

Full Length Research Paper

Creation of alternative energy by bio- ethanol production from pineapple waste and the usage of its properties for engine

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The world is facing problems of fossil fuels depletion. The problem of using fossil fuels can have an environmental impact due to the oxidation of CO₂, SO₂ and NO_x emission. In order to overcome those problems, there is an alternative fuel that can replace fossil fuel such as bioethanol and biodiesel. Bioethanol can be derived from biomass with many different varieties of feedstocks such as corn, sugarcane, wood and fruits wastes that are renewable and sustainable resources, which are easily accessible and reliable and can help to clean the environment from the wastes. The experiment was conducted to prove that, bioethanol can be produced from rotten pineapples waste through the biochemical reaction called fermentation by commercial yeast, *Saccharomyces cerevisiae* which is suitable for running petrol engine. The influencing parameters that affect the production of bioethanol from pineapples wastes were optimized. The effects of pH, temperatures, fermentation period, substrate concentration with and without water, components of pineapples from rotten and fresh ones were investigated. From the results, the optimal yield of bioethanol in the parameters such as pH, temperatures, fermentation period, substrate concentrations was found to be 8.7% having pH 4 at 30°C using 3 g/l. The result for viscosity was found under American Society for Testing Materials (ASTM) standard in different concentration of yeast. The anhydrous ethanol was analyzed and it was found that, there was no dangerous element in its acceptability as a transportation fuel based on ASTM standard. The elements that were mostly contained in the samples of ethanol production from pineapples wastes were Fe, Cu, Sn, Mn, Ag, Mo, Zn, P, Ca, Mg, Si, Na, B and V, but there was no significant difference among all elements.

Key word: Bioethanol, waste pineapple, yeast, temperature, viscosity.

INTRODUCTION

Energy from the sun arrives and heats the earth mainly in the form of visible light (Infrared, IR). About 30% of the sunlight is scattered back into space, but the rest of it reaches the earth's surface with slow moving energy type (infrared radiation). Infrared radiation (IR) carries slowly a lot of air currents and green house gases (GHG) such as: water vapor, CO₂, ozone and methane, which delay its eventual escape into space. The atmosphere is warm by this mechanism and in turn, emits IR radiation with a portion of this energy which warms the surface and lower

atmosphere. As a result, the temperature of the earth could maintain about 30°C higher than it would be without atmospheric and reradiation of IR energy (Handerson-Sellers and Robinson, 1986; (Kellogg, 1996; Peixoto and Oort, 1992) . However, problems may arise when the atmosphere concentration of GHG increases. One of the causes of those problems is the burning of fossil fuels. When it is burnt, it could increase the net of CO₂, NO_x, SO_x etc. Energy consumption around the world has increased 17-fold in the last century as effects of the burning of fossil fuel mainly used in transportation sector, causes the primary atmospheric pollution. By oxidation of CO₂, SO₂, NO_x emission (Ture et al., 1997). IPCC (2001), it is reported that global temperature increased from

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1.4 to 5.8°C between 1990-2100. The emissions that have been producing fossil fuel burning can give bad impact to the human health. Carbon monoxide (CO) in large dosage can cause fatal heart disorders and affects the nervous system. Oxidation of CO also, can extremely cause disturbance of oxygen carrying in the blood by forming carboxy-hemoglobin. The other factor of distribution of the other alternative fuel is the continuous rising of petroleum price, due to the expansion of the transportation sector. Thus, the awareness of the researcher to create a new source of alternative fuel, that is, bioethanol from wastes such as pineapples wastes, will be used to convert invaluable product to valuable products as well as to clean the environment from wastes and reduce the pollution. Biofuels are substitute for petroleum fuels. It can be used alone or blends together with the petroleum (Demirbas 2002; Demirbas 2003). Biofuels give more benefit since it comes from renewable resources. It's sustainability reduces green house gas emission, regional development, social structure, agriculture and security supply (Demirbas 2006; Demirbas 2008; Unal and Alibas, 2007; Ikilic and Yucesu 2008). Pineapples waste have the potential for recycling in order to get valuable raw material, convert into useful and higher value products, food or feed after biological treatment and even as raw material for other industries (Kroyer, 1991). One example of raw material is pineapples waste that is converted to bioethanol production (Hossain et al., 2008). The wastes contain valuable components such as: sucrose, glucose, fructose and other nutrients (Sasaki et al. 1991; David et al., 2008). In addition, the conversion of pineapples waste to useful products such as ethanol production can help to clean the environment from wastes and also, it has economic usefulness, when the wastes are converted to valuable product. The objectives of this study were:

1. To know the extract bioethanol percentage from pineapple (*Ananas comosus*) waste through fermentation process using the yeast, *Saccharomyces cerevisiae*.
2. To clean the environment from rotten pineapples wastes.
3. To increase the biorenewable energy resources from the wastes.
4. To investigate the composition of trace elements of bioethanol and make sure that sample achieved the standard to prove that it can be use in petrol engine.

