Reaction Kinetics Modelling for Dry Anaerobic Digestion of Hura Crepitans Invasive Species Lignocellulosic Biomass

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Research Article

Abstract

In this research study, the impact of the feedstock to the inoculum (F/I) amount ratio in the dry anaerobic digestion (DAD) of *Hura crepitans* leaves was evaluated. Measured biogas volumes, as well as the chemical kinetic predictions for exponential, logistic and Gompertz model, depicting the agreement of the simulations over time, were also determined. From the F/I equivalents 2, 4 and 6 at 22 % of packed total solids, which were considered in analysis test procedure, the DAD digester with F/I number 4 was the most promising in terms of biogas' production rate. Its daily methane/carbon dioxide was 690 mL, while cumulative generation productivity was greater than 2 L/sample, respectively. On the other hand, the DAD reaction with F/I contained 6, recorded the lowest related expressed primary matter of < 1 L. An associated early commencement of the organic material breakdown in all bio vessels was indicative of a good start-up phase, which is one of the challenges, often encountered in DAD process. Furthermore, applied experimental methods revealed the direct correlation phenomena between biodegradability physical constants, measured molecular CH_4/CO_2 synthesis and simulations. *Hura crepitans* being an invasive plant species makes its lignocellulosic fractions desired in terms of valorisation, as it is not competing with agricultural crop products. Modelling can, moreover, contribute to consecutive operation optimisation, scaling and integrating, also taking dynamics under consideration. As opposed to bio-refining wood residues, where individual cellulose, hemicellulose or lignin biopolymers can be attained, degradation to yield CH_4 is robust, as well as compatible in combustion.

Introduction

Dry anaerobic digestion (DAD) also known as solid-state anaerobic digestion (SSAD) refers to a process operated at a total solid of 20-55% [1]. It has gained more prominence in recent years because of the benefits associated with it in comparison to liquid or wet anaerobic digestion (LAD or WAD). These benefits include mitigation of floating and stratification of substrates in the digester, lower energy requirement, lower water consumption, less wastewater generation [2, 3].

DAD has been used to digest different organic wastes such as municipal solid wastes, agricultural wastes, with promising results that have encouraged further research efforts [4, 5]. DAD can be operated under the three temperature regimes used in WAD namely psychrophilic, mesophilic and thermophilic temperature. However, mesophilic and thermophilic temperature regimes are commonly used with thermophilic outperforming mesophilic system in terms of biogas yield but due to its sensitivity to temperature fluctuations and high cost of operation (energy requirement), mesophilic system is still preferred for commercial operation [6]. Zhu and Jha [7] conducted DAD of cow dung under psychrophilic conditions with a significant increase in yield when the amount of low temperature adapted inoculum was increased from 30−50%. Li *et al*. [8] conducted DAD of raw and pretreated corn stover at mesophilic and thermophilic temperatures of 37 °C and 55 °C with some encouraging results. In another study, DAD of rice straw was carried out at three feedstock-to-inoculum ratios of 6, 8 and 10 under mesophilic and thermophilic conditions with thermophilic generally performing better than the mesophilic temperature regime [9].

Feedstock-to-inoculum ratio plays a significant role in process efficiency of DAD. It has been observed that operating DAD at a higher F/I could lead to process failure due to accumulation of volatile fatty acids (VFAs) [10].

There is need therefore to explore more feedstocks in order to discover their biogas potentials under this AD system and by so doing enhancing competiveness with WAD system. *Hura crepitans* (figure 1), which is also known as the Sandbox tree, is a fast-growing, semi-deciduous tree with a heavy bole and limbs that are covered in spines [11]. In closed forests, it can grow up to 50 meters tall, but in more open sites, it is usually rather smaller, in the range of 12 -20 metres [12]. The straight, cylindrical bole is often basally swollen, or has small buttresses. It can be unbranched for up to 30 metres and boles 200 cm in diameter have been reported, though 90 – 150 cm is more common [13].

