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The transformation of palm oil mill effluents via anaerobic fermentation for yield bioethanol production

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ABSTRACT:
The focal point lies in biomass, an innovative element that holds promise as a substrate for the generation of biofuels. This has spurred a concerted global effort towards replacing conventional liquid fossil fuels with sustainable and renewable alternatives. The investigation into biomass, a distinct material suitable for biofuel production, has emerged as a worldwide imperative. Through anaerobic treatment of highly concentrated organic wastewater, such as palm oil mill discharge, bioethanol can be derived, offering a viable substitute for food-based raw materials in the utilization of agricultural and industrial residues for alternative energy production. Processes involving acidogenic degradation also offer avenues for bioethanol production. In the acidogenic phase of organic decomposition, bioethanol synthesis becomes feasible. In this study, palm oil mill discharges are subjected to treatment in an anaerobic circulating batch reactor (CBR) for 72 hours under varying pH conditions (5, 6, and 7), utilizing a substrate with a chemical oxygen demand (COD) concentration of 27,400 mg/L and employing mixed bacterial cultures as biomass. Acidogenesis byproducts are monitored at six-hour intervals during sampling. Notably, the reactor operating under pH 5 conditions exhibits the highest bioethanol production efficiency within the 12-hour duration of the process, yielding a highest output rate of 9,89 mgCOD/L/hour and resulting in 102,94 mgCOD/L bioethanol production.

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I. INTRODUCTION

Fossil fuels represent a finite energy resource that is anticipated to be depleted in the foreseeable future. Consequently, the imperative for exploring alternatives to fossil fuels arises, not only to address the looming issue of resource scarcity but also to mitigate carbon emissions. [1]. Scholarly investigation into biofuels centers on methodologies of production, operational efficiency, environmental ramifications, and their viability as a renewable energy solution. [2], [3]. The utilization of bioconversion techniques significantly contributes to the advancement of renewable energy, particularly in the production of bioethanol, derived from the fermentation of biomass like lignocellulose, serves as a viable renewable fuel source, [1], [2], [4] offering an alternative to fossil fuels and mitigating dependence on non-renewable energy resources.

The conversion of palm oil mill discharges biomass into energy (bioethanol) encourages institutions/researchers to use the bioconversion process method optimally. However, bioethanol research has made it difficult for researchers to obtain maximum conversion results because it is influenced by complex factors when using sources from biomass. Research sourced from palm oil mill discharges to bioenergy generally tends to the results of biogas and biohydrogen research, [5], [6], [7]. Biomass that contains high organic content can be used as a substrate for bioconversion to ethanol (through switching acidogenesis pathways). Biomass that has a high organic content helps researchers in developing as a substrate for the formation of biofuels such as ethanol, methanol, and hydrogen [8]. Bioethanol contributes to overcoming fossil fuel dependence, thus answering the challenges of renewable energy This opens up new opportunities for researchers in obtaining suitable biomass to be converted into bioethanol.

Prior studies have demonstrated the feasibility of utilizing wastewater characterized by elevated organic content as a substrate for bioethanol production through anaerobic processes employing mixed bacterial cultures. Palm oil mill discharge represents a notable example of such wastewater, distinguished by its substantial concentrations of organic constituents including carbohydrates, proteins, oils, and fats are accompanied by heightened levels of mineral constituents and organic substance, notably cellulose, and hemicellulose. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values in palm oil mill discharges typically range from 24,500 to 70,514 mg/L and 45,200 to 110,245 mg/L, including both [9]. The utilization of wastewater characterized by a high organic content presents an opportunity for the bioconversion process, facilitating the production of biofuels such as ethanol, methanol, and hydrogen. This experiment is governed by the anaerobic pathway, which unfolds in four distinct stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. [10], [11], [12]

During the acidogenic phase, ethanol and its derivatives are generated. It has been previously noted that ethanol production by anaerobic bacterial mixed cultures is accompanied by the formation of diverse by-products. Minimizing the production of these by-products is essential to enhance the efficiency of ethanol formation and overall product yield. It is widely acknowledged that the pH of the medium exerts significant influence not only on microbial growth and fermentation rate but also on the yield of end products. [11], [13]. Nevertheless, the intricate matrix comprising starch, protein, and oil/fat has received limited scholarly attention. Therefore, this investigation seeks to elucidate the attributes of the extant palm oil mill discharge with the specific aim of assessing the influence of pH regulation on bioethanol production.

