International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249 – 8958, Volume-3, Issue-5, June 2014

Kinetic Assessment of Biogas Production from Lignocellulosic Biomasses

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Abstract-In this paper the kinetics of biogas production was studied by performing a series of laboratory experiments using different lignocellulosic biomass mixed with fresh cattle dung at three different temperatures. Laboratory digesters each of 1000 ml capacity were used for the laboratory experiments in batch mode. Five different types of lignocellulosic biomasses such as bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk were considered for biogas production, each mixed with fresh cattle dung, in the ratio of 1:3. Water was mixed with the prepared feed material in 1:3 ratio for digestion in the aforementioned digesters. The experiments were carried out in the temperature range 45°C-55°C in a step of 5°C. The purpose of this research was to study the biogas production kinetic from lignocellulosic biomass in batch mode anaerobic digestion. Modified Gompertz equation was used to compare the data obtained from the experiments. It was found that the kinetic parameters such as biogas production rate (U ml/gm/day) and maximum biogas production potential (A ml/gm) improved with increase in temperature for all the biomasses, whereas the lag phase period (λ days) reduces with increase in temperature.

Keywords: anaerobic digestion, kinetics, biogas production, lignocellulosic biomasses, batch mode.

I. INTRODUCTION

Biogas can be produced by anaerobic digestion of lignocellulosic biomass which includes agricultural wastes, energy crops, wood residues and municipal paper. They represent relatively unused source for biogas production. Lignocellulose is plant biomass, mainly consists of three major constituents such as Cellulose, hemicellulose and lignin. The other components such as water and proteins do not participate in forming the structure of the material [1]. Many factors inhibit the digestibility of hemicellulose and cellulose present in lignocellulosic biomass. These factors include lignin content, crystallinity of cellulose and particle size [2]. Although biogas production from cattle dung is getting a very good response due to its economical and eco-friendly usage, it is not abundant in south Asian countries like India. Whereas various bio-wastes with high cellulose content like waste from saw mill, bamboo mill, crop residue like rice husk, rice straw and bio-waste like sugarcane bagasse are obtainable in plenty in this region. These wastes are either uneconomically used or disposed of as they are, thereby causing serious pollution problems. These bio-wastes also contain lignin rendering its anaerobic digestion slow with conventional digestion methods. As a result these bio-wastes cannot be directly used for biogas production. To break the lignin content various pretreatment methods can be applied which include mechanical/physical, chemical and biological pretreatment. The most significant physical pretreatment include the particle size reduction [3], which eventually leads to the increase in available surface area and the release of intracellular components [4,5]. Das Ghatak and Mahanta, 2013 [6] characterized cattle dung and found that it exhibit by a very low carbon to nitrogen ratio (C:N) which eventually leads to limited biogas yield. Das Ghatak and Mahanta, 2013 [6] also characterized lignocellulosic biomass such as bamboo dust (BD), sugarcane bagasse (SB), saw dust (SD) and rice straw (RS) and found that the C:N ratio of the biomasses varied widely from 32 to 82:1. On the other hand Hills and Roberts (1981) [7] reported that the performance of digesters containing dairy manure and field crop residues is the maximum when the C:N ratio of the feed mixtures was between 25 to 30:1. Addition of lignocellulosic biomass with high C:N ratio balances the C:N ratio of the livestock manure. Anaerobic digestion mainly take place at either mesophilic (25°C -40°C) or thermophilic temperatures (45°C -60°C) [8]. Several researchers have worked on effect of temperature on biogas production from cattle dung [9], laminaria digitata, commonly known as seaweed biomass [10], lignocellulosic substrate such as maize chaff [8], lignocellulosic biomass such as bamboo dust and saw dust [11] and reported that temperature plays a very important in biogas production. Garba, 1996 [12] worked on biogas production from lignocellulosic material and found that at thermophilic temperature biogas production was the highest. Van Liar, 1995 [13] have reported in his Ph.D thesis that usually 43-45°C is considered as the upper limit of mesophilic condition and lower limit of thermophilic condition. Various investigators have stated that the effect of temperature on anaerobic digestion is very vigorous beyond 45°C (13, 14, 15, 16, 17, 18). It is observed from literature review that most of the study on effect of temperature on anaerobic digestion at thermophilic condition was studied mainly on animal manure, wastewater, food waste etc. Very few literature is available on effect of temperature (mesophilic as well as thermophilic) on aforementioned lignocellulosic biomass. Furthermore, kinetic models are reported to be useful tool to optimize the co-digestion processes [19]. Several models have been developed during the last few years but appropriate mathematical models are needed in order to overcome the problem of instability of system and also to design and operate anaerobic systems. Various researchers [20, 21, 22, 23, 24, 25] have used modified Gompertz equation which was modified by Zwieetering et. al, 1990 [26] to make the kinetic model of biogas production assuming that biogas production rate in batch mode is proportional to the specific growth rate of methanogenic bacteria in the biodigester. Lo et al., 2010 [27] utilized this modified equation for modelling biogas production from organic fraction of municipal solid waste (OFMSW) at a temperature of 35°C, while Budiyono et al., 2010 [20]