Hura crepitans Linns which belongs to the family *Euphorbiaceae* has ovate leaves that could grow up to two feet wide [14, 15, 16]. *Hura crepitan* leaves are one of the unexplored materials that can be used as a potential feedstock for biogas production. There have been various reports on the uses of different parts of *Hura crepitans* tree in literature but none to the best of authors' knowledge, has been reported on the production of biogas from *Hura crepitans* leaves using DAD. The author in a previous work produced biogas from *Hura crepitans* leaves but with WAD [17]. The aim of this study was to determine the biogas potential of *Hura crepitans* leaves under DAD system with focus on the effect of feedstock-to-inoculum ratio on production yield.

Materials And Methods

Hura crepitans Linns leaves were collected from Auchi, Etsako West Local Government Area, Edo State, Nigeria. The leaves were sun-dried, ground and passed through 300 microns mesh sieve and stored in an air-proof plastic bottle prior to DAD process and analysis. The cow dung was collected from a local cattle market and stored in an anaerobic condition for 30 days before it was used as inoculum.

Dry Anaerobic Digestion of Hura crepitans Leaves

Digesters were prepared with F/I ratios 2, 4 and 6 based on the volatile solids (VS). Appropriate amount of water was added to obtain 22% total solids (TS). The samples were charged into 1 L glass reactors and tightly closed with rubber stoppers. The digesters were codenamed DAD2, DAD4 and DAD6, where the number denotes the F/I ratio, respectively. Biogas volume was measured by water displacement method every 24 hours while the cumulative volume was calculated. All tests were conducted in duplicate at ambient temperature of 36±2°C for a retention time of 30 days. Reactors were manually shaken once a day for improved substrate-microorganism contact.

Analytical Methods

Hura crepitans leaves were analyzed for TS, VS, ash, carbon, nitrogen, extractives, lignin, cellulose and hemicellulose while the inoculums was analyzed for ash, TS and VS according to standard methods [18,

19]. The initial and final pH values of the slurries were determined using a hand-held digital pH meter (Hanna Instruments, Italy).

Kinetic Studies

The kinetics of the anaerobic digestion process was evaluated using a first-order kinetic model to determine the biodegradability constants according to the following equations:

$$G = G_m[1 - \exp(-kot)\ (1)$$

Equation (1) was linearized to give equation (2)

$$\ln\left[\frac{Gm}{G_m - G}\right] = kot\ (2)$$

A plot of $\ln\left[\frac{Gm}{G_m - G}\right]$ vs time gave the biodegradability constants as shown in Table 2

In order to describe cumulative biogas yield (P), exponential, logistic and Gompertz model were used as Equations 3-5, respectively. P_m represents maximal P, t time, k (digestion) reaction rate constant, R_m highest biogas production and λ initial process lag.

$$P(t) = P_m\left(1 - e^{-kt}\right)$$

3

$$P(t) = P_m\left(1 + e^{(4R_m(\lambda-t)/P_m+2)}\right)^{-1}$$

4

$$P(t) = P_m exp\left(-e^{(eR_m(\lambda-t)/P_m+1)}\right)$$

5

Results And Discussion

Physicochemical properties of the samples are shown in Table 1. The ash, TS and VS were determined to be 14.22%, 97.00% and 82.79% for Hura *crepitans* leaves and 5.42%, 30.14% and 24.72% for the inoculum. The C/N ratio Hura *crepitans* leaves was 32.2 while its lignin, cellulose and hemicellulose contents were measured to be 28.26%, 32.70% and 39.05% respectively. As earlier mentioned, Hura *crepitans* leaves were thoroughly mixed with the inoculum and water added to produce the three F/I ratios used in the DAD.

Sample DAD6 had the highest lignin content while DAD2 had the least. Lignin usually forms a complex network with the carbohydrates thus making the lignocellulosic biomass recalcitrant to microbial degradation, which in turn could lower biogas yield [9].

