

# Assessment of Biochemical Methane Potential and Kinetic Studies on Municipal Solid Waste for Methane Production

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This study evaluated the biochemical methane potential (BMP) and its kinetic studies of municipal solid waste using a total of five solid waste mixtures. Mixture A consisted of 74% organic waste and 26% inorganic waste, mixture B consisted of 72% organic waste and 28% inorganic waste, mixture C consisted of 60% food waste, 30% inorganic waste, and 10% garden waste, mixture D consisted of 30% food waste, 60% paper waste, and 10% diaper waste, and mixture E consisted of 10% food waste, 30% plastic waste, and 60% textile waste. The BMP assay was conducted in a 250 mL serum bottle with 70% of the working volume. The samples were then incubated at 37°C for 37 days. The BMP assay showed that mixture B had the highest methane yield (310.91 mL CH<sub>4</sub>/g VS), followed by mixture C, mixture D, mixture A, and mixture E with 269.61 mL CH<sub>4</sub>/g VS, 240.85 mL CH<sub>4</sub>/g VS, 229.91 mL CH<sub>4</sub>/g VS, and 218.13 mL CH<sub>4</sub>/g VS, respectively. For the kinetic study, the findings revealed that the modified Gompertz model (MGM) fitted well with the predicted methane generation potential with R<sup>2</sup>>0.97. The findings of this paper provided baseline data for effective municipal solid waste management practices.

**Keywords:** Biochemical methane potential; Kinetic studies; municipal solid waste; Modified-Gompertz model; anaerobic degradation

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One of the persistent challenges among developed and developing countries around the world is the rapid increase in municipal solid waste (MSW). MSW is defined as any discarded and unwanted products in the solid state. They are derived from human activities and made up of heterogeneous waste compositions like food, paper, garden waste, plastic, diapers, textiles, and inorganic waste. These unwanted products are finally disposed of at a landfill. The increase in the human population is in line with waste generation. As a result, the rapid growth of the human population and an increase in MSW have put waste managers under intense pressure due to land scarcity to provide new landfills.

MSW dominates the waste stream by weight that is produced from human activities in residential, commercial, institutional, and industrial areas. Asian nations currently produce MSW at a rate of 1 Mt/day, and by 2025, the value increased to 1.8 Mt/day [1]. According to the UN Environment Programme Annual Report [2], Malaysia ranked third in ASEAN in 2016 in terms of waste generation per individual, with a value of 1.17 kg/capita/day. Additionally, daily waste generation in Malaysia experienced a 5.19% increase from 2015 (38,563 tonnes) to 2020 (49,670 tonnes), with 38,000 tonnes of waste generated daily in 2018 [3]. To support recycling efforts, the Malaysian

MSW management system implemented solid waste separation in September 2015. Even so, the recycling rate in the country in 2022 was 30.67%, as stated by Solid Waste Corporation (SWCorp), which was lower than other Asian nations such as Singapore (59%), Korea (49%), and Taiwan (60%).

However, MSW is highly diversified according to regions and nations. Factors influencing the MSW biodegradability are its composition, such as the amount of carbohydrates, proteins, and lipids, and its degradable fraction, such as lignocellulose and volatile solid content. Meanwhile, the main limiting factor in its degradation process is substrate composition. Substrate composition affects the particulate substrates in the hydrolysis process and the large differences in hydrolysis rates for various particulate components [4]. Besides, the kinetic behaviour varies with the substrate composition because each product of the subsequent hydrolysis is digested by a different bacterial population [5].

Alternative methods in managing solid waste have received great concern recently. Among them is the anaerobic digestion (AD) process. Anaerobic digestion offers energy recovery through methane combustion over traditional aerobic treatment. It has the ability to degrade poorly biodegradable substrates

at high concentrations and short incubation times, at minimal energy. The method is agreed upon as an environmentally friendly method of managing waste by producing methane-rich biogas that can then be converted to electrical energy [6]. Therefore, AD of MSW has received a lot of interest among researchers, especially in identifying the anaerobic biodegradability of MSW in different countries. For example, Nielfa et al. [7] evaluated the influence of each fraction in the final mixture of MSW biodegradability, Sandoval-Cobo et al. [8] determined the methane potential and biodegradability of MSW disposed of in Colombia's landfill, Bilgili et al. [9] evaluated the biochemical methane potential (BMP) of MSW obtained from Turkey's landfill, and Sohoo et al. [10] assessed BMP of MSW in Pakistan.