Manuscript Received on June 2014.

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applied the equation in the study of biogas yield from cattle manure at room temperature and 38.5°C. Agulanna et. al, 2012 [28] applied this model to study anaerobic digestion of organic fraction of municipal waste at 37°C. Adiga et.al, 2012 [25] used the modified Gompertz equation to study the kinetics of anaerobic digestion of Water Hyacinth, Poultry Litter, Cow Manure and Primary Sludge at 35°C. Very few literatures are available which have used modified Gompertz equation to study the kinetics of anaerobic digestion of above-mentioned lignocellulosic materials. Application of the modified Gompertz equation in thermophilic range is also hardly observed. The aim of the current study is to assess the effect of temperature on biogas production rate from lignocellulosic biomass by anaerobic digestion process and study the kinetic parameters from mathematical model concerning biogas production rate in batch anaerobic digestion processes

II. MATERIALS AND METHODS

Substrates that were utilized in this research were bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk each mixed with fresh cattle dung. The biomasses were physically pretreated by ball milling prior to being used for biogas production. The chemical analysis of the biomasses were carried out to determine total solid and volatile matter using standard test methods ASTM E1756-08, and E872-82 (Reapproved 2006) respectively. Carbon and Nitrogen content of the biomasses were determined by a high resolution Scanning Electron Microscope (SEM) (Make: Carl Zeiss, Model: LEO 1430 VP) with an attachment of energy dispersive X-ray (EDX) system (Make: Oxford, UK).

Table 1.
Characteristics of Lignocellulosic Biomasses (Dry Weight Basis)

	Bamboo Dust	Sugarcane Bagasse	Saw Dust	Rice Straw	Rice Husk	Cattle Dung
Total Solid (%)	88.23	86.17	86.77	87.33	89.4	19.02
Volatile Solids (%)	84.24	84.175	82.79	65.15	74.04	66.2
Carbon (%)	49.79	50.39	63.17	32.19	32.79	35
Nitrogen (%)	0.99	0.83	0.77	0.98	0.4	1.6
C:N ratio of biomass before mixing with cattle dung	50.29	60.71	82.03	32.84	81.97	21.8
C:N ratio of biomass after mixing with cattle dung	26.73	27.6	30.19	24.06	26.49	

Table 1 presents the results of the characterization of the lignocellulosic biomasses on dry weight basis. Total solid (TS) of all the biomasses were in the range from 86 to 90% and that of cattle dung was 19.02%. The C:N ratio of the biomasses varied widely from 32 to 82:1, whereas that of cattle dung was 21.8:1. Hills and Roberts, 1981 [7] reported that the performance of digesters containing dairy manure and field crop residues is the maximum when the C:N ratio of the feed mixtures was between 25 to 30:1 and total solid of the slurry was 8%. . It is because microorganisms in the fermentation process utilize carbon 25-30 times faster than nitrogen [29, 30] Budiyono et al. (2010) [20] stated that TSs content of 7.4 and 9.2% in cattle dung exhibit the best performance for digestibility. Mahanta et al., 2004 [9] reported that for cattle dung at 35°C temperature maximum gas production was obtained with 8% total solid. That is why the biomasses were mixed with cattle dung and tap water in such a manner so that their C:N ratio come between 25-30:1 ratio and the total solid of the slurry become 8-9%. In the present case 25% biomass and 75% fresh cattle dung was used in the mixtures and water was added to the mixtures in 1:3 ratios respectively. The C:N ratio of the biomasses after mixing with cattle dung is shown in Table 1. From the characterization of the biomasses it was observed that all the biomasses have fairly good amount of volatile matter contents in the range of 82-85% indicating fairly good potentiality to generate biogas. However, it was observed that volatile matter in rice straw and rice husk sample was found to be low as compared to saw dust, bamboo dust and sugarcane bagasse indicating lower potentiality to produce biogas.