Both samples DAD2 and DAD4 had higher contents of hemicellulose and cellulose than DAD6 which are the major components from which biogas is produced [20]. The highest ash content was found in sample DAD2 followed by DAD6. The cellulose content for DAD2 was close to 51.30% reported for organosolv-pretreated pinewood at 150 °C for 30 minutes by Mirmohamadsadeghi [21]. The hemicellulose content on the other hand was higher than 19.1% reported for corn cob by Liew *et al* [22].

The C/N ratios of DAD4 and DAD6 were well outside the range recommended for AD, that is, between 20:1 and 30:1 [23] while DAD2 was slightly above (30.95%) the range. The C/N ratios of DAD4 and DAD6 were however, below 97.6% reported for sunflower stalk by Kurt *et al.* [24]. Despite the high C/N ratios (with the exception of DAD2) there was still reasonably high biogas production. This observation has been reported in literature [25, 26] which could be attributed to the fact that C/N is not the only parameter responsible for effective running of AD. The overview done by Deublein and Steinhauser (2011) have pointed out no direct correlation between C/N ratio and biogas yield. [27] Their presumable conclusion was that C/N ratio might not in any way affect biomethane (biogas) yield. They based their argumentation on a three-year study on buffalo manure collected under varying conditions with C/N ratios ranging from 9 to 50. Their findings showed that there was significant biomethane production outside the range often reported in literature as optimal for AD. The argument can be laid to rest when we consider the fact that there are other factors that contribute to biogas production beside C/N ratio. There is need for further research in this area because of the contradictory results that have been reported in literature in order to have a better understanding of the role of C/N ratio on AD. However, substrates high in C/N ratio, such as samples DAD4 and DAD6 could serve as good co-digestion feedstocks for substrates that are low in carbon content [27].

Table 1

Physicochemical properties of the samples used in dry anaerobic digestion

Parameters	*Hura crepitans* leaves	Inoculum	DAD2	DAD4	DAD6
Ash content (%)	14.22±0.15	5.42±0.31	15.32±0.17	13.54±0.76	14.29±0.54
TS content (%)	97.00±0.05	30.14±0.05	ND	ND	ND
VS content (%)	82.79±0.15	24.72±0.3	ND	ND	ND
Carbon content (%)	47.66±0.08	ND	47.05+0.05	47.73+0.42	47.62+0.30
Nitrogen content (%)	1.48+0.28	ND	1.52+0.83	0.63+0.04	0.57+0.07
C/N ratio	32.20	ND	30.95	75.76	83.54
Lignin (%)	28.26±0.74	ND	26.77+0.53	36.48+0.04	44.50+0.54
Cellulose (%)	32.70+0.34	ND	50.33+0.04	45.76+o.29	38.58+0.5
Hemicellulose (%)	39.05±0.39	ND	22.91+0.55	17.75+0.25	16.94+1.03
ND – not determined					

The pH values of the initial and final samples are shown in figure 2. The values ranged from 5.4-8. The initial pH of F/I 2 was 8.00 while the final pH was 5.60. For F/I 4 the initial pH was 7.60 while the final pH was 5.40. Digester F/I6 also had initial pH of 7.60 but a final pH of 6.00. Overall, there was a decline in pH values in all the digesters at the end of the anaerobic digestion, a fact that has been attributed to accumulation of volatile fatty acids [28].

Daily And Cumulative Biogas Production

Figure 3 shows daily and cumulative biogas production from the three weighted samples. There was no lag phase in all the digesters as production commenced within the first 24 hours which was indicative a good start up/hydrolysis stage in the DAD process. It has been observed that operating DAD at a higher F/I ratio could slow down the initial stage as shown elsewhere [10] but the results from this study revealed that the F/I ratios adopted were appropriate for rapid beginning phase of the DAD. Digester DAD6 peaked earlier (day 7) than other digesters with peak production of 280 ml. Digester DAD2 peaked on day 8 with 410 ml while digester DAD4 achieved its highest peak value on day 18 (690 ml) which was longer than other digesters. Biogas continued till the last day of the experiments which shows that the process efficiency was healthy which could be as a result of no or low inhibitory substances in the system.