Aleluia and Ferrão [11] found MSW produced in Asia's emerging nations high in organic percentage, which often accounts for more than 50% of MSW composition. This is in line with Malaysia's waste composition that consists of more than 70% organic fractions (i.e., 45% food waste, 8% garden waste, 8% paper waste, 8% diapers, and 5% textile waste) [12]. Despite a high percentage of organic fraction, other characteristics of MSW, such as high volatile solid content, make this waste a potential substrate in the AD process. Accordingly, the current study was conducted to (i) evaluate the biochemical methane potential of the variety fraction of MSW in Malaysia and (ii) study the kinetic behaviour of the measured substrates. From this study, baseline data could be established for a possible Malaysian MSW management system solution and guidance for waste-to-energy (WTE) parties.

## EXPERIMENTAL

### Substrate and Inoculum

Data obtained from Majlis Bandaraya Shah Alam (MBSA) revealed seven categories of solid waste:

food, paper, garden, plastic, diapers, textile, and inorganic. In order to study the effects of waste composition on methane potential yield, five different solid waste mixtures were used as substrates. They were mixture A, mixture B, mixture C, mixture D, and mixture E. Mixture A represented Shah Alam waste composition, mixture B was a fair mixture of seven categories of solid waste, while mixtures C, D, and E were the mixtures of the waste in a range of 0% to 100% for biodegradable waste like food, textile, garden, and paper. Since plastic, diapers, and inorganic waste do not have the potential to generate gas by themselves, their range was designated between 0% and 40%. The total mixture of waste components in the serum bottles was set at 100%. Table 1 summarises the five waste mixtures that were used in this study.

The food waste in the current study was food leftovers collected from the UiTM Shah Alam cafeteria, while other waste (i.e., paper, garden, plastic, and inorganic waste) was obtained around UiTM Shah Alam. However, textile waste was obtained from local tailors at Section 7, Shah Alam, and diaper waste was collected from the baby changing rooms in shopping malls. For inoculum, a sample was collected from the anaerobic digester of a domestic wastewater treatment plant located at Setiawangsa, Kuala Lumpur. The waste components were cut into small pieces with a size smaller than 10 mm.

### Substrate and Inoculum Characterisation

Standard Method for the Examination of Water and Wastewater (APHA, 2012) [13] was used to conduct analytical methods. All substrate mixtures were characterised chemically and physically, with the parameters including moisture content (MC), total solids (TS), volatile solids (VS), pH, and chemical oxygen demand (COD). To ensure the validity of data, this analysis was measured in triplicate for each sample.

**Table 1.** Summary of waste composition percentage in five different solid waste mixtures.

| Waste composition | Percentage (%) |            |            |            |            |
|-------------------|----------------|------------|------------|------------|------------|
|                   | Mixture A      | Mixture B  | Mixture C  | Mixture D  | Mixture E  |
| Food waste        | 45             | 15         | 60         | 30         | 10         |
| Garden waste      | 8              | 15         | 10         |            |            |
| Paper waste       | 8              | 14         |            | 60         |            |
| Plastic waste     | 18             | 14         |            |            | 30         |
| Diapers           | 8              | 14         |            | 10         |            |
| Textile waste     | 5              | 14         |            |            | 60         |
| Inorganic waste   | 8              | 14         | 30         |            |            |
| <b>Total</b>      | <b>100</b>     | <b>100</b> | <b>100</b> | <b>100</b> | <b>100</b> |

Based on Angelidaki [14], food waste should be oven-dried at 65°C ( $\pm 5^\circ\text{C}$ ) to avoid volatilisation of organic matter. Accordingly, all mixtures in the current study were oven-dried at 65°C ( $\pm 5^\circ\text{C}$ ) until they reached a constant weight to determine MC and TS. Then, samples were cooled at room temperature in a desiccator before the total solid weight was measured. The moisture content percentage of all mixtures was calculated as in (1):

$$\text{Moisture content (\%)} = \frac{\text{wet weight} - \text{dry weight}}{\text{wet weight}} \times 100 \quad (1)$$

Samples from moisture content analysis were weighed in three porcelain crucibles before igniting at 550°C for about two hours in a LENTON furnace. After combustion, the ash weight was weighed, and a calculation for the determination of volatile solid percentage was made as in (2):

$$\text{Volatile solids (\%)} = \frac{\text{dry sample weight} - \text{ash weight}}{\text{dry sample weight}} \times 100 \quad (2)$$

The closed reflux colorimetric method was used in the determination of COD by digesting samples with dichromate in the Hach DRB200 digital reactor. Meanwhile, pH was measured using a pH meter from Mettler Toledo. For inoculum characterisation, additional analyses were conducted, which are volatile fatty acid (VFA) and alkalinity analysis. VFA was identified using a HACH DR1900 spectrophotometer, and a titration-based method was used in the determination of the total alkalinity by titrating the inoculum with 0.1 N of sulphuric acid until achieving an endpoint of pH 4.3 to pH 4.7.

