The effect of biogas desulfurization to acidity of lubricant oil of the biogas fuelled engine

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Abstract This research is established for the purpose of the understanding the stability of the acidity of lubricant oil in biogas fuelled engine due to the absence of hydrogen sulfide (H₂S). As was recognized that other than Methane (CH₄), there are also other gas impurities in the biogas such as carbon dioxide (CO₂), hydrogen sulfide (H₂S), moisture (H₂O) and ammonia (NH₃). Due to H₂S contents in the biogas fuel, the engine was found failure. This is caused by corrosion in the combustion chamber due to increase of lubricant acidity. To overcome this problem in practical, the lubricant is increased the pH to basic level with the hope will be decrease to normal value after several time use. Other method is by installing pH measurement sensor in the engine lubricant so that when lubricant is known turn to be acid, then lubricant replacement should be done. In this research, the effect of biogas desulfurization down to zero level to the acidity of lubricant oil in the four stroke engine was carried out with the hope that neutral lubrication oil to be available during running the engine. The result indicates that by eliminating H₂S due desulfurization process, effect on stability and neutrality of pH lubricant. By this method the engine safety can be obtained without often replacement the lubricant oil.

1. Introduction

Biogas is promoted to be a fuel for stationary engine. It is about not efficient to storage in the form of compressed biogas in the steel container as compression natural gas (CNG). The biogas is directly flowed from the digester to the temporally storage and continued to be injected as a fuel of the four stroke engine on site to run an electric generator. Pure methane is not possible to be obtained directly from anaerobic digestion process. The gas that is obtained (biogas) generally consist amount of trace such as water (H₂O), hydrogen sulfide (H₂S), and ammonia (NH₃). The main composition of biogas are methane (CH₄) and carbon dioxide (CO₂) [1,2].

The function of a lubricant in the engine or machine is to create a film as a barrier between moving mechanical parts. The function of this barrier is to reduce friction and wear. The lubricant also acts as a coolant, to prevent corrosion and avoiding harmful formation of deposit. The base oil that is used for lubricant can not cover all of these requirement. The additives are added to the lubricant formulation which include anti oxidant, anti wear, corrosion inhibitor, detergent and viscosity modifier [3]. The additive usually neutralize acidic components taht is generated during running the engine, and give effect on reducing corrosion. Additives also improve overall efficiency in the engine. To extend the lifetime of the lubricant is also become concern for the reason of efficiency [3]. The lubricant oil must free from components which corrode metal parts of an engine or a machine. High sulfur fuels such as biogas will generates by-products of acidic sulfate. The increase of oxidation and sulfating by-
products results in an increase in acidity levels and oil viscositys. These by-products increase the production of sludge and varnishes which significantly degrade lubrication performance[3]. Recently for practical purpose and simplicity, The company that produce biogas engine is completed the engine with special oil lubricant which has high basic number (BN) with the hope will act as reserve alkalinity which is to become neutral for several hour of operation [4]. But still the instability of oil viscosity need to be investigates if this technique will be a choice of the user. Other alternative that is develop to avoid biogas engine failure due to H$_2$S in the biogas fuel without any concern for elimination H$_2$S contents in biogas is by monitoring the oil acidification by using a chemical sensor. An early work regarding this method is developed by using copper film that was deposit on titanium [5]. This method was improved by using a sacrificial layer (600 nm of lead metal film) that is immersed into the oil. There will be a material loss due to corrosion. This material loss is monitored by measuring the capacitive coupling between sacrificial layer and readout electrodes[6]. Due to irregularity concentration of H$_2$S in the biogas, the acidity of lubricant will also have fluctuation and this condition can be monitored by using this method. The lubricant should be changed when the acidity reach its critical value [6]. This method is not addressed to prolong the life time of the lubricant.

Biogas desulfurization previously is not attracting attention in utilization of biogas as fuel of an engine. This condition was caused by limitation of appropriate technology for biogas desulfurizer. In the early work of utilization biogas as an engine fuel in china for example, the H$_2$S is ignored and let it burn in the combustion chamber. The system is simple by compressed in the cylinder than, passing trough mixer and mixed with diesel fuel [7]. It is sure then the engine will failure in the very soon.Recently, desulfurizer is known can be prepared even from waste material. Example for this idea is by using iron chips from manufacturing waste [8]. The chips just annealed and compacted, then biogas is flowed in to this filter. It was reported that this type of desulfurizer is possible for regenerative used [2]. Other example of using waste material for desulfurizer is by using zinc case from used zinc-carbon battery [9].This research is investigate and effect of eliminating H$_2$S from the biogas to the acidity of the lubricant of the biogas fuelled engine.