III. EXPERIMENTAL SET-UP AND PROCEDURE

The schematic diagram of the experimental set-up is shown in Fig. 1. It consists of a laboratory bio-digester made of borosilicate glass of capacity 1000 ml with air tight rubber cork fitted into its opening. Thermometer and copper tube were fitted through the rubber cork for measuring the slurry temperature and fitting the connecting tube. The other end of the connecting tube was passed through a 500 ml solution bottle containing brine solution. Thus, the biogas produced in the biodigester by the anaerobic digestion process was delivered through the connecting tube to the solution bottle containing brine. The pressure of the biogas produced caused displacement of the brine solution which is then collected in a 200 ml beaker placed on the other side of the solution bottle. The amount of solution collected in the beaker represented the amount of biogas produced in the biodigester. A sampling port was provided through the cork fitted with a valve to take out sample from time to time testing of sample for total solid, volatile solid and pH.

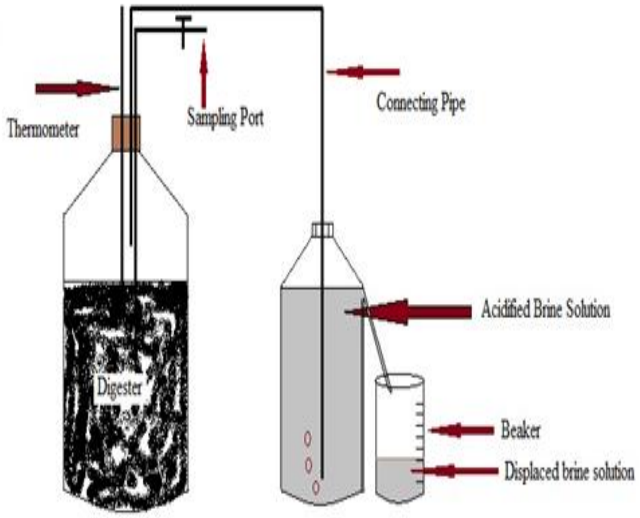

Fig. 1 Schematic Diagram of Experimental Set-Up [Das Ghatak and Mahanta, 2013]

A weighing balance was used to measure the required mass of cattle dung and biomasses. The mercury-in-glass thermometer (range -10°C to 110°C) fitted to the bio-digester through the cork was used to measure the daily temperature of the slurry and a digital pH meter was used to determine the pH of the fermentation slurry. The constant temperatures of the digesters were maintained by putting the digesters in the water bath at fixed temperature. The feed materials used in this research were bamboo dust, sugarcane bagasse, saw dust, rice husk and rice straw. Three sets of digesters each consisting of 5 units were prepared using bamboo dust, sugarcane bagasse, saw dust, rice husk and rice straw each mixed with cattle dung in 1:3 ratio. The mixture was further mixed with water in 1:3 ratio thus reducing the total solid to 8-9%. The feedstock was filled upto 90% of the 1000 ml borosilicate bottle and was kept in water bath at 45°C, 50°C and 55°C respectively to study the effect of temperature on biogas production rate. The temperature of the feedstock was measured twice a day with the help of the thermometer fitted through the cork. The biogas productions were monitored daily and measured every five days by means of water displacement method. The lab-scale experiment was carried out for 50 hydraulic retention days until biogas production reduced significantly. It was found that the biogas production was very slow at the beginning and at the end of observation. This is because the biogas production in batch condition directly corresponds to specific growth rate of methanogenic bacteria in bio-digesters [9].

IV. KINETIC MODEL OF BIOGAS PRODUCTION

The scope of this research was restricted to the study of the cumulative biogas production at three different digestate temperatures from lignocellulosic biomass using modified Gompertz equation [20, 21, 22, 23, 24, 25, 31]. The experimental data was analysed using non-linear regression for determining the kinetic constants. It is seen that the model data obtained from this equation were quite comparable with the experimental data.

While using the modified Gompertz equation it was assumed that biogas production rate in batch mode corresponds to the specific growth rate of methanogenic bacteria in the biodigesters [20, 21, 22, 23, 24, 25, 31]. The modified Gompertz equation is as follows-

$$P = A.\exp\{-\exp\left[\frac{Ue}{A}(\lambda - \mathrm{t}) + 1\right]\} \qquad (1)$$

where, P is the cumulative of the specific biogas production (ml/gm VS), A is the biogas production potential (ml/gm VS), U is the maximum biogas production rate (ml/gmVS.day), λ is the lag phase period or the minimum time required to produce biogas (day). The constants A, U, λ were determined using the non-linear regression approach with the aid of the solver function of the MS Excel Toolpak. Here the kinetic constant of biogas production rate is expressed by the maximum biogas production rate (ml/gmVS.day), U. The higher the maximum biogas production rate, higher is the biogas production rate.