### Biochemical Methane Potential (BMP) Assays

BMP assays were conducted in 250 mL amber glass bottles with 70% of working volume and 30% of headspace. To achieve 10 g/L of substrate concentration as recommended by Filer et al. [15], about 5.8 g of substrate and 116 mL of inoculum were filled in substrate bottles. Control represents known substrate (microcrystal cellulose) and inoculum; meanwhile, blank represents a reference of methane generation from inoculum only and was also prepared. All controls, blanks, and samples were conducted in triplicate to ensure repeatable results. The substrate-to-inoculum ratio (SIR) used in this study was 1:2. According to Holliger et al. [16], all samples should have an initial pH of 7.2.

Then, nitrogen gas ( $\text{N}_2$ ) was purged into each bottle for approximately three minutes before they were all sealed airtight with rubber caps to create the anaerobic condition [17]. All samples were incubated at 37°C (mesophilic condition) for 40 days, and all bottles were manually shaken once a day.

Nonetheless, BMP assays could be discontinued if the daily methane production over three days was less than 1% even the incubation period was set at 40 days [18]. Lastly, the Agilent 7890A Gas Chromatography-Flame Ionisation Detector was used to measure methane production three times per week.

### Kinetic Studies

First-order kinetic model (FOKM) and modified Gompertz models (MGM) were applied in this study to assess the predicted methane potential of substrates. Throughout the process, the prediction models accounted for the substrate's experimental biodegradability. Nevertheless, a relative error was calculated as in (3) to generate the perfect circumstances and models that were in agreement with the experimental results.

$$\% \text{ error} = \frac{\text{BMP}_{\text{exp}} - \text{BMP}_{\text{theoretical}}}{\text{BMP}_{\text{exp}}} \quad (3)$$

#### First-order Kinetic Model (FOKM)

FOKM is a model that assumes accumulated methane production follows an exponential increase to the maximum. Two variables are needed to identify the predicted methane potential of FOKM (4).

$$P = \gamma \times (1 - \exp(-\mu t)) \quad (4)$$

where P was the predicted methane potential,  $\gamma$  (mL  $\text{CH}_4/\text{g VS}$ ) was the maximum volume accumulated at an infinite digestion time (t), and  $\mu$  ( $\text{d}^{-1}$ ) was the speed of microorganism growth.

#### Modified Gompertz Model (MGM)

MGM explains the relationship between cumulative methane production and incubation time by considering the maximum rate of methane production and the duration of the delay phase. Equation (5) has been recognised as a good experimental model of nonlinear regression and is commonly used in the simulation of methane accumulation [19].

$$P = \gamma \exp\left(-\exp\left(\frac{K(\lambda - t)e^1}{\gamma} + 1\right)\right) \quad (5)$$

where P was the predicted methane potential,  $\gamma$  (mL  $\text{CH}_4/\text{g VS}$ ) was the maximum volume accumulated at an infinite digestion time (t), K was the specific rate constant, and  $\lambda$  (d) was the lag phase time constant.

To identify the best-fitted kinetic model, a comparative analysis of root mean square error (RMSE) and coefficient of determination ( $R^2$ ) was performed.