In this study, the sample DAD6 with highest lignin content produced the least amount of biogas. Although no clear relationship between the amount of biogas produced and lignin contents of the substrates in this study, yet the least biogas produced was from the sample with the highest lignin content.

Results of cumulative biogas production revealed that digester DAD4 was 2.4 fold higher than that of DAD6 which produced the least volume (940 mL) of biogas. Digester DAD2 produced a volume of 2005 ml while digester DAD4 produced a highest volume of gas with a total of 2210 ml. This shows that biogas production is best carried out at this F/I ratio.

Kinetic Study

There was a direct correlation between biodegradability constant and biogas yield. DAD4 with the highest biogas yield had the highest constant biodegradability value of (K_o) of 1.110 d^{-1} followed by DAD2 0.569 d^{-1} with sample DAD6 having the least value of 0.347 d^{-1}. The results revealed that digester DAD6 had highest utilization of the substrate, which translated to increased biogas production compared to other digesters. The K_o for DAD2 was higher than 0.9185 reported for 3% Organosolv pretreated rice husk by Olugbemide *et al.* [17].

Table 2
Chemical kinetics parameters regressed for various proposed models/data.

Data	DAD2	DAD4	DAD6
Exponential			
P_m/L	2.05	2.21	1.01
k/day^{-1}	0.146	0.064	0.094
Logistic			
P_m/L	1.92	2.58	0.90
R_m/(L day^{-1})	0.272	0.124	0.066
λ/day	1.80	5.72	0.24
Gompertz			
P_m/L	1.94	3.42	0.92
R_m/(L day^{-1})	0.273	0.102	0.068
λ/day	1.58	3.45	0.12

Results show that exponential kinetic model provides the poorest measurement agreement, not being able to describe the lag in production, which is clearly seen, in particular with the data 2, where maximal production rate is achieved only after day 17. Logistic or Gompertz models provide approximately the same prediction/ measurement agreement, whereas the data 1 or 3 can be described excellently, while for 2, we not only see a lag in production, but also a bimodal digestion process. Correspondingly, this hints

towards two predominant fractions, which are being digested at a much dissimilar rate/lag of cascade digestion process, which should have been described by a reaction in series kinetic model, regressing also intermediate.

Conclusion

Hura crepitan leaves, as one of the underutilized feedstocks, have shown potential to be used for biogas production. Herein, dry anaerobic digestion (DAD) of *Hura crepitans* leaves was carried out with the aim of determining the effect of different feedstock-to-inoculum ratios on biogas production. The results revealed that anaerobic digestion of *Hura crepitans* leaves carried out at F/I4 (22% TS) was the optimum condition for generating maximum amount of biogas. However, in terms of peak value, digester DAD2 outperformed other digesters in reaching its maximum peak value at the earliest time in comparison to other digesters. The use of *Hura crepitan* leaves for biogas production could help increase the number of viable substrates that can be used for energy recovery via AD; more so now that the technology is gaining prominence around the world. Further studies need to be done though to explore how best to improve biogas yield from this underutilized but readily available substrate.

Declarations

Declaration of Competing Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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Figures