V. RESULTS AND DISCUSSION

In this research characterization of the aforementioned lignocellulosic biomass were first carried out as shown in Table 1. Based on the chemical analysis of the biomasses fresh cattle dung was mixed with each biomass and water was added to the substrates in 1:3 ratio thus making the total solid of the feed stock 8-9%. The cumulative biogas production was observed for 50 days HRT. The investigation was performed at temperature range 45°C-55°C, at a step of 5°C. Further, modified Gompertz equation was applied to study the kinetics of biogas production from lignocellulosic biomass in the thermophilic range. This research was carried out to study the influence of temperature on the kinetics of biogas production from lignocellulosic biomasses respectively in 1000 ml volume digesters. The working volumes of the biodigesters were maintained at 900 ml volume and ran under controlled temperature. The various substrates considered are saw dust, rice straw, rice husk, sugarcane bagasse and bamboo dust mixed with fresh cattle dung in 1:3 ratio. Water was added to these mixtures in 1:3 ratio thus making the total solid around 9%. as shown in Fig. 2. This research was carried out to study the influence of above mentioned temperature range on biogas production kinetic. Fig. 2 shows the comparison of cumulative biogas production saw dust (SD), bamboo dust (BD), sugarcane bagasse (SB), rice straw (RS) and rice husk (RH) at different temperatures. It shows that the biogas production rate tend to follow the sigmoid function (s-curve) which generally occurred in batch growth curve. Biogas production at the start and the end period of digestion is very low as biogas production in batch mode is proportional to the specific growth rate of bacteria. The cumulative biogas production was studied for 50 days hydraulic retention time (HRT). Biogas production kinetic was studied by developing the modified Gompertz equation for biogas production in batch system. The kinetic constants biogas production potential, A (ml/gm VS), maximum biogas production rate (ml/gmVS.day), U and lag phase period, λ (day) were determined using non-linear regression. In this study, experimental data obtained from the research was solved using non-linear regression. Kinetic constants

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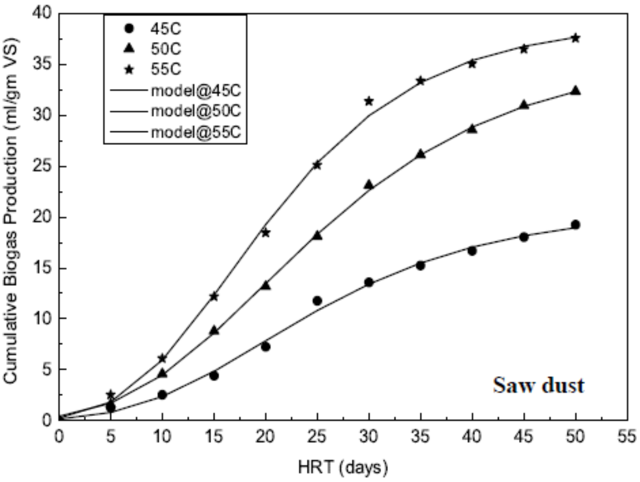
obtained are presented in Table 2. The data of cumulative biogas production obtained from the experiments were fitted to the modified Gompertz equation which describes cumulative biogas production in batch mode assuming that that biogas production rate in batch mode is a function of the specific growth rate of methanogenic bacteria in the biodigesters. After plotting the experimental data and the simulation of modified Gompertz equation (Eq. 1) the graphs as illustrated in Fig. 2 is obtained. The high values of regression co-efficient, R^2 demonstrates the appropriateness of the proposed model for accurate estimation of the anaerobic digestibility of the biomass.

