased with the increase in inhibitor concentration as seen in the figure 6. But the effect of substrate concentration remains the same as in the presence of varying the pH. The results could be expected because the increase in the inhibitor concentration will increase the methanogenesis inhibition which will subsequently favour the growth of hydrogen producing microorganisms, which results in higher yield.

Fig. 6. Response surface (A) and Contour plots (B) between inhibitor concentration and substrate concentration

(A)



(B)

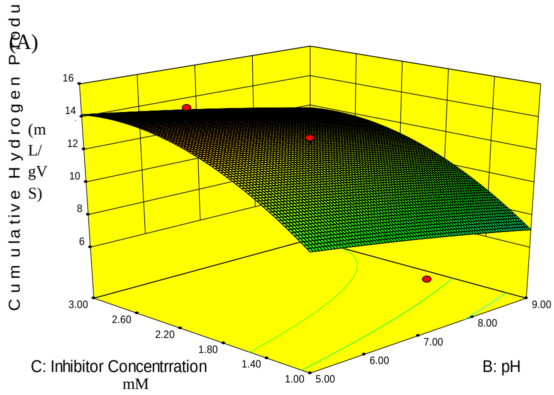


Effect of pH and inhibitor concentration

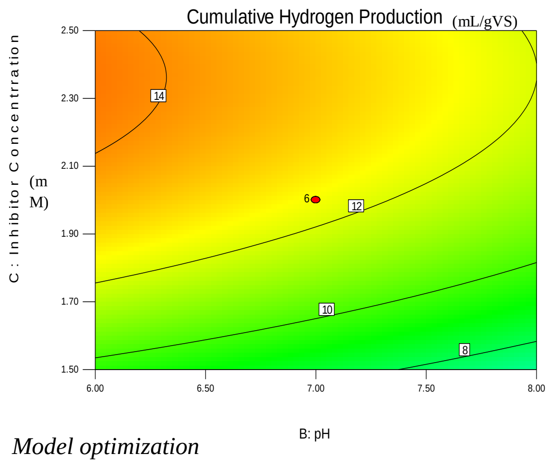
The circular plot indicates the insignificance between the interactions between the parameters. However it can be noted that the maximum hydrogen yield occurred at low pH and high inhibitor concentration. This result was consistent with most previous works, in which the optimum pH value for hydrogen-producing system occurred in the range of pH from 5.0 to 7.0 (Fan et al., 2006b; Li and Fang, 2007b). However, it was different from the results reported by Cai and co-workers, in which the maximal hydrogen yield of 16.6 mL/g-TS occurred at pH of 11.0 using the alkaline pre-treated sludge by anaerobic fermentation (Cai et al., 2004). The results showed that the proper pH control in the reactor could stimulate the microorganisms to produce hydrogen and would achieve the system having a maximum hydrogen yield, but the activity of hydrogenase would be inhibited by low or high pH values in overall hydrogen fermentation (Lay et al., 1999; Fan et al., 2004).

Fig. 7. Response surface (A) and Contour plots (B) between inhibitor concentration and pH

(A)



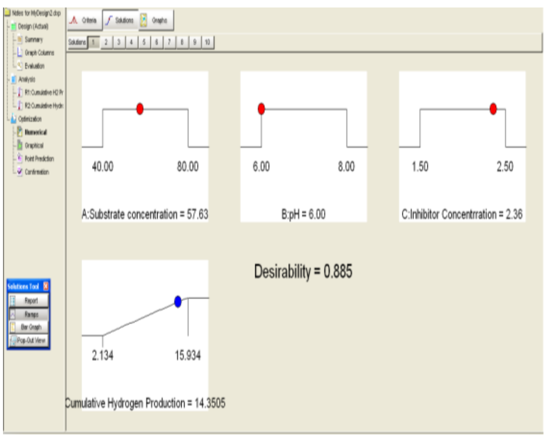
(B)



Model optimization

According to the statistical design, the optimized conditions for maximum yield of cumulative hydrogen production of 23.1995 mL/gVS were substrate concentration of 57.63 g VS/L, initial pH of 6, inhibitor concentration of 2.36 mM. This optimization gave maximum desirability of 0.885 for the model.

Fig. 8. Optimized parameters for the model



Acknowledgement

Authors would express their sincere gratitude to Dr. A. U. Ravishankar, Head, Department of Civil Engineering for having allowed to do this project.

References

Anonymous (2006). Clean Urban Transport for Europe (CUTE) a detailed summary of achievements. A hydrogen fuel cell bus project in Europe 2001-2006. Internet document, accessed 1.3.2008.

Antoni D, Zverlov VV, Schwarz WH (2007). Biofuels from microbes. Applied Microbiology and Biotechnology 77: 23-35.

Busby RL (2005). Hydrogen and fuel cells: A comprehensive guide. 1st edition. Penn-Well Corporation, Tulsa, U.S. pp. 445.

Cai M, Liu J, Wei Y (2004). Enhanced bio-hydrogen production from sewage sludge with alkaline pretreatment. Environmental Science and Technology 38: 3195-3202.

Claassen PAM, Lier JB, Lopez Contreras AM, Niel EWJ, Sijtsma L, Stams, AJM, de Vries SS, Weusthuis RA (1999). Utilisation of biomass for the supply of energy carriers. Applied Microbiology and Biotechnology 42: 741-755.

Dincer I (2002). Technical, environmental and exergetic aspects of hydrogen energy systems. International Journal of Hydrogen Energy 27: 265-285.