2. Experiment
The engine that was used for this purpose was non contact transistor ignition (TCI), 4-stroke biogas fuelled engine, inclined single cylinder, compression ratio 9:1, with displacement 196 cc. The engine was coupled with electric generator for capacity 1000 watt . The engine need about 0.5 litters lubricant oil during operation. The lubricant that was used for this purpose was SAE 10W30, with viscosity index 141, the colour was brown, density 0.8858 °Cg/cm$^3$, and flash point 218. The schematic of the experiment can be seen in Fig. 1. The biogas was produced in an anaerobic digester (1) and was streamed to the biogas desulfurizer (2). The biogas desulfurizer was made from iron or steel chips that was previously annealed and compacted to become a billet for easy installation and handling inside the pipe as explained in the previous publication [2]. The biogas that was released from desulfurizer was ensured to be free from H$_2$S impurities by using H$_2$S gas detector (3). If the H$_2$S still detected in the stream, then the billet of the iron chips is added in the desulfurizer. Biogas bag was prepared for biogas storage (4) and from here biogas was pumped to the part of the mixer in the biogas fuelled engine (5) to be mixed with oxygen from the air. The engine was let running for 100 hours. The engine was stopped running for every 10 hour, and the pH was measured with 3 time repetition for validity. The result is plotted in a graph and analyze.
3. Result and discussion

The engine is found still in good performance up to 100 hours operation and keep produce power up to its maximum capacity of 1000 watt. The desulfurizer working well and no H2S impurity is detected in the biogas. The result of pH measurement for 100 hour operation can be seen in Fig. 2. The fluctuation of the pH was about to found during early hour of operation until reach 50 running hour. The fluctuation range is from 7.6 the lowest and to reach 7.9 the highest. After passing 50 hour operation until final testing at 100 hours operation the pH is found stable around range 7.4 to 7.5. It can be understood that since the H2S is eliminated from the biogas, the other impurities that active is ammonia (NH3). With the moisture (H2O) existence in the biogas, the reaction between NH3 and H2O possible to occur with resulting fluctuation to more base following reaction in Equation 1.

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\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-
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(1)

The NH3 is polar molecules and have an ability to form hydrogen bonds. This give explanation related with high solubility of ammonia in water. The chemical reaction also occurs when ammonia dissolves in water. Ammonia acts as a base in aqueous solution, hydrogen ion is acquired from H2O to yield hydroxide ions (OH-) and ammonium (NH4+). The production of hydroxide ions when ammonia dissolves in water gives aqueous solutions of ammonia which have basic (alkaline) properties. From this stand point the, the operation of biogas fuelled engine give the user 3 options related with avoiding failure of the engine due to H2S corrosion. The 1st alternative is by using special oil lubricant that have performance as reserve alkalinity [10]. The price of the Lubricant may expensive since should be created for special purpose. The advantage of this alternative is, the lubricant replacement is not necessary to be conducted so often. The 2nd alternative is by mounting the chemical sensor of oil acidification [5,6]. This alternative gives the user an accurate time for oil replacement.
The oil that will be used may be regular oil that available in the market with reasonable price, but this alternative come with disadvantage that the oil should be replacement quite often. The environmental issue related with waste of used oil, and the sensor that is consumable may increase the cost for maintenance. The 3rd alternative is by installation of desulfurizer as was explained in this paper. This alternative gives opportunity to the user to use regular oil that available in the market with reasonable price. The oil replacement is not so often. And by recent development in biogas desulfurization technology, which make possible by using waste material [2] for desulfurizer, this can reduce the cost of production desulfurizer. The desulfurizer is also possible to be used repetitively. Other benefit is the biogas installation is free from dangerous and toxic H2S gas that may harmful if there is a leak in the installation system. It can be completed id this discussion that by progress in production of activated carbon [11], which is make availability of activated carbon with reasonable price, the system then can be improved with biogas purification from CO2 impurities to increase calorific value of biogas.

4. Conclusion
The biogas desulfurization give advantages in application of biogas as a fuel of an engine by keeping the pH of the Engine lubricant in neutral condition so that corrosion and engine failure can be avoided. This method make possible for the use of regular oil that available in the market with reasonable price. The replacement of the oil lubricant can be performed not so often. The method have more advantage because recent biogas desulfurization technology can be realize by using waste material such as iron chips which is available abundantly and can be use repetitively.

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