**Table 2.** Results for the characterisation of the substrates.

| Parameters           | Mixture A         | Mixture B         | Mixture C         | Mixture D         | Mixture E         |
|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Moisture content (%) | 22.32±1.53        | 9.67±0.13         | 18.71±1.56        | 10.78±1.72        | 11.25±0.27        |
| Total solid (%)      | 77.68±1.53        | 90.24±0.13        | 81.01±1.56        | 89.22±1.72        | 88.75±0.27        |
| Volatile solid (%)   | 73.60±2.87        | 24.09±1.39        | 45.7±2.88         | 50.18±3.55        | 67.42±5.39        |
| COD (mg/L)           | 15400.00±<br>8.72 | 19000.00±<br>3.59 | 13500.00±<br>6.36 | 17000.00±<br>8.96 | 12900.00±<br>6.59 |
| pH                   | 6.05±0.54         | 7.22±0.99         | 5.78±0.68         | 7.21±0.36         | 7.07±0.99         |

## RESULTS AND DISCUSSION

### Substrate and Inoculum Characterisations

Table 2 lists the mean value and standard deviation for the characteristics of each measured substrate. The results revealed that some of the values in Table 2 were inconsistent with other researchers [7, 8, 9, 10]. This distinction could be due to the differences in lifestyle and culture, population, economic growth, geography, climatic factors, and waste management practices [20].

The moisture content is measured by the amount of water lost from materials upon drying at a constant weight. It is directly affected by the physical and chemical properties of the material, which enable it to absorb the existing water in the environment [21]. Mixture A resulted in the highest percentage of moisture content with a value of 22.32%, followed by mixture C, mixture D, mixture B, and mixture E. The data indicated that a waste mixture containing a high percentage of food waste composition resulted in a high percentage of moisture content.

According to Aghdam et al. [22], moisture content determines the method preferred for the management and disposal of MSW. In addition, it is an important parameter to consider in planning the AD process. This is because the moisture content influences the choice of the digester's technology, whether wet, semi-wet, or dry [23]. Besides that, the total solid content is also useful in determining the type of digester used in the anaerobic process. Total solid content less than 10% is suitable for

wet processes, 10% to 20% can be considered for semi-dry processes, and more than 20% of total solid content is practicable for dry processes [24]. In this study, mixture B had the highest total of solid content with a value of 90.24%, while the lowest one was mixture A with a value of 77.68%.

Volatile solid (VS) content is an indicator of the present organic matter in the materials. Therefore, in an anaerobic process, it is essential to monitor the efficiency of organic matter removal based on VS analysis [25]. Mixture A contained the highest VS content (73.60%). According to Filho et al. [26], substrates containing more than 60% of VS content can yield high production of potential biogas. Chemical oxygen demand (COD) quantifies the amount of oxygen in a sample that oxidising agents can consume [27]. The measured COD content values allow an accurate mass balance of the digester to be determined, ultimately providing a better understanding of the system, as the total digestible material entering the digester will be known [28]. The COD content of all measured substrate mixtures ranged from 12,900.00 mg/L to 19,000.00 mg/L.

A wide range of pH was identified for all substrate mixtures, which was from slightly acidic to neutral conditions (pH 5.78 to pH 7.22). All inoculum parameters that were identified in this study were in line with the recommended range. The pH of the inoculum should be in a neutral to slightly basic ( $7 \leq x \leq 8.5$ ) condition so that it is allowed to correct the substrate pH. Table 3 presents the characterisation of the inoculum in this study and recommended range values.

**Table 3.** Characterisation of inoculum and recommended range.

| Parameter                                | Present study | Recommended range [16] |
|------------------------------------------|---------------|------------------------|
| pH                                       | 7.94±0.025    | $7 \leq x \leq 8.5$    |
| VFA (g CH <sub>3</sub> COOH/L)           | 0.21±0.06     | <1                     |
| NH <sub>4</sub> (g HN <sub>4</sub> /L)   | 0.42±0.027    | <2.5                   |
| COD (g/L)                                | 20.767±0.15   | NA                     |
| Alkalinity (g CaCO <sub>3</sub> /L)      | 3.42±0.43     | >1.5                   |
| Methane yield (NL CH <sub>4</sub> /g VS) | 20            | ~50                    |