EurObserver (2007b). Biogas barometer systemes solaires - Le Journal des Energies Renouvelables 179: 51-60.

European Commission (EC) (1997). Communication from the commission. Energy for the future: Renewable sources of energy. White paper for a community strategy and action plan. Internet document, accessed 1.3.2008, available at: http://ec.europa.eu/energy/library/599fi_en.pdf

European Commission (EC) (2003a.). Directive 2003/30/EC of the European parliament and of the council of May (2003) on the promotion of the use of biofuels or other renewable fuels for transport. Internet document, accessed 1.3.2008, available at: http://ec.europa.eu/energy/res/legislation/doc/b iofuels/en_final.pdf.

EC 2003, European Commission (2003b). Hydrogen and fuel cells: A vision for our future. European commission, Directorate-General for Research, Directorate-General for Energy and Transport, EUR 20719 EN. Internet document, accessed 19.12.2007, available at: https://www.hfpeurope.org/uploads/59/hydrogen-vision- report_HLG_2003_en.pdf.

Fan Y, Li C, Lay J-J, Hou H, Zhang G (2004). Optimization of initial substrate and pH levels for germination of sporing hydrogen-producing anaerobes in cow dung compost. Bioresource Technology 91: 189-193.

Fan Y-T, Zhang G-S, Guo X-Y, Xing Y, Fan M-H (2006b). Bio-hydrogen production from beer lees biomass by cow dung compost. Biomass and Bioenergy 30: 493-496.

Fang HHP, Li C, Zhang T (2006). Acidophilic bio-hydrogen production from rice slurry. International Journal of Hydrogen Energy 31: 683-692.

Fang HHP, Liu H (2006). Effect of pH on hydrogen production from glucose by a mixed culture. Bioresource Technology 82: 87-93.

Hu R, Li J, Wang Z (2005). China's renewable energy law and biomass energy. Industrial Biotechnology 1: 222-227.

IEA (2007). International Energy Agency, World energy outlook 2007. Executive summary. China and India insights. Internet document, accessed 1.3.2008, available at: http://www.iea.org/Textbase/npsum/WEO2007SUM.pdf.

IPCC (2007). Intergovernmental panel on climate change fourth assessment report. Climate change (2007): Synthesis report. Summary for policymakers. Internet document, accessed 1.3.2008, available at: http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr_spm.pdf.

Koroneos C, Dompros A, Roumbas G, Moussiopoulos N (2004). Life cycle assessment of hydrogen fuel production processes. International Journal of Hydrogen Energy 29: 1443-1450.

Lay J-J, Lee Y-J, Noike T (1999). Feasibility of biological hydrogen production from organic fraction of municipal solid waste. Water Research 33: 2579-2586.

Li C, Fang HHP (2007b). Inhibition of heavy metals on fermentative hydrogen production by granular sludge. Chemosphere 67: 668-673.

Liu Y, Xu H-L, Yang S-F, Tay J-H (2003). Mechanisms and models for anaerobic granulation in up flow anaerobic sludge blanket reactors. Water Research 37: 661-673.

Plombin C (2003). Biogas as vehicle fuel. A European overview. Trendsetter Report No 2003:3. Internet document, accessed 1.3.2008, available at: http://213.131.156.10/xpo/bilagor/20040115134708.pdf.

Rind D (2002). The Sun’s role in climate variations. Science 296: 673-677.

Rogner H-H, Zhou D, Bradley R, Crabbé P, Edenhofer O, Hare B, Kuijpers L, Yamaguchi M (2007). Introduction. In Climate Change (2007): Mitigation. Contribution of working group III to the Fourth assessment report of the intergovernmental panel on climate change. Edited by: Metz B, Davidson OR, Bosch PR, DaveR, Meyer LA. Internet document, accessed 1.3.2008, available at: http://www.ipcc.ch/pdf/assessment-report/ar4/wg3/ar4-wg3-chapter1.pdf.

Schlapbach L, Züttel A (2001). Hydrogen – storage materials for mobile applications. Nature 414: 353-358.

Solanki SK, Usoskin IG, Kromer B, Schüssler M, Beer J (2004). Unusual activity of the sun during recent decades compared to the previous 11,000 years. Nature 1084-1087.

Speece RE (1983). Anaerobic biotechnology for industrial waste water treatment. Environmental Science and Technology 17: 416A-427A.

Svensmark H (1998). Influence of cosmic rays on Earth's climate. Physical Review Letters 81: 5027-5030.

Svensmark H, Friis-Christensen E (2007). Reply to

Lockwood and Fröhlich - The persistent role of the sun in climate forcing. Danish National Space Center Scientific Report 3/2007.

Turner JA (2004). Sustainable hydrogen production. Science 305: 972-974.

United Nations (UN) (1997). Kyoto protocol to the United Nations framework convention on climate change. Internetdocument, accessed 4.3.2008, available at: http://unfccc.int/resource/docs/convkp/kpeng.pdf.

Venkata Mohan S, Lalit Babu V, Sarma PN (2008). Effect of various pretreatment methods on anaerobic mixed microflora to enhance bio-hydrogen production utilizing dairy wastewater as substrate. Bioresource Technology 99: 59-67.

Zhang M-L, Fan Y-T, Xing Y, Pan C-M, Zhang G-S, Lay J-J (2007a). Enhanced bio-hydrogen production from cornstalk wastes with acidification pretreatment by mixed anaerobic cultures. Biomass and Bioenergy 31: 250-254.