MATERIALS AND METHODS

The basic instrumentations used for this research were spectrophotometer, viscometer, titrator, multi element oil analyzer (MOA II), incubator, pH meter, water bath, conical flasks, schott bottles, water bath and volumetric flask.

Raw material

The fresh pineapples were bought from grocery at Bangsar. They

were kept at room temperature until it fully ripen and became rotten before undergoing the fermentation. These were washed before they were cut and chopped for fermentation to avoid other contamination.

Yeast

The microorganisms were obtained from the commercial supermarket (commercial dry yeast) and ABO lab. *S. cerevisiae* was used as yeast. 10% of water was added to it and it underwent warming in water bath at 40°C for 15 min.

Chemicals and reagents

The chemical reagents were purchased from Chemolab, the chemicals were sodium hydroxide (NaOH), hydrochloric acid (HCl) and Ethano assay reagent (potassium dichromate, sulfuric acid, diphenylcarbazine and 95% ethanol).

Fermentation

In order to produce bioethanol production, there are two methods which are via chemical analysis and fermentation. This research was focused on bioethanol production via fermentation by using yeast, *Saccharomyces cerevisiae*. The pineapples were bought from a supermarket at Bangsar and was left in the box at room temperature for 10 days to get it fully ripen and rotten. The pineapples were washed and chopped into smaller pieces together with the skin and were blended with the juice blender. After that, the juices were collected and then poured into 1 L schott bottle. The fresh weight was measured, while the total soluble solid (TSS) of samples was measured before fermentation.

The pH of the pineapples was measured. The original pH for pineapple was from range 3.6 to 3.8. The pH was adjusted from 5 to 5.8 using 5 M sodium hydroxide (NaOH) to increase the pH and 1 M acid hydrochloride (HCL) to decrease the pH. *S. cerevisiae* was added to the schott bottle that contained pineapples and it was shook afterwards. The fermentation was conducted in the incubator and it was set up at 30°C for 3 days. After 3 days, the samples were taken out from the incubator for filtration step.

Fermentation of pH parameter

The fermentation method of pH was same as previously stated. The pH of samples was adjusted to 4, 5 and 6.

Fermentation of yeast parameter concentration

The fermentation method of yeast concentration was same as stated above. The concentration of yeast was used as 1, 3 and 5 g/l.

Fermentation of temperatures

The fermentation method was same as stated above, instead of change in the temperatures to 28, 30 and 32°C.

Filtration

After 3 days, the samples were taken out from the incubator. The samples were filtrated by using cheese cloth and then poured to the

beaker that was covered with the cloth from the schott bottle. The samples filtrated through the cloth into the beaker and were left for approximately 2 h, until there was nothing coming out from it. The raw ethanol's yield was measured by ethanol assay using dichromate colorimetric method (Williams and Darwin, 1950), glucose content, pH and total soluble solid (TSS).

Ethanol yield calculation

Ethanol's yield was determined by the measurement of ethanol absorbance at 575 nm. After completion of the ethanol assay reagent step using spectrophotometry, it was compared to the ethanol standard graph that was used to calculate the percentage of bioethanol. Glucose content was calculated from basic glucose and ethanol equation by knowing the molecular weight of ethanol and glucose as well as ethanol's percentage.

Chemical analysis

The 3 parameters which are: 1) pulp, skin and mixture 2) concentration of yeast 3) rotten and fresh, were sent for chemical analysis (multi element oil analyzer (MOA) II) at the Faculty of Engineering in University of Malaya to measure the composition of elements in the bioethanol.

Viscosity analysis

Viscosity analysis for components of pineapples (skin, pulp and mixture) was sent to the Faculty of Engineering, University of Malaya to measure the viscosity. The samples of the concentration of yeast conducted in lab by Prof Datin and Dr. Aishah Salleh were put in the beaker and heated up at 40°C and were then measured with a viscometer. The viscometer is set with the rpm of 30, then the spindle with the size of 63 is used.

RESULTS AND DISCUSSION

Bioethanol yield was investigated at different pH content from rotten pineapple (Table 1). The bioethanol yield at pH 4 showed the highest with 7.8%, followed by pH 6 which slightly decreased to 7.48% and pH 5 at 7.43%. The range percentage of bioethanol production between pH 4 to 6 did not show the significant difference which only ranged from 7.43 - 7.8% of ethanol production. Ogunya et al. (2006) reported that the lower pH was found when the experiment was conducted at 3.4 and 4.1 which produced much greater of ethanol concentration as well as the rate of ethanol production from pineapples juices. The pH did not affect the ethanol's yield in the range of 3.5 to 6.0 when using pineapple effluent as substrates (Muttamara et al., 1982). Prior et al. (1981) found about 4% (v/v) bioethanol yield from pineapple cannery effluent when worked with pineapples wastes.

From Table 1, it can be stated that there was a significant variation at pH 6 before and after fermentation. At pH 4, before fermentation dropped slightly, the initial pH which was 4.26 finally reduced to 4.11. In the case of pH 5, the pH value decrease from 5.11 to 4.88 and also for pH 6, the pH values decreased gradually to 5.10. In

the case of Total Soluble Solid (TSS), the TSS values had showed significant difference before and after fermentation for all parameters of pH. At pH 4, TSS values were decreased from 13 to 4.03 and both pH 4 and 6, has same initial values of 13.1 which was reduced to 4.

According to the parameter stated in Table 2, the results of bioethanol production from different concentrations of yeast (1, 3 and 5 g/l), shows that *S. cerevisiae* were obtained. The bioethanol productions were linear to the concentration of yeast. As the concentration of yeast increases, higher percentages of bioethanol yield were produced. The 1 g/l concentration of yeast produced about 7.81% of ethanol yield, while 3 g/l produced about 7.96% and 5 g/l produced the highest of ethanol yield with 8.11%. Based on the results in Table 2, the pH values for all concentration of yeast were reduced after the fermentation. For 1 g/l, the pH values before fermentation was 5.67 and reduced to 4.74, while for 3 g/l, pH before fermentation was 5.71 but reduced to 4.69 and also for 5 g/l, pH values showed reduction from 5.58 to 4.97 after fermentation. For TSS values, all concentration of yeast showed the reduction of TSS after fermentation. Before fermentation, all concentration of yeast had same TSS value which was 12.8 and after the fermentation, 1 g/l reduced to 3.93 while 3 and 5 g/l reduced to 4. There was no significant difference of glucose (%) at different yeast concentration.

The percentages of bioethanol production were shown at different temperatures for 28, 30 and 32°C using rotten pineapples wastes fermented with yeast, *S. cerevisiae* (Table 3). It was observed that the maximum ethanol yield production was at temperature 30°C with 8.7%, followed by 32°C with 7.42% and at room temperature, 28°C produced 7.2% of ethanol yield that was the lowest among the parameters. Hence, the strain of yeast, *S. cerevisiae* was performed better at 30°C than other temperatures.

Kouakou et al. (2006) reported the ethanol concentration obtained at the range of 22.10 to 35.10 g/l at 25°C, 27.17 to 46.60 g/l at 30°C and 27.17 to 40.32 g/l at 32°C. Ogunya et al. (2005) reported that the ethanol concentrations of about 91.60% can get at temperatures of 27°C at pH 3.4 on pineapples juices. However, the ethanol concentration from 28°C at 48.71% is only about half of the Ogunya (2005) report. The experiment at 28°C produced the lowest yield compared to the others parameters which is 30 and 32°C. This is because, at low temperatures, the reaction rates of all metabolic functions was slowed down and it reduced the substrate and product diffusion rates for higher ethanol yields. However, this statement is not supported for experiments carried out at 30 and 32°C, where the ethanol yield obtained at 30°C was much higher than 32°C. From Tables 3 and 4, the pH values of the fermented pineapples for all samples of temperatures parameters were decreased gradually, in which the input of pH for 28, 30 and 32°C was 5.55, 5.56 and 5.57, but reduced to 4.30, 4.31 and 4.39, respectively.

Table 1. Showing the pH, total soluble solid in different pH parameters. Different letters (a, b) showed difference at 5% level of significant by least significant difference (LSD) test.

Parameter	Bioethanol yield (%)	pH		Total soluble solid (TSS)		Glucose content (%)
		Before	After	Before	After	
pH 4	7.8a	4.0a	4.26a	13a	4.03a	3.97a
pH 5	7.43a	5.0a	4.88a	13.1a	4.0a	3.78a
pH 6	7.48a	6.0ab	5.10a	13.1a	4.0a	3.80a

Table 2. Showing the pH, total soluble solid (TSS) and residue for parameter concentration of yeast. Same letters (a, a) showed no difference at 5% level of significant by least significant difference (LSD) test.

Parameter (g/l)	Bioethanol yield, (%)	pH		Total soluble solid (TSS)		Glucose (%)
		Before	After	Before	After	
1	7.81a	5.67a	4.74a	12.8a	3.93a	3.9a
3	7.96a	5.71a	4.69a	12.8a	4.0a	4.05a
5	8.11a	5.58a	4.97a	2.8a	4.0a	4.13a

Table 3. Showing the bioethanol yield, pH, total soluble solid (TSS) and glucose content in different temperatures. Same letters (a, a) showed no difference at 5% level of significant by least significant difference (LSD) test.

Parameter (°C)	Bioethanol yield (%)	pH		Total soluble solid (TSS)		Glucose (%)
		Before	After	Before	After	
28	7.2a	5.55a	4.30	11.1a	3.83a	3.67a
30	8.7b	5.56a	4.31	11.1a	4a	4.43a
32	7.42a	5.57a	4.39	11.1a	4.2a	3.78a

Table 4. Showing the viscosity of different concentrations of yeast at 40°C. Same letters (a, a) showed no difference at 5% level of significant by least significant difference (LSD) test.

Viscosity (g/l)	Value (cst)
1	2.4a
3	1.5b
5	1.5b

The TSS also decreased during the fermentation period in which the initial TSS was 11.1 for all temperatures of 28, 30 and 32°C and reduced to 3.83, 4 and 4.2, respectively. The residue for 28, 30 and 32°C were 23.43 g, 23.89 g and 23.05 g. Kouakou et al. (1984) reported the ethanol concentration obtained at the range of 22.10 to 35.10 g/l at 25°C, 27.17 to 46.60 g/l at 30°C and 27.17 to 40.32 g/l at 32°C. For viscosity analysis, components of pineapples and concentrations of yeast were measured. While for concentration of yeast, 1g/l of yeast had the highest value of viscosity with 2.4 cst and 3 and 5g/l had the same value of viscosity with 1.5 cst. The viscosities results were compared with research done by Ghobadian

et al. (2008) which measured the viscosity value of bio-ethanol with 1.1 cst. The viscosity of ethanol is 1.52 cst at 20°C (Sinor et al., 1993). From the results, all the samples had acceptance value of viscosity since it had a small value than the pure petrol and did meet the requirement of petrol standards. The anhydrous ethanol was blending with the petrol to get the results of lower viscosity and was suitably used for fuel engines. The lower fuel viscosity led to the greater pump and injector leakage which can reduce maximum fuel delivery and power output. Lower viscosity also, can overcome hot restart problems as insufficient fuel is injected at cracking speed, when fuel leakage in the high pressure pump is amplified due to the reduced viscosity of fuel.

Metal content

From the results, there are several additive metals present in samples of concentration of yeast (1, 3 and 5 g/l) which had been plotted in the graphs as stated in Figures 1a, b and c. Additive metal consists of Zinc (Zn), Phosphorus (P), Calcium (Ca), Magnesium (Mg) and Boron (B). The concentration of yeast, 3 g/l got the highest values for Zn concentration with 6 ppm, while

both 1 and 5 g/l shared the same values of Zn concentration of 5 ppm. For phosphorus elements concentration of yeast, 5 g/l contained the highest P concentration of 75.5 ppm, followed by pulp with 69.5 ppm and skin with 65 ppm. For Ca elements, it was observed in the concentration of yeast, that 5 g/l showed the highest Ca concentration with 51 ppm, while for both 1 and 3 g/l, it produced the same concentration with 42.5 ppm. The concentration of yeast of 5g/l produced the highest Mg concentration with 194.5 ppm, followed by 3 and 1 g/l with 173.5 and 167.5 ppm, respectively. The presence of Boron was small in the concentration of yeast. All concentration of yeast showed the same concentration of Boron with 1 ppm. The presence of wearable metals were Ferum (Fe), Cuprum, Silicon (Sn), Argentum (Ag) and Vanadium from the results as stated in Figures 1a, b and c. For yeast concentration, the highest values were 1 and 5 g/l, which shared same value of 3 ppm, and 3 g/l produced Fe concentration of 2.5 ppm. The concentration of yeast of 1 and 3 g/l showed the highest value of Sn concentration of 41.5 ppm, while 5 g/l showed slightly the reduction to 40.5 ppm. For Ag concentration, 5 g/l produced the highest with 235.5 ppm, followed by 1 g/l with 96.5 ppm and 3 g/l with 31.5 ppm. The presence of vanadium concentration was produced at the same concentration of yeast with 5 ppm in all the samples. The presence of contaminant metals were Silicon (Si) and Sodium (Na) from the results as stated in Figures 1a, b and c. For Si elements, the increase of Si was linear from smaller concentration to the highest concentration. The production of Si concentration for 1, 3 and 5 g/l was 18, 19 and 20 ppm, respectively. Concentration of yeast for 5 g/l produced among the highest concentration of Na with 129 ppm, followed by 1 g/l at 113.5 ppm, meanwhile, for 3 g/l, it produced Na concentration of 112.5 ppm. The multi-source elements present in the samples, comprised of molybdenum (Mo) and manganese (Mn) as plotted in the graph that is stated in Figures 1a, b and c. For Molybdenum (Mo), only 1 g/l showed the production of Mn with 0.5 ppm. There was no production for Mn in 3 and 5 g/l. The Mn concentration of 5 g/l showed the highest of Mn concentration with 5 ppm, while for 1 and 3 g/l, they shared the same concentration value at 4.5 ppm.

The results in Figures 1a, b and c, demonstrated that the samples did not contain the dangerous elements based on American Society for Testing and Materials (ASTM) D4806 and ASTM D5709 standards. The presence of elements Zn and Ca gave the benefit of doubt, because these compounds provide an alkaline reserve to neutralize acidic by-products of combustion, and thus can reduce the formation of insoluble compound and avoid corrosion (Larry et al., 1995). Additive metal that consists of Zn, P, Ca, Mg and Boron were present in this sample.

The presence of additive elements such as Zn, P, Ca and Mg might be gotten from raw material (pineapples) that were used as substrates in bioethanol production. According to the Williams (2008), he stated that the trace

metals that contained in pineapples juices consist of Pb (0.009 ppm), Mn (15 ppm), Ni (0.29 ppm), Zn (0.90 ppm) and Sn (0.45 ppm).

Camara et al. (1994), reported in their experiment in the investigation of chemical characterization of pine-apple juices, that the level of mean value and standard deviation (mg/100 ml) of mineral elements of pineapples juices consists of Na (2.24 ± 0.855), K (124 ± 9.572), Ca (11.5 ± 4.2888), Mg (15.4 ± 5.105), P (3.16 ± 0.261), Cu (0.059 ± 0.0019), Fe (0.265 ± 0.028), Mn (0.295 ± 0.072) and Zn (0.0074 ± 0.013). It is note-worthy that the mineral concentration of pineapples juices varies, depending on the composition of growing soil and irrigation of water in where the cultivars are harvesting. The mean (mg/l) chemical or mineral elements composition of pineapple cannery effluent are Zn (2.23), Ca (57.24), Copper (0.45), Fe-iron (29.24), potassium (191.54), Mg (35.78), Mn (1.54) and Na (54.98) (Prior and Potgieter 1981). There were several elements presented in these samples that might have come from it. In addition, it might be contaminated from the beaker, pH electrode and other equipment during experiment. The elements such as Fe (iron) and silicon (Si) may come from samples as well as the aluminum foil that were used during experiment. Accordingly, the elements of aluminum foil in mass per-centage (%) consist of aluminum, Al (51.35%), oxygen, O (46.88%), Ferum, Fe (0.95%) and silicon, Si (0.82%). A surface exhibit a layer of aluminum oxide due to the presence of a big amount of oxygen, which covers almost half of the contains. The pure aluminum is a reactive metal that forms oxide layers that was bonded strongly to its surface, and that if damaged, it reformed immediately in most environments (Pierre, 2000). Fe and Silicon (Si) contains in aluminum foil can cause a contamination as it exhibits the surface of aluminum foils. Ag (silver) was believed to come from the pH electrode that was being used in measuring the pH of the samples. The electrode contains a small amount of AgCl that precipitate the inside glass electrode. The Ag elements have been oxidized and mixed together with the samples. Na element came from sodium hydroxide (NaOH) that was used in increasing the pH of the samples for fermentation. NaOH is made up by elements of sodium (Na), hydrogen (H), and oxygen. The NaOH when dissolved in water will decompose into hydroxide (OH^-) and sodium ions (Na^+). Thus, Na elements that come from NaOH are used as catalyst to increase the pH