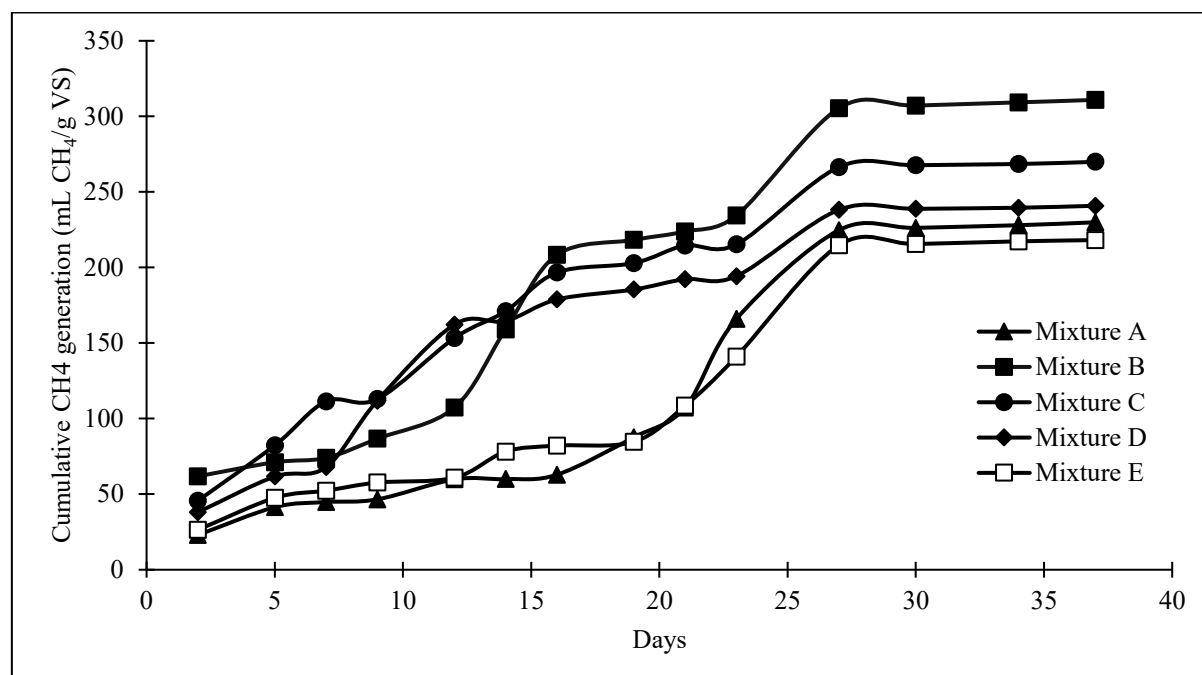


Figure 1. Cumulative methane production for experimental BMP.

Table 4. Results of kinetics studies.

| Waste     | FOKM                                      |                             |                |       |              | MGM                                       |               |                                      |                |       |              |
|-----------|-------------------------------------------|-----------------------------|----------------|-------|--------------|-------------------------------------------|---------------|--------------------------------------|----------------|-------|--------------|
|           | $\gamma$<br>(mL CH <sub>4</sub><br>/g VS) | $\mu$<br>(d <sup>-1</sup> ) | R <sup>2</sup> | RMSE  | Error<br>(%) | $\gamma$<br>(mL CH <sub>4</sub><br>/g VS) | $\lambda$ (d) | K<br>(mLCH <sub>4</sub> /<br>g VS/d) | R <sup>2</sup> | RMSE  | Error<br>(%) |
| Mixture A | 554.18                                    | 0.01                        | 0.90           | 25.76 | 141.04       | 366.32                                    | 5.83          | 8.61                                 | 0.93           | 20.86 | 59.33        |
| Mixture B | 367.95                                    | 0.04                        | 0.95           | 21.02 | 18.35        | 366.42                                    | 0.09          | 11.47                                | 0.97           | 16.98 | 17.85        |
| Mixture C | 316.37                                    | 0.06                        | 0.98           | 9.49  | 17.34        | 291.46                                    | 2.75          | 10.34                                | 0.99           | 8.77  | 8.10         |
| Mixture D | 281.59                                    | 0.06                        | 0.97           | 11.86 | 16.92        | 246.40                                    | 0.61          | 11.30                                | 0.97           | 11.06 | 2.30         |
| Mixture E | 598.42                                    | 0.01                        | 0.91           | 20.58 | 174.34       | 413.51                                    | 3.44          | 7.27                                 | 0.93           | 18.17 | 89.57        |

As mentioned in [16], the production of CH<sub>4</sub> by the inoculum should not exceed 20% of the total measured production (inoculum + substrate) to accurately examine the possible impact of endogenous CH<sub>4</sub> production during BMP tests.

#### Biochemical Methane Potential (BMP) Yield

Figure 1 shows the trend of cumulative CH<sub>4</sub> generation during the incubation time. In general, all mixtures produced different curve trends due to the variety of mixed waste composition in all series. The production of CH<sub>4</sub> gas that began immediately, with no lag phase in all series, indicated that microorganisms in all samples provided a suitable environment to start the degradation process [10]. Mixture A and mixture E

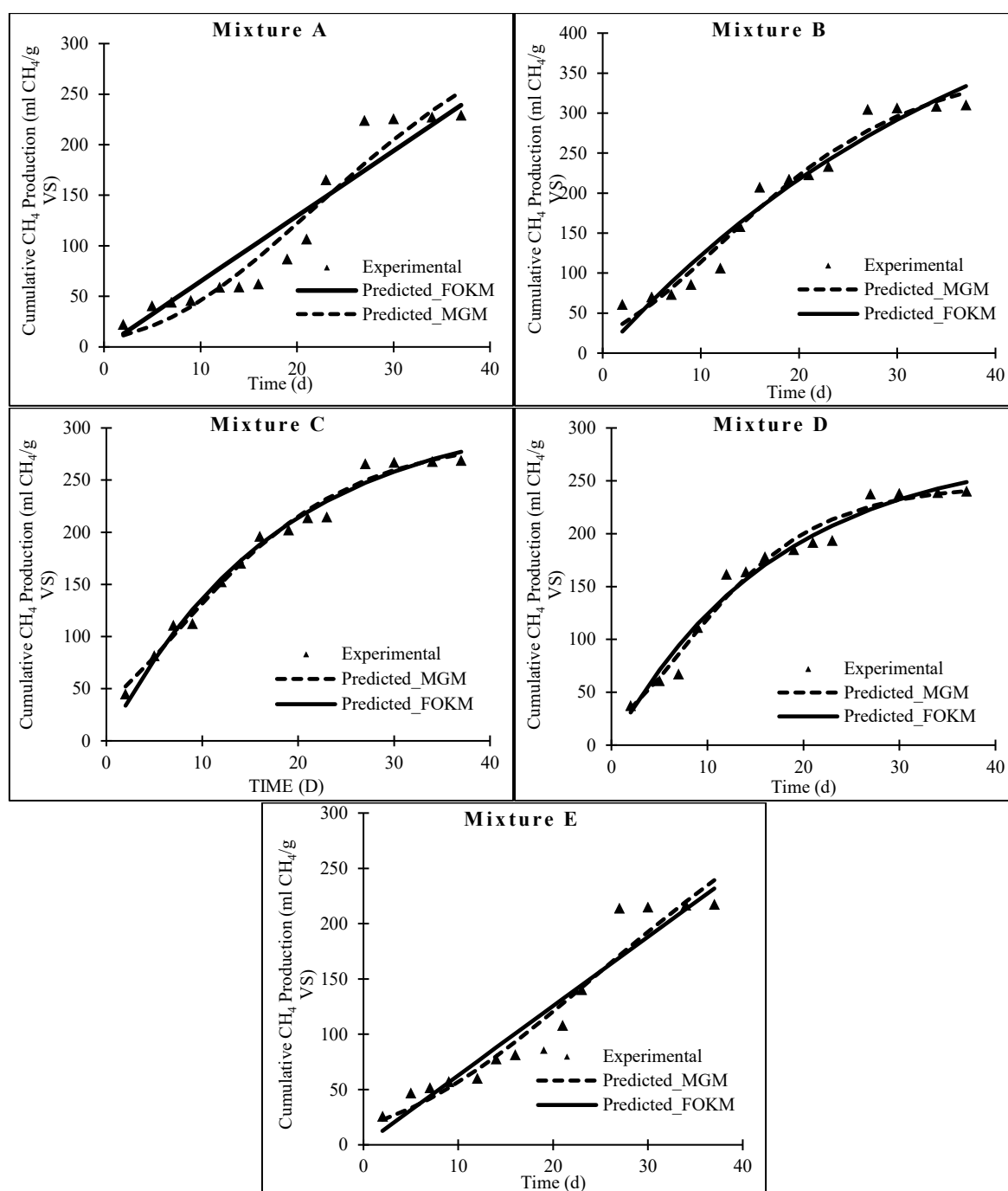
had slightly similar cumulative CH<sub>4</sub> generation curves, with a rapid increase observed from day 19 until day 27, followed by a stabilisation phase from day 27 until day 37. The stabilisation phase was due to some factors, such as substrate depletion, that altered microbial communities and environmental conditions [29].

However, for mixtures B, C, and D, the rapid increase phase occurred earlier than for mixtures A and E, which were at day 9, due to the presence of a high percentage of biodegradable waste components, as tabulated in Table 1. Mixture B produced the highest CH<sub>4</sub> production at 310.91 mL CH<sub>4</sub>/g VS, with a standard deviation of 5.40%. This was followed by mixture C, mixture D, and mixture A with cumulative CH<sub>4</sub> production of 269.61±3.78 mL CH<sub>4</sub>/g VS, 240.85±

3.44 mL CH<sub>4</sub>/g VS, and 229.91±2.16 mL CH<sub>4</sub>/g VS, respectively. Mixture E produced the lowest CH<sub>4</sub> production at 218.13±3.70 mLCH<sub>4</sub>/g VS. The mixture was composed of a high percentage of poorly biodegradable waste components (60% textile waste), which was the reason that it contributed to the lowest CH<sub>4</sub> production compared to the other mixtures. Although mixture A contained a high amount of easily biodegradable waste components, specifically 45% food waste, its low methane potential production was due to the accumulation of volatile fatty acids resulting from an imbalance between the acidogenesis and methanogenesis phases [8].

## Kinetic Studies

In this study, FOKM and MGM evaluated the kinetic behaviour of substrates. FOKM offers information about the maximum accumulated biogas production and the growth speed of microorganisms. Meanwhile, MGM assumes a direct relationship between the biogas production rate and microbial activity, estimating the maximum accumulated methane production, the specific rate constant, and the lag phase. The summary of the kinetic study results was tabulated in Table 4.



**Figure 2.** Cumulative methane production for experimental BMP and kinetic study fitting curves.

According to statistical indicators, MGM had the lowest percentage error in a range of 2.30% to 89.57%, compared to FOKM. MGM, represented by lower RMSE (8.77-20.86) and high  $R^2$  values ( $>0.95$  for all mixtures except mixture A and mixture E), was fitted perfectly with experimental BMP. RMSE employs a metric for assessing the discrepancies between predicted values and actual values. A lower RMSE value is preferable since it signifies that the model's predictions are closer to the actual values, indicating a more precise model. An  $R^2$  value approaching 1 is typically seen as superior, as it signifies that the model accounts for a substantial percentage of the variance in the dependent variable, enhancing the accuracy of the model's predictions with the actual data. The result suggests that to attain the ideal adjustment for some of the substrates, which may have a lag phase or an adaptation time, an additional parameter in the equation ( $\lambda$ ) may be required [30].

From Table 4, mixture B had a shorter lag phase (0.09 d), and mixture A experienced the longest lag phase (5.83 d). The lag phase was inversely proportional to the degradation rate constant, as shown in Table 4. Mixture B had higher degradation with a value of 11.47 mL CH<sub>4</sub>/g VS/d, while mixture E had the lowest degradation with a value of 7.27 mLCH<sub>4</sub>/g VS/d.

Figure 2 illustrates the cumulative CH<sub>4</sub> generation potential and both kinetic models' fitting curves. There are many reasons for the presence of the latency phase in the AD process. One reason is the disruption of methane generation during the early stage of degradation, which occurs due to the accumulation of volatile fatty acids that increase the acidogenesis rate relative to the methanogenesis rate. Besides that, fibre content in the waste composition also contributes to the delay phase in the methane generation process [31]. In this study, both models overestimated experimental methane potential when compared with predicted values. The type of substrates were the main reason for the overestimation or underestimation obtained from kinetic study models [32].

## CONCLUSION

The BMP yield results confirmed that mixture B had higher potential in methane production than the other mixtures. This higher potential is attributed to the presence of a variable waste composition that serves as a nutrient that enhances the methane degradation rate. From the MGM equation for the degradation rate, mixture B had a high methane generation potential (11.47 mL CH<sub>4</sub>/g VS/d) in a short lag phase (0.09 d). In contrast, mixture E, composed of a high percentage of poorly biodegradable waste components, had the lowest methane generation potential (218.13 mL CH<sub>4</sub>/g VS) with the lowest CH<sub>4</sub> degradation rate (7.27 mL CH<sub>4</sub>/g VS/d). The current study concluded that MGM was more effective in explaining the mixture

series in this study than the FOKM, indicating that some substrates need an adaptation period or latency phase before the degradation process occurs. This paper supplies baseline data for future researchers and parties involved in identifying potential solutions for improving the MSW management system and in planning and designing waste-to-energy projects in Malaysia.

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## CONFLICT OF INTEREST STATEMENT

The authors declare no competing interests related to the publication of this research.

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