Figure 1

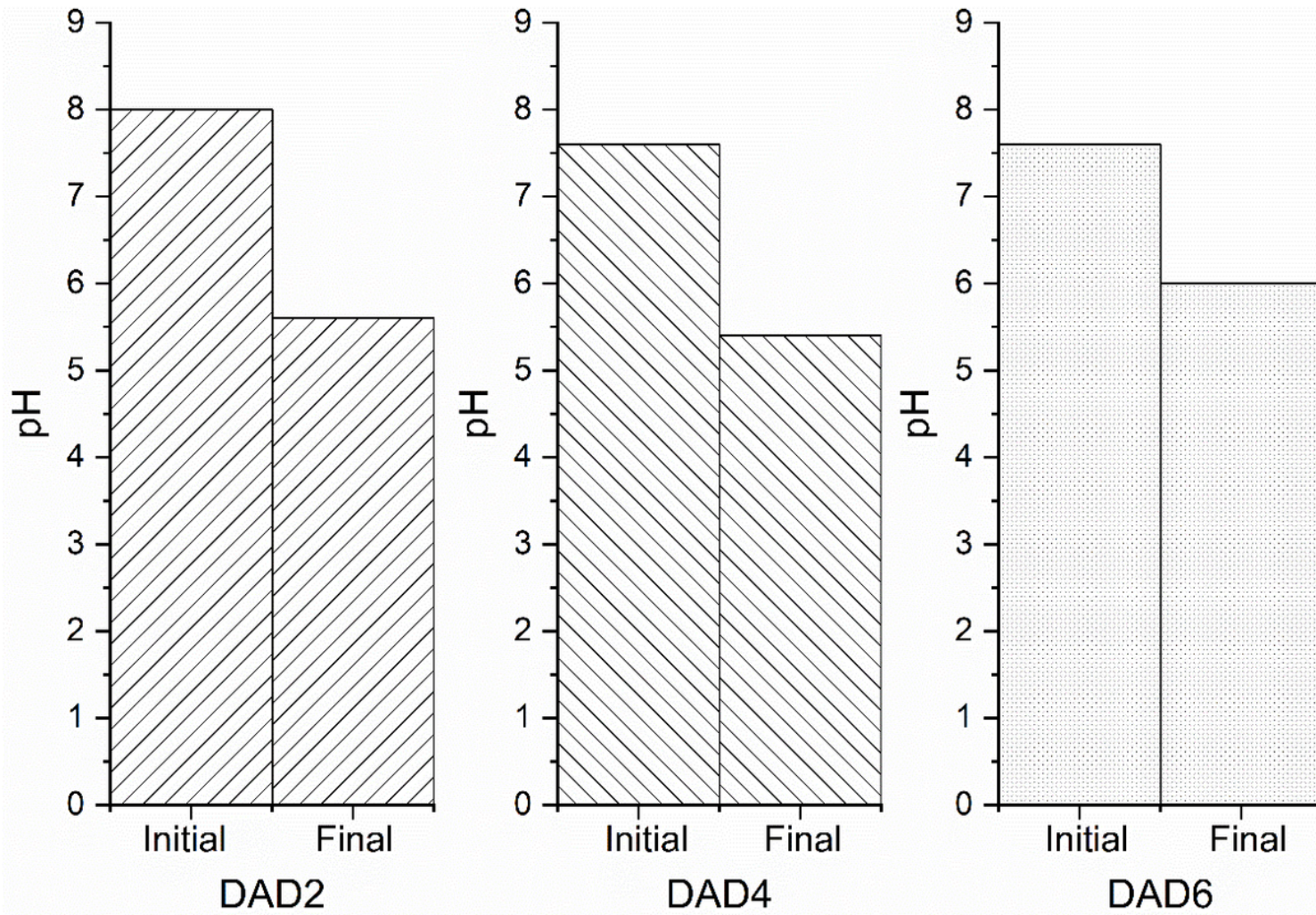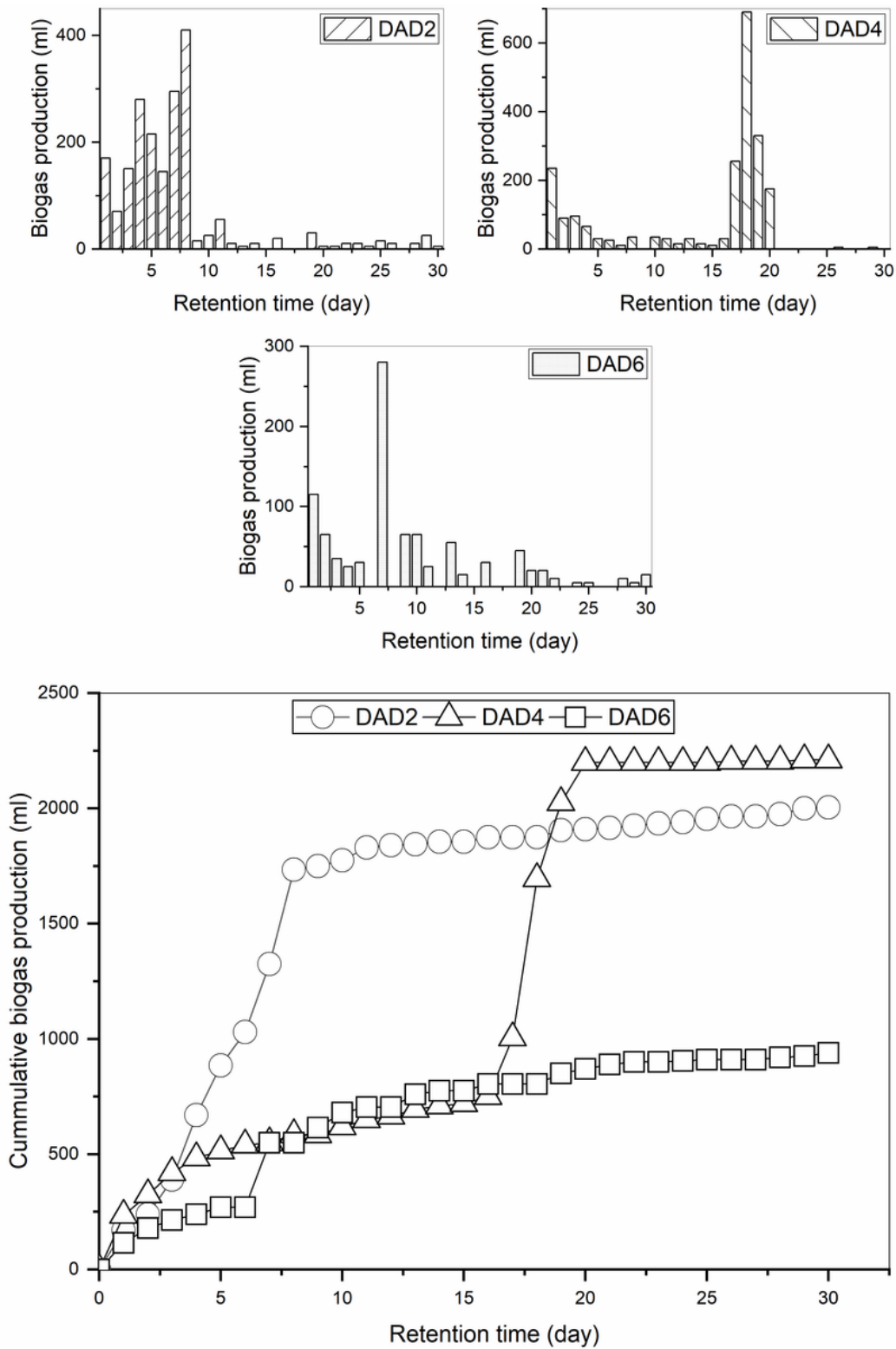a. Hura crepitans tree b. Hura crepitans leaves and seeds