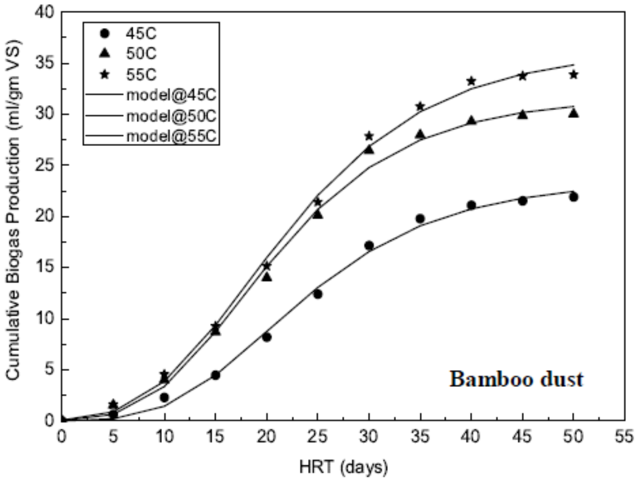
Table 2
Kinetic Constants of Biogas Production Rate, Cumulative Biogas Production and Regression Co-Efficient

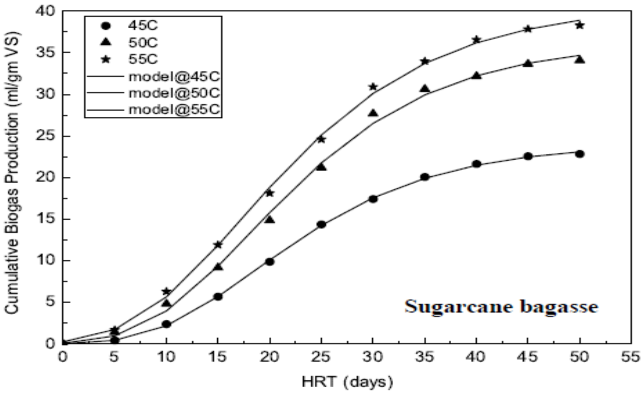
Substrates/Temperatures		**45°C**	**50°C**	**55°C**
SD	A, (ml/gm VS)	20.644	35.770	39.106
	U, (ml/gm VS/day)	0.613	0.994	1.406
	λ, days	7.192	6.444	6.228
	Cumulative Biogas Production, ml/gm VS	19.24	32.34	37.57
	R^2	0.998	0.999	0.999
RS	A, (ml/gm VS)	19.150	31.820	34.317
	U, (ml/gm VS/day)	0.759	1.445	1.493
	λ, days	9.760	9.621	8.735
	Cumulative Biogas Production, ml/gm VS	18.24	30.73	32.93
	R^2	0.998	0.998	0.998
RH	A, (ml/gm VS)	13.945	19.956	24.444
	U, (ml/gm VS/day)	0.482	0.811	0.875
	λ, days	9.589	9.640	9.444
	Cumulative Biogas Production, ml/gm VS	13.41	19.41	22.74
	R^2	0.998	0.998	0.998
SB	A, (ml/gm VS)	24.080	36.259	40.744
	U, (ml/gm VS/day)	0.897	1.304	1.405
	λ, days	8.732	7.876	6.570
	Cumulative Biogas Production, ml/gm VS	22.84	34.07	38.26
	R^2	0.999	0.998	0.999
BD	A, (ml/gm VS)	23.447	31.576	36.278
	U, (ml/gm VS/day)	0.899	1.293	1.340
	λ, days	10.247	8.260	8.053
	Cumulative Biogas Production, ml/gm VS	21.92	30.02	33.89
	R^2	0.998	0.997	0.998

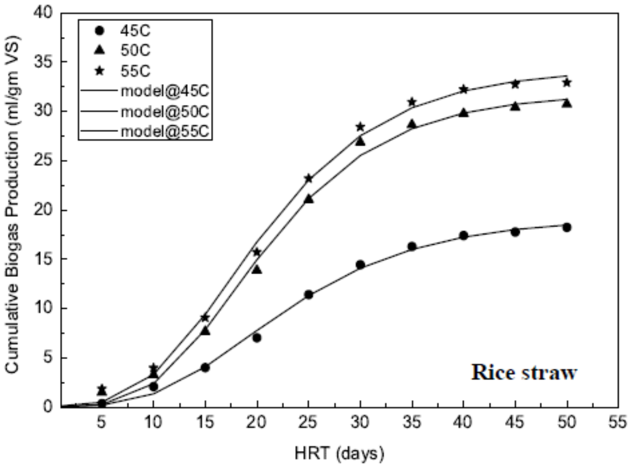
It is observed from Table 2 that the biogas production potential (ml/gm VS) and the maximum biogas production rate of the biomasses increases with increase in temperature. This is because temperature is a very important parameter in anaerobic digestion process. It can be concluded that in thermophilic condition the optimum temperature for methanogenic bacteria is 50°C to 55°C. on the other hand, the lag phase period (minimum time required to produce biogas) of the biomasses decreases with increase in temperature. The reason may be due to high rate of breakage of fibre material at high temperature surrounding the cellulose. Further it is observed that at 55°C the biogas production potential (ml/gm VS) of the biomass was the highest in case of sugarcane bagasse mixed with cattle dung (40.744 ml/gm VS) followed by saw dust (39.106 ml.gm VS), bamboo dust (36.278 ml/gm VS) rice straw (34.317ml/gm VS), and rice husk powder mixed with cattle dung (24.444 ml/gm VS). The maximum biogas production rate of the biomasses at the same temperature is shown as follows: Saw Dust mixture (1.406 ml/gm VS/day)> Sugarcane bagasse mixture (1.405 ml/gm VS/day)>Rice straw mixture (1.493 ml/gm VS/day)>Bamboo dust mixture (1.340 ml/gm VS/day)> Rice husk powder (0.875 ml/gm VS/day). The most important fact that is observed from the Table 1 is that the behaviour of kinetic parameters at different temperatures follow similar trend for all the biomass. In almost all the cases, the biogas production potential as well as the maximum biogas production rate was the highest at 55°C followed by 50°C and 45°C respectively. Garba, 1996 [12] reported that the digester containing lignocellulosic biomass maintained at 60°C produced more gas than the digester maintained at 40°C. Kim et. al, 2006 [32] studied the effect of temperature on anaerobic digestion of food waste and found that the rates of biogas and methane production by thermophilic digesters were higher than those by mesophilic digesters regardless of HRT. It is observed from the present investigation that with increase in temperature from 45°C-55°C, the biogas production rate increases for all the five biomasses. So, temperature has significant effect on cumulative biogas production and biogas production rate. In the present study it is observed that saw dust, bamboo dust and sugarcane bagasse shows significant response to change in temperature. Whereas rice straw and rice husk powder are reluctant to the effect of temperature. This may be due to the presence of lignin and high amount of silica (approximately 21%-27%) in rice straw and rice husk. Table 2 and Fig. 2 shows that for all kind of lignocellulosic biomass biogas production rate is higher for higher temperature. In addition the kinetic constants biogas production potential, A (ml/gm VS), maximum biogas production rate, U (ml/gmVS.day) increases with increase in temperature whereas lag phase period, λ (day) decreases with the increase in temperature.



The graphs suggest that the model defines experimental data in a suitable way.







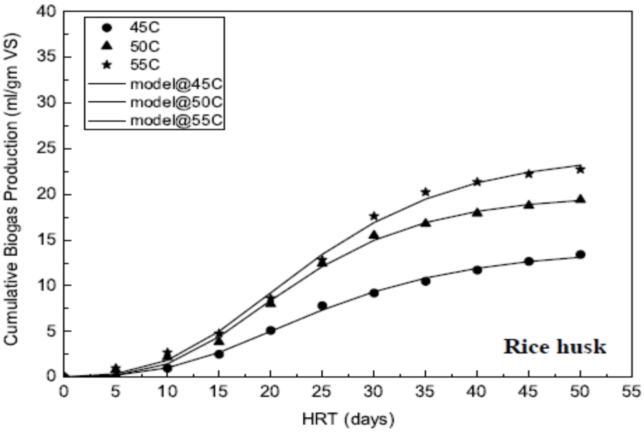


Fig 2 Comparison of model data and experimental data of cumulative biogas production from saw dust, bamboo dust, sugarcane biogases, rice straw and rice husk at different temperatures.

VI. CONCLUSIONS

Kinetics of biogas production was studied here by applying modified Gompertz equation and it was found that the data predicted by the model are quite close to the experimental data with ±10% error. It is also observed that with increase in temperature both maximum biogas production rate (U) and biogas production potential (A) of all the lignocellulosic biomass improves. Further, minimum time required for biogas production from the biomasses reduces with increase in temperature of digestate. Thus, temperature improves the production as well as the efficiency of the digester. On the other hand, there is no significant improvement in biogas production after 55°C temperature of digestate. Therefore the data obtained after 55°C are not reported here. On the other hand biogas production at 50°C was found to be almost near to the value at 55°C temperature, so to reduce the power consumption the anaerobic digestion process at 50°C is better as compared to 55°C from economic point of view. The modified Gompertz equation well explains cumulative gas production as a function of retention time.

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