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The Implementation of Methanogenesis Reaction for Chemistry Subject on Senior High School Using Chemistry, Life, Universe and Everything (Clue) Approach

Nur Azlina Oktavianti[1,2*], Muhamad Abdulkadir Martoprawiro[3], Badra Sanditya Rattyananda[4]

[1] Magister of Teaching Chemistry, Faculty of Math and Natural Science, Bandung Institute of Technology, Bandung, Indonesia.
[2] Vocational State High School 1, North Tambusai, Rokan Hulu Regency, Riau Province, Indonesia.
[3] Inorganic and Physical Chemistry Laboratory, Faculty of Math and Natural Science, Bandung Institute of Technology, Bandung, Indonesia.
[4] National Research and Innovation Agency (BRIN), Bandung, Indonesia.

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Corresponding Author:
NurAzlinaOktavianti
nuroktavianti70@guru.smk.belajar.id

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Abstract: Palm Oil Mill Effluent (POME) is the biggest waste from palm oil production. This liquid waste contain much methane gas (CH_4) which has potential as renewable energy, namely biogas. The last stage of processing biogas called methanogenesis reaction, the process of synthesis methane and carbon dioxide. The methanogenesis reaction can be studied by computational studies as learning media source for SeniorHigh School Chemistry with the Chemistry, Life, Universe, and Everything (CLUE) approach. According to learning outcomes of Merdeka Curriculum, the methanogenesis reaction can be used as a learning source forthree chapters in F phase. The chapters areChemical Bonding, Rate of Reaction,and Thermochemistry. The chapter of Chemical Bonding describe hydrogen bonding in acetic acid intermediate species and its effect on the molecular characteristics. The chapter Rate of Reactiondiscuss the result of computational calculation to determine the activation energy (AE). Methanogenesis reaction have two transition states (TS), with AE of each TS are 228.56 kJ.mol^{-1} and 281.31 kJ.mol^{-1}, while the second stage act as the rate-determining step. The last, for Thermochemistry chapter, the content material is define the quantity of thermodynamic variables on methanogenesis reaction.The value ofΔS = 50.14 kJ.mol^{-1}T, ΔG = 139.7 kJ.mol^{-1}, and ΔH =168.84 kJ.mol^{-1}.

Keywords: CLUE; Computational study; Methanogenesis reaction; POME

Introduction

In 2022, the Indonesian of Ministry Education and Culture released the Merdeka Curriculum with anew programme called Pancasila Student Profile Strengthening Project (P5), which aims to develop students character to think critically and be able to solve the problems in their environment with a project-based learning and correlate with Pancasila's characters(Irawati et al., 2022; Nurhayatiet al., 2022; Nurmawanti et al., 2023; Dasmo, et al., 2023). Sustainability Lifestyle is one of the topics that can be discussed for P5 at the Senior High Schoollevel. This theme encourages students how to analyze the impacts of daily human activities to the environment (Rusnainiet al., 2021; Muaziyahet al., 2023).

The related issue with the Sustainability Lifestyle topic is waste management. The waste issue isa common problem for every region, include in Riau Province with industrial waste from palm oil production.In addition, this province has approximately 2.89 million hectares of oil palm plantations, the largest oil palm plantation area in Indonesia (BPS Riau Province, 2020; Syahza, 2020; Descals, 2020). Furthermore, the problems aboutPalm Oil Industry wastecan be discussed as student project topic and learning sources,because it known as local

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knowledge and relevant with student's environment (Tahyaet al., 2022).

One of the significant waste frompalm oil industryis liquid waste called Palm Oil Mill Effluent (POME), approximately 70-80% from total waste (Lam & Lee, 2011; Nuryadiet al., 2019). According to Saleh, et al. (2012), this waste contains methane and carbon dioxide gases, whichcaused greenhouse effects. However, POME waste is also classified as biomass, one of the renewable energy source, that can be converted into biogas(Ahmad et al., 2016; Aziz et al., 2020).

The processing of POME into biogas involves four distinct phases of reaction: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Winanti et al., 2019). The whole reaction process occurs in a closed system and involves anaerobic bacteria(Choon et al., 2018; Mao et al., 2015). One of the stages is the methanogenesis reaction, the final reaction of converting POME waste to biogas (Woraruthai et al., 2020). Methanogenesis reactions can take place in several reaction mechanism pathways, one of them is reaction between acetate ion and water molecule (Li et al., 2019).

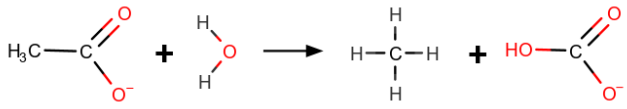


Figure 1. Methanogenesis reaction between acetate ion and water

Since the methanogenesis reaction occurs with the presence of bacteria, it is possible to predict the mechanism reactions if without bacteria. An approach that can be learn is through computational studies.Computational studies can be applied to predict the reaction mechanism. Computational studies for chemistryalso provide information about the mechanisms and energies along the chemical reactions(Snyder &Kucukkal, 2021; Mustika et al., 2022). Furthermore, computational offer a visualization to construct understanding about representation levels on chemistry, such as macroscopic, symbolic and and submicroscopic (Daninet al., 2023). For example, computational offers visualization how molecule bonds are rearranging while the reaction occurs.

The outcomes of computational calculations on methanogenesis reactions can be utilized as a learningsource forsenior high schoolchemistrymaterial and as preliminary material for P5 activities. The method that been usedto determine the mapping chemistry content with methanogenesis reaction is Chemistry, Life, Universe, and Everything (CLUE)approach. This method was developed by Melaney Copper and Klymkowski, focusing on integrating chemistry materials with daily life phenomena to achieve a coherent and holistic comprehension(Cooper &Klymkowsky, 2013). CLUE divides Chemistry into four fundamental topics: Bonding and Interaction (BI), Structure and Properties (SP), Energy (E), and Change and Stability (CS) (Cooper, et al., 2019). So, the chemistry material that relate methanogenesis reaction will classified into topics in CLUE approach.

Method

This research uses two methods: the computational study to calculate the energy of the methanogenesis reaction and the literature review to determine the relevance between chemistry for high school and the result of computational study.

Software

Computational studyfor the methanogenesis reaction mechanism using several software applications: Avogadro (ver. 1.90) for drawing molecules(Hanwell et al., 2012), Notepad++ (ver. 7.9.2) for editing command scripts, ORCA (ver. 5.0.1) for quantum chemical simulation(Neese, 2022; Neese et al., 2020), Termius (ver. 7.47.2) to connect a PC to a network host, and Chemcraft (ver. b592b) to visualize the results of quantum chemical calculations.

Procedure

This research begins with computational calculation on methanogenesis reaction, then the result of calculation is analyzed with CLUE approach. The outcome is used as source of chemistry learning in senior high school that applicable with P5 program.

Thecomputational calculation starts with determining the optimal structure of the species in the methanogenesis reaction. B3LYP def2-SVP is used as the functional theory and basis set. The implicit solvent water is inserted to make the research as realistic as possible. The results of a structure optimization is continued with the search for transition states and intermediate compounds which is formed during the reaction. The energetic data obtained from the transition state can be utilized to determine the activation energy, spontaneousity of reaction, and type of reaction (whether exothermic or endothermic).

The result of calculation, including energetic data and reaction mechanism visualization, is modified to correlate for the high school chemistry syllabus. The material is relate with the competence of the syllabus in the Merdeka Curriculum, specifically for Phase F in XI and XII grade.Since the Merdeka Curriculum only

provides Learning Outcomes in each phase, the material development is driven by the Revised 2013 Curriculum's Basic Competencies. Basic Competencies are derived from Permendikbud No. 37 of 2008 regarding Core Competencies and Basic Competencies in the 2013 Curriculum Revision. Moreover, the learning sourcefrom methanogenesis reaction also considers from the main topic of the CLUE approach.

Resultand Discussion

The outcome ofcomputational calculation on methanogenesis reactions is used as chemistry course material in high school, particularly for the XI grade. The chapters such as, Chemical Bonding, Rate of Reaction and Thermochemistry are correlated with the computational result. These chapters are associatedwith the main topics of the CLUE approach, especially:Structure, Intermolecular Bonding and Properties; Change and Stability (CS); and Energy (E). The flow diagram that shown the relevance between chemistry materialand CLUE approach, can be seen in Figure 1.

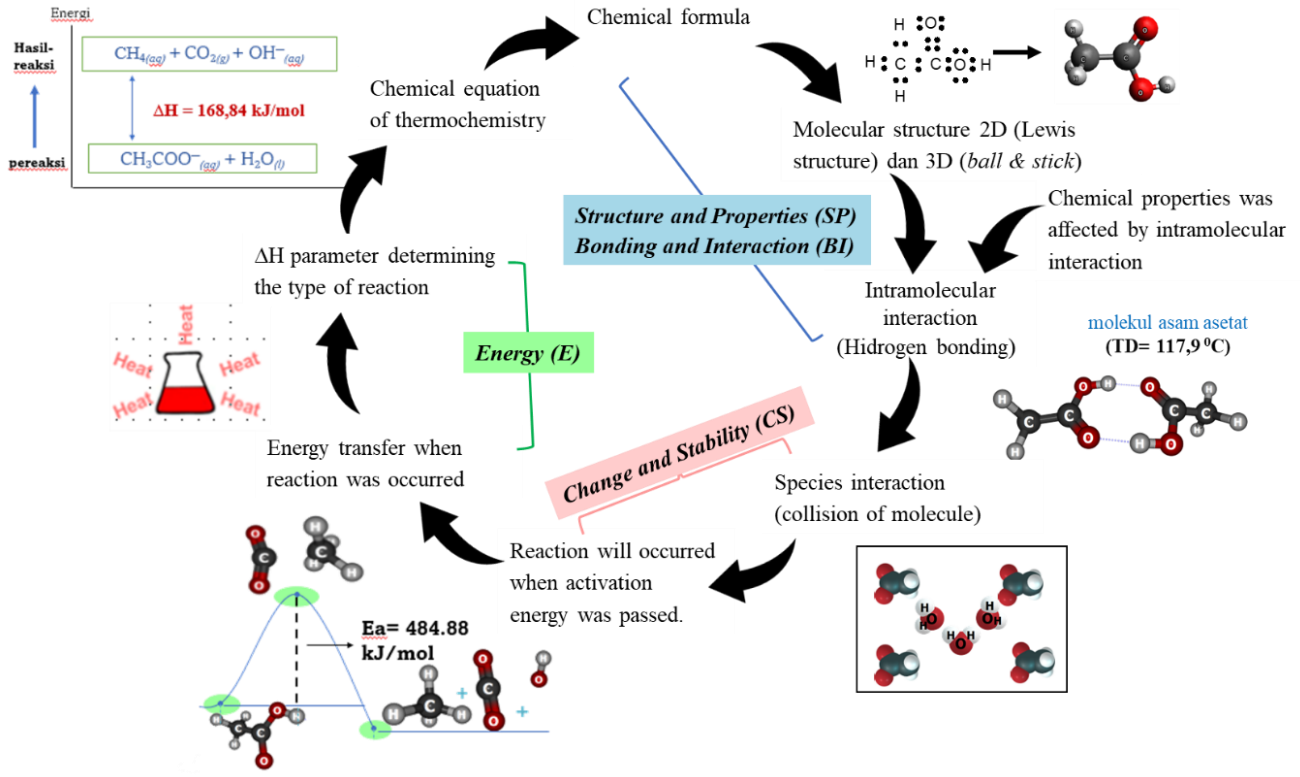


Figure 2. CLUE diagram for methanogenesis reaction

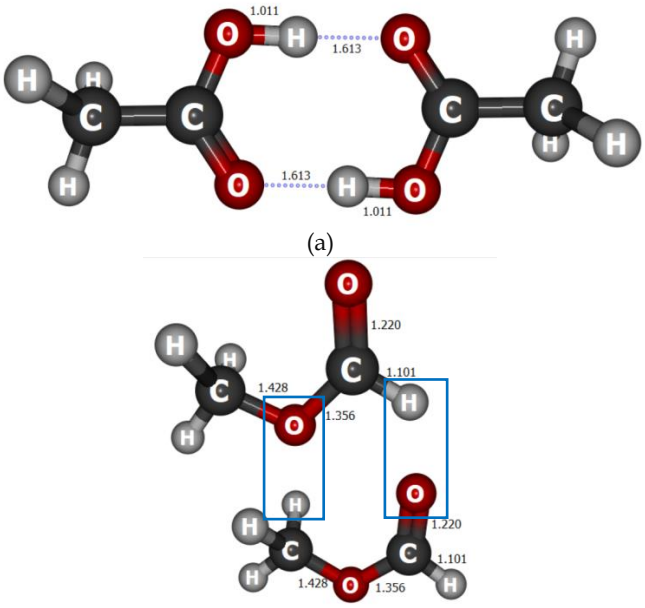
Structure, Intermolecular Bonding and Properties

Bonding and Interaction (BI) and Structure and Properties (SP) are the main CLUE topics discussed in this section. This primary topic discusses the impact of intermolecular bonds on the properties of compounds involved in methanogenesis reactions. The intermolecular bonding material is discussed in the chapter Chemical Bonding of the High School Chemistry material. Acetic acid and water are the species that discussed for this topic. Acetic acid is an intermediate, whereas water is a reactant.

Both water and acetic acid have intermolecular interactions of hydrogen bonds. This bond gives both molecules high boiling point because need additional energy to break the bonds of these intermolecular interactions.This evidence can be use to describe physical properties of water species and acetic acid. Although water molecules have a small relative molecular mass (Mr), 18 gr/mol, it has a boiling point closes to acetic acid (Mr = 60.05 gr/mol).The boiling points of water and acetic acid at room temperature are 100^0C and 117.9^0C. It is due to water molecule have hydrogen bonding stronger than acetic acid.The hydrogen bonds of them represent in Figure 2.

Furthermore, acetic acid is compared with methyl formate to proofthe correlation of hydrogen bonds on the properties of compounds. Both of these compounds have the samefunctional groupsand molecular formula, $C_2H_4O_2$. However, the boiling points of the two are quite far apart. The boiling point of acetic acid is 117.9^0C, while methyl formate around 32^0C. The high boiling point of acetic acid is because this compound

can form hydrogen bond (Figure 3a), while methyl formate doesn't have it (Figure 3b). Computational studies can provide data in the form of comparisons of bond lengths in these compound. For example, the length of the O-H bond in an acetic acid compound is 1.011 Å, while the distance of the O-H in the hydrogen bond is 1.613 Å.

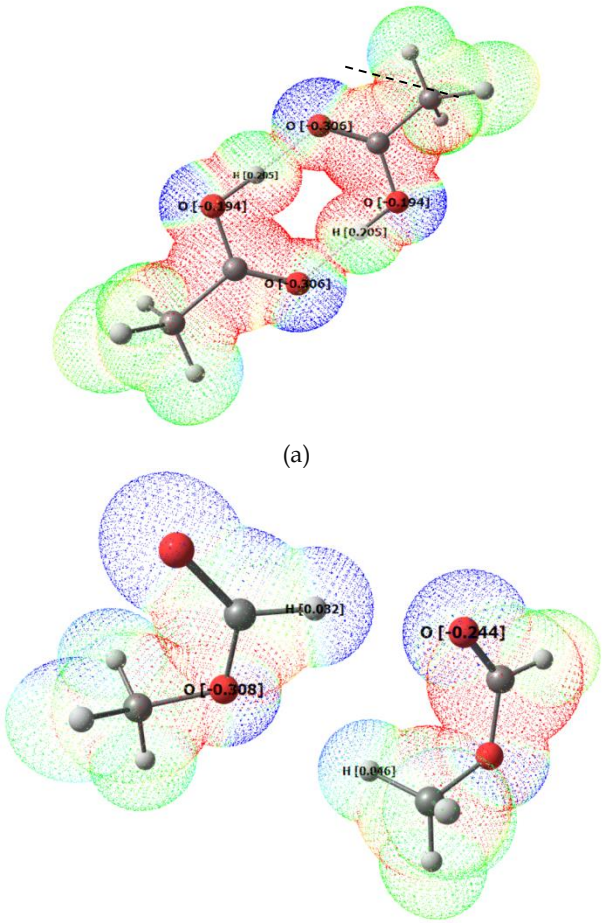


(a)

(b)

Figure 3. Interaction between 2 molecules of: (a) acetic acid compound which generated hydrogen bond and (b) Methyl Formatewhich haven't hydrogen bond

A common misconception by the student about hydrogen bonding is that it happens when the H atom reacts with a more electronegative atom (such as F, O, or N). Moreover, there is an additional requirementthat the H atom must also be bonded to a electronegative atom so that the H atom's characteristics are more positive such as interaction between 2 acetic acid molecules which showed on figure 4.(a). However, if the H atom is bonded to a less electronegative C atom like interaction between 2 methyl formate which showed on figure 4.(b), there will be no hydrogen bonding between the H atom.



(a)

(b)

Figure 4. Electrostatic potential surfaces and charge of hydrogen between 2 molecules of (a) acetic acid and (b) methyl formate

Change and Stability (CS)

The subject matter explained for the core topic of CS is Reaction Rate. The material described focuses on collision energy and the relationship between collision energy and activation energy. Since the reaction occurs stepwise, students will also be introduced to theterms such as, intermediate, transition states and their differences.

The results of computational calculations of methanogenesis reactions show that this reaction can occurs by stepwise mechanisms. The reaction occurs in 2 reaction stages, producing 2 transition states and 1 intermediate compound. The reaction step showed on figure below:

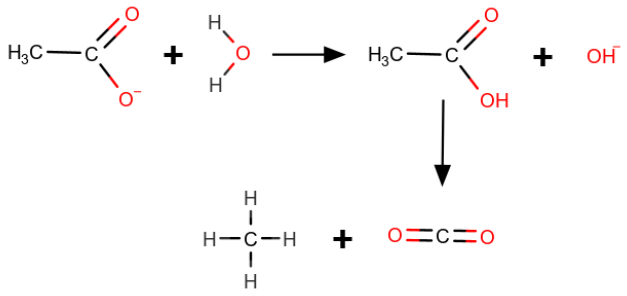
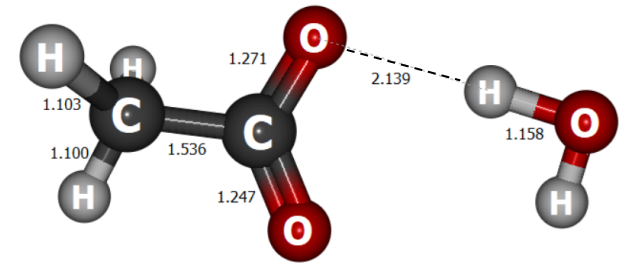
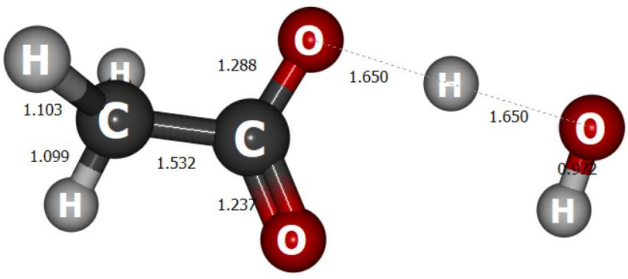


Figure 5. Stepwise methanogenesis reaction scheme

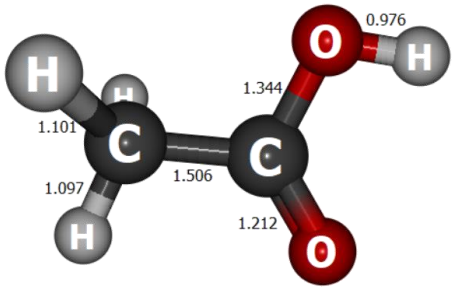
A *transition state*is defined as the configuration of a compound at a reaction coordinate. This compound is characterized by a short time appearance and an unstable state. Typically, on the energy graph, the transition state has the highest energy level compared to other species because, under this condition, there is a rearrangement of chemical bonds, as seen in Figure 6. In the transition state, the atom is preparing to react,so the position of bonding is between the release and joining of the bond, which is depicted with an imaginary line.



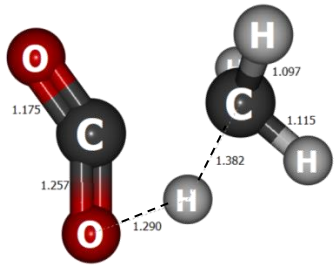
Reactant



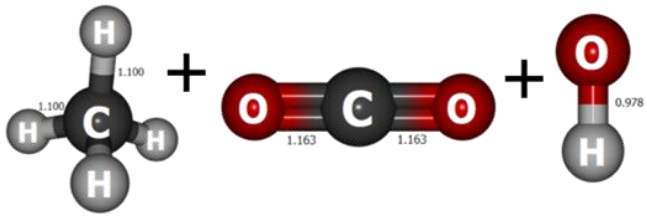
Transition state-1



Intermediete



Transition state-2



Product

Figure 6. The species structure of methanogenesis reaction

Meanwhile the *intermediate compounds* are species which is formed before the reactant forms the product. The difference between intermediate and transition state is intermediate more stable and can sometimes be used as side-products other than the main product. In writing the total reaction equation, intermediate compounds can be removed because they will undergo further reactions to form products. In this methanogenesis reaction, the intermediate compound is acetic acid, which results from the first stage reaction. Acetic acid will then decompose to produce methane gas and carbon dioxide. The comparison of reactant structure, transition state-1, transition state-2, intermediate and product can be seen in Figure 6. While the energy graph resulting from the methanogenesis reaction can be seen in Figure 7.

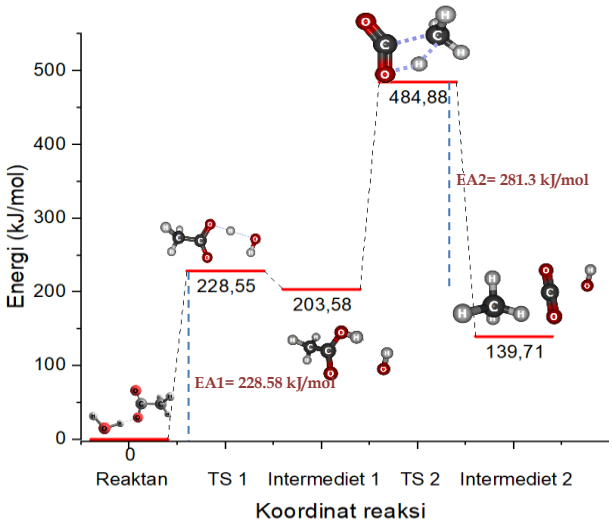


Figure 7. Energy graph of methanogenesis reaction

The first stage of the methanogenesis reaction occurs following the equilibrium principle, namely the acid-hydrolysis reaction. This reaction has an activation energy of 228.58 kJ/mol. This activation energy is lower than the activation energy of the acetic acid decomposition reaction in the second stage, which is 281.3 kJ/mol. The high activation energy of the second stage indicates that the reaction stage of methane gas formation is a rate-determining state because, at this stage, the reaction proceeds slowly.

Energy (E)

Computational studies also provide data related to changes in Gibbs free energy (ΔG), changes in entropy (ΔS) and changes in enthalpy (ΔH). The value of the ΔG value of this reaction is 139.7 kJ/mol, which indicates that this reaction does not proceed spontaneously at room temperature. The acetic acid decomposition reaction can only run at temperatures around 500K – 700K (Li et al.,2017). While calculations in computational studies follow standard states (STP) to assess the probability of reactions at room temperature. In fact, with the help of bacteria, this reaction can occur in a closed digester at a temperature of 310 K (Woraruthaiet al., 2020).

The second thermodynamic variable is ΔS of 50.14 kJ/molT. This increase in entropy value is due to the products formed, namely methane and carbon dioxide, both in gaseous phases. Because the phase the reactant is liquid while the product is gases, so the entropy value in the methanogenesis reaction increases. Gas molecules have random movements that increasing the quantity of entropy.

The last variable is ΔH of 168.84 kJ/mol, which indicates that the methanogenesis reaction is exothermic. The energy diagram of the methanogenesis reaction can be seen in Figure 8. Although it has been mentioned that methanogenesis reactions cannot take place spontaneously (ΔG>0).In fact, methanogenesis reactions can occur under two circumstances. In the first state, the reaction is endothermic (ΔS>0 and ΔH>0). In this case, the methanogenesis reaction can take place better if there is an increase in heat in the system. The second state is that the reaction is exothermic (ΔS<0 and ΔH<0); this is because insufficient concentrations of the reactants forming acetate ions (resulting from hydrolysis and acidogenesis reactions) inhibit the formation of acetate ions. The computational studies follow the initial endothermic and entropy-price positive case (Oh & Martin, 2010).

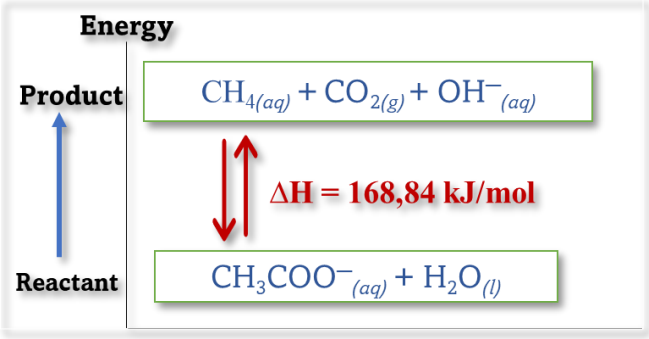


Figure 8. Exotherm energy diagram of methanogenesis reaction

Conclusion

The results of computational studies on methanogenesis reactions can be used as teaching materials for XI grade onsenior high school using the CLUE approach. The Chemistry material discussed along with the relevant CLUE core topics: Chemical Bonding for Structure, Intermolecular Bonding and Properties (BI-SP), Rate of Reaction Chapter for Change and Stability (CS), also Thermochemistry for Energy (E). The computational study provide the visualization of hydrogen bonding in acetic acid and proof their effect on molecular properties. In the chapter Rate of Reaction, computational study alsogive calculation for activation energy data in two transition states that form along the reaction, approximately 228.56 kJ.mol^{-1} and 281.31 kJ.mol^{-1}, with the reaction rate of the second stage as the rate-determining step. The final chapter on thermochemistry focuses on thermodynamic variables resulting from methanogenesis reactions, including S = 50.14 kJ.mol^{-1}T^{-1}, G = 139.7 kJ.mol^{-1}, and H = 168.84 kJ.mol^{-1}.

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Author Contributions

Nur Azlina Oktavianti was the main writer of this research, Muhamad A. Martoprawirowasthe corresponding author supervisor, and BadraSandityaRattyanandadid many parts of this research simulation.All Author wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

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Conflicts of Interest

The authors declare no conflict of interestin this paper publication process. All the author was the first contributor and if in future have any discrepancies were found, we were willing to be responsible for the discrepancies.

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