Figure 2

Initial and final pH values of DAD2, DAD4 and DAD6.

Figure 3

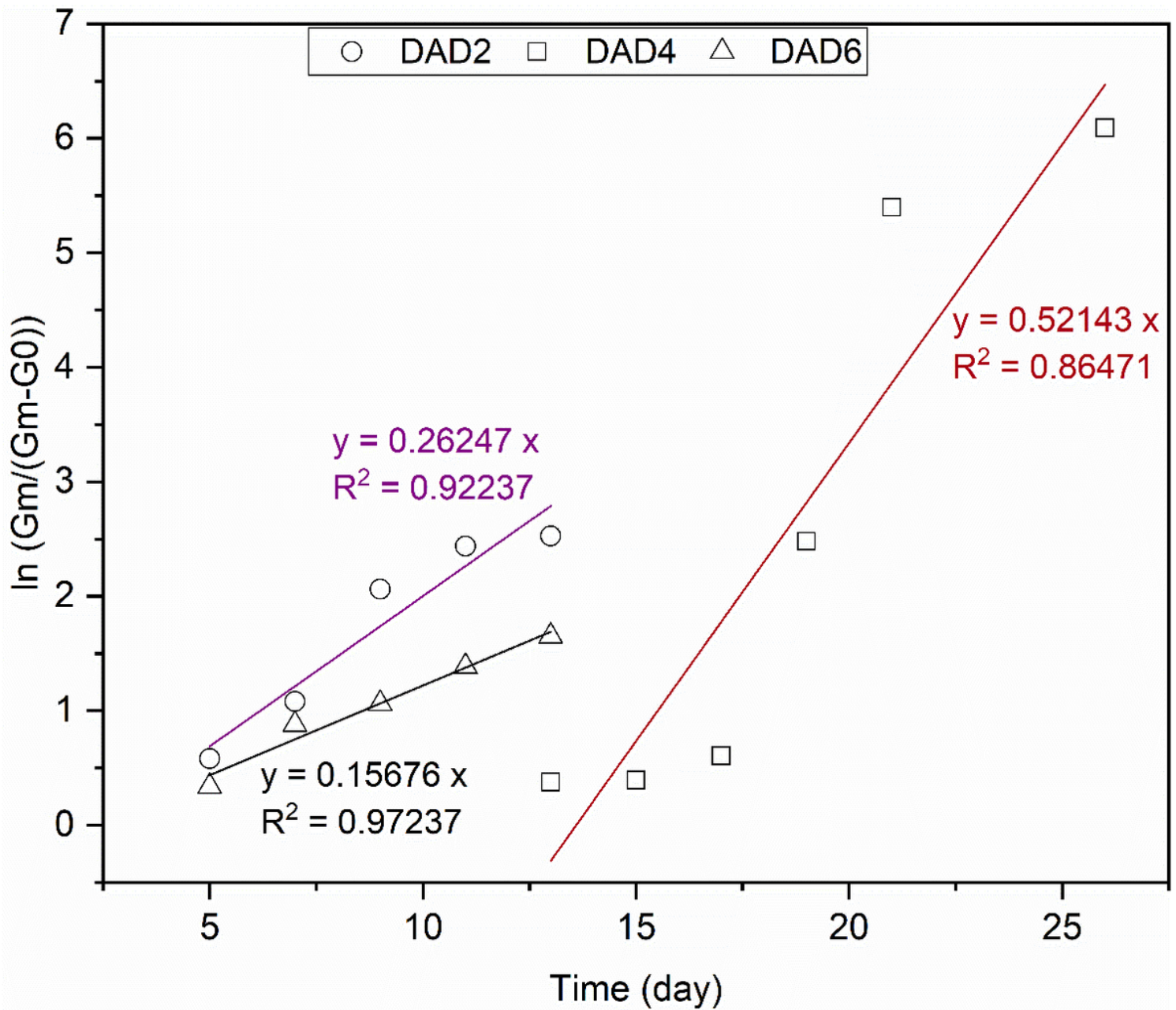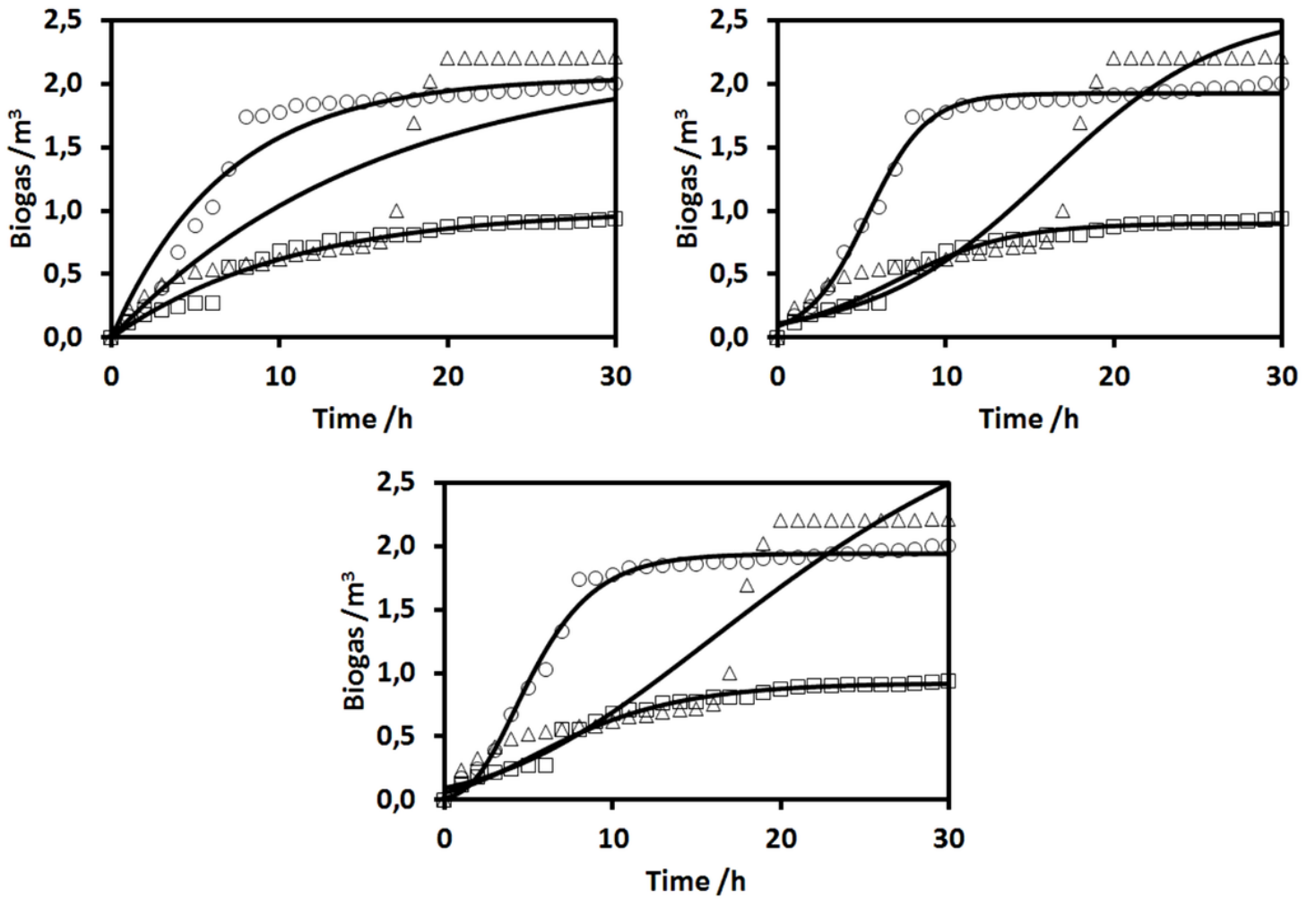Daily and cumulative biogas production of digesters DAD2, DAD4 and DAD6.

Figure 4

Plot of ln Gm/Gm-Go against retention time of digesters DAD2, DAD4 and DAD6.

Figure 5

Measured biogas volumes (the circles for 1, triangles for 2 and squares for 3), as well as the chemical kinetic predictions for exponential (top left), logistic (top right) and Gompertz (bottom) model, depicting the agreement of the simulations over time.