II. MATERIALS AND METHODS

Organic wastewater discharge

The initial sample of untreated palm oil mill discharge was procured from the influent basin at the facilities of PT. Condong Garut, located in Bandung city, Indonesia. For the purposes of this investigation, a composite biomass sample was obtained from the sludge of the palm oil mill discharges and cow rumen as mixed culture bacteria, with a proportionate ratio. Subsequently, this biomass underwent an acclimation process to adapt to the palm oil mill discharges environment. The resultant acclimated biomass, characterized by mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS), exhibited concentrations of approximately 954 mg/L and 4860 mg/L, respectively, and was utilized in the anaerobic batch reactor experiments.

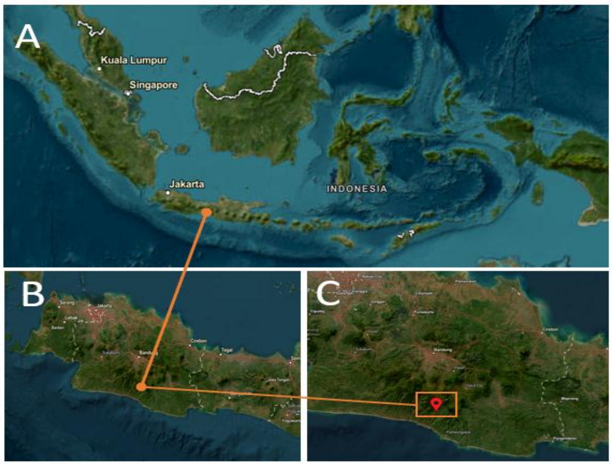

Fig. 1 Sampling site at PT Condong Garut, Bandung

Analytical methods and reactor

Biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), oil and grease content, total nitrogen concentration, and pH level were assessed utilizing established methodologies. Bioethanol quantification was conducted employing a GC Shimadzu flame ionization detection.

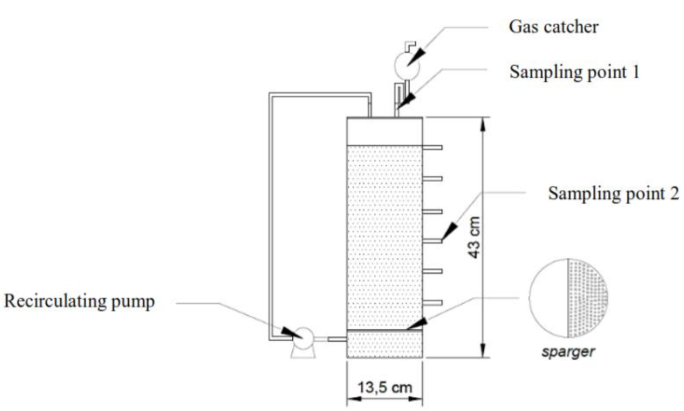

Fig. 2 Scheme for the experimental setup.

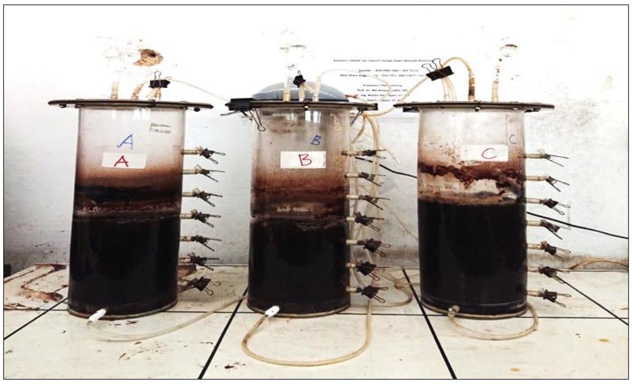

Fig. 3 Anaerobic circular batch reactor on a laboratory scale (CBR)

Experimental design

Anaerobic batch reactors, each having a working volume of 5 liters, were subjected to a continuous N2 flushing rate of 1 liter per minute for a duration of 24 hours, followed by an additional 72 hours of operation fueled by internal biogas generation (refer to Figure 1). The reactors were initially loaded with a mixture comprising 20% (v/v), equivalent to 1 liter, of a diverse mixed bacterial culture and 70% (v/v), equivalent to 4 liters, of palm oil mill discharge as the substrate for subsequent anaerobic processing. The experimental setup involved three reactors denoted as (A), (B), and (C), each maintaining distinct pH conditions, specifically pH 5, pH 6, and pH 7, respectively. All reactors underwent identical treatments for comparative analysis.

Calculation

Mass balance analysis was employed to quantify the substrate conversion leading to the production of bioethanol during fermentation, facilitating the examination of the effects of pH variation and sterilized substrate on the bioethanol synthesis pathway. The calculation of this analysis involved converting each acidogenic product into its equivalent theoretical soluble chemical oxygen demand (COD), following the methodology outlined by Haandel and Der Lubbe. Expressed in Equation 1

$$COD_{theoretical} = 8\cdot(4x+y-2z) / (12x+y+16z) \text{ gCOD.g-1 CxHyOz} \quad (1)$$

where:
x = C; y =H and z = O.

$$DE = \frac{(\text{Ethanol})}{influent\ of\ soluble\ COD} \frac{[\text{mgCOD/L}]}{[\text{mgCOD/L}]} \quad (2)$$

DE = Degree of ethanol

$$\text{Formation flowrate (mgCOD/L/hour)} \ \frac{[Product\ concentration_{end} - Initial\ concentration_{in}]}{\text{time}} \frac{[\text{mgCOD/L}]}{[\text{hour}]} \quad (3)$$

III. RESULTS AND DISCUSSION

In this investigation, the wastewater utilized originated from the palm oil mill discharge, subsequently subjected to analytical scrutiny to ascertain its fundamental properties. The findings of the wastewater analysis are delineated in Table 1. The waste slated for treatment exhibited total COD concentrations of 27,400 mg/L and dissolved COD of 5400 mg/L. Subsequently, the waste was introduced into the Circulating Bed Reactor for further processing.

Table 1. The properties of palm oil mill wastewater

Parameter	Unit	Results
Acidity level (pH)	-	3,98
Soluble COD	mg/L	5,400
Total COD	mg/L	27,400
BOD	mg/L	7.600
Volatile fatty acids (VFA)	mg/L	70,562
Nitrogen Total	mg/L -N	224

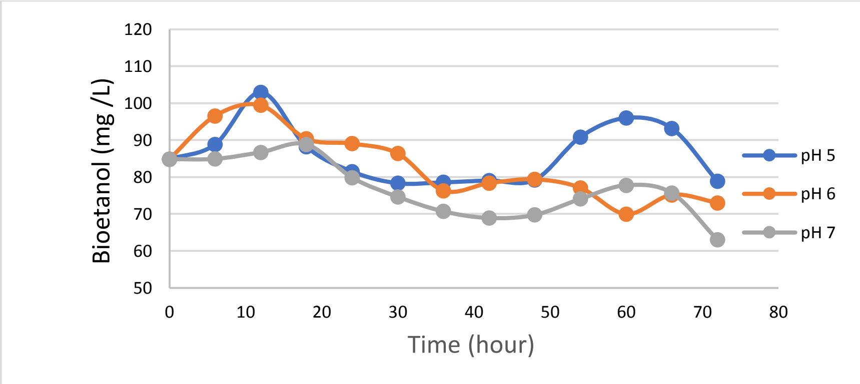

Fig. 4 Research Findings on Bioethanol synthesis by pH variations

Figure 4 illustrates a notable trend of increasing bioethanol concentration across all reactors. Bioethanol synthesis commenced approximately 12 hours post-inoculation in each reactor, under varying pH conditions. The reactor exhibiting a pH variation of 5 demonstrated the highest bioethanol yield, reaching 105,89 mg/L, with a degree of ethanol of 0.037 mg/L, and a maximum production rate of 9,84 mg/L/hr. Bioethanol concentration exhibited a steady increase until the 12-hour mark. Similar trends were observed across other pH conditions, wherein bioethanol concentration peaked at 12 hours before stabilizing. Reactors with pH levels of 6 and 7 yielded lower bioethanol concentrations compared to the pH 5 reactor. Specifically, the highest bioethanol concentration achieved at pH 6 was 99.58 mg/L, with a production rate of 3.23 mg/L/hr. Meanwhile, the pH 7 reactor recorded a peak concentration of 87.98 mg/L, with a flowrate of 1.27 mg/L/hr. Variations in the synthesis of bioethanol were ascribed to environmental variables including thermal condition, acidity level, levels of dissolved oxygen, and the presence of enzyme regulators. [14] and Nitrogen flushing has the potential to induce a metabolic shift favouring the generation of acetyl CoA, subsequently facilitating its oxidation into bioethanol via the action of alcohol dehydrogenase enzyme. [15].

The pH 5 condition was previously investigated using a mixed culture of bacteria obtained from the thickener of a sewage treatment plant [16]. The research revealed that bioethanol production reached 102,94 ± 79.26 mg/L, attain at a Retention Time of nine hours. Moreover, under the pH 6 condition, the utilization of the identical substrate, when subjected to a combination of micronutrient supplementation and 24-hour Nitrogen flushing, resulted in the highest bioethanol concentration of 99.44 mg/L, with a peak flowrate production of 3.23 mg/L/hr. The outcomes derived from the calculation of volatile acids and their corresponding levels of acidogenesis throughout the investigative inquiry are depicted in Figures 5 and 6. **Figure 5 – 6**

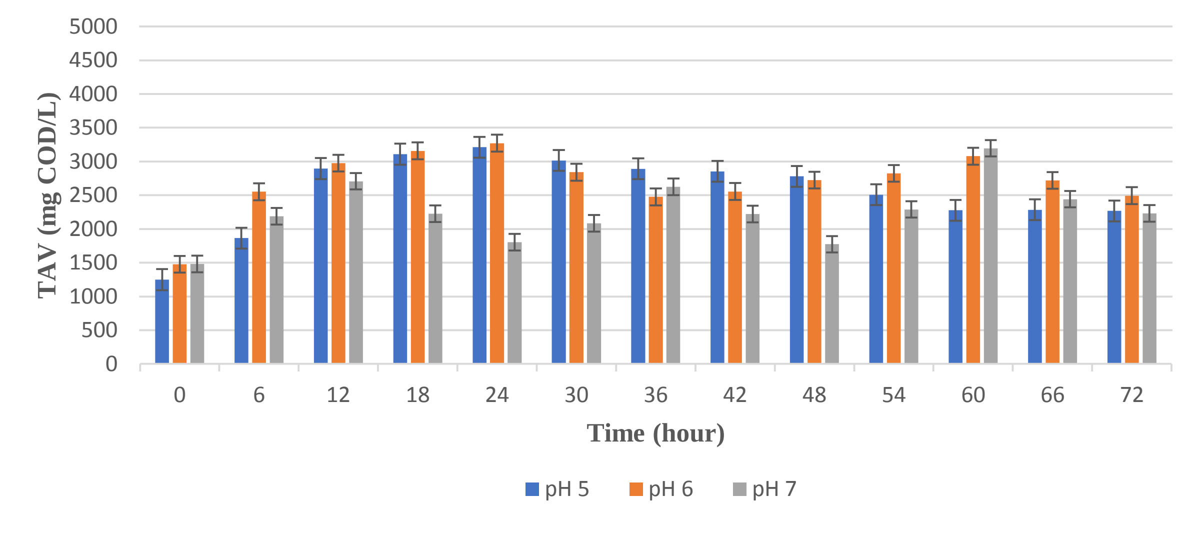

Fig. 5 Research Findings on Acidity level (pH) Variations and Total Volatile Acid (mgCOD/L)

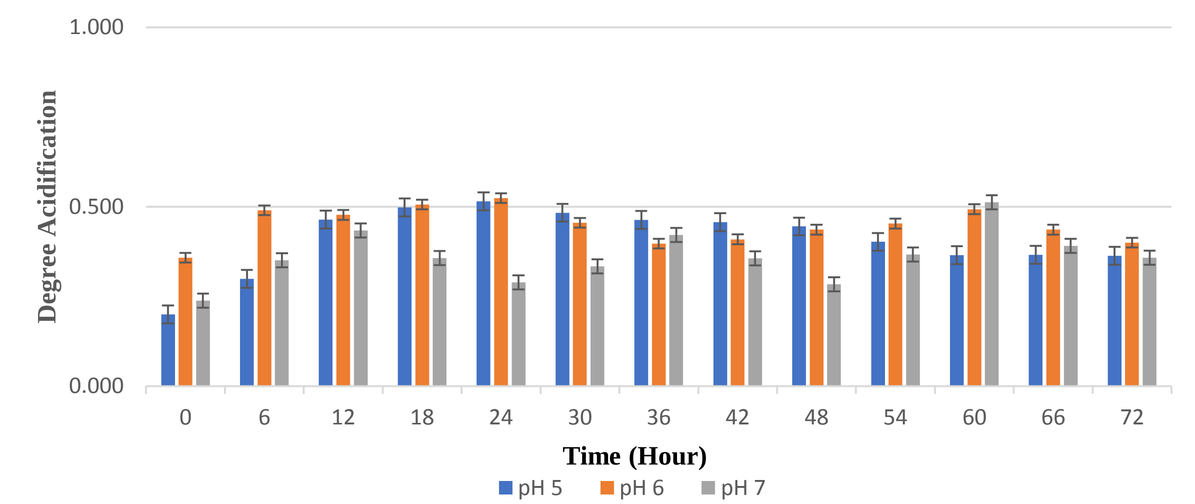

Fig. 6 Research findings on degree of acidification of Acidity level (pH)

IV. CONCLUSION

According to the findings of this investigation, the pH level of 5 significantly influences the production of Bioethanol. Analysis of the properties of effluent discharged from palm oil mills indicates that the optimal duration for bioethanol synthesis is 12 hours, resulting in a Bioethanol fixation of 0.037 mg/L and a increased rate production of 9.89 mg/L/hour, leading to a bioethanol yield of 102.94 mg/L. Throughout the process, in addition to bioethanol, volatile acids are also generated. This suggests that palm oil mill discharges possess promising potential for the advancement of renewable fuel bioconversion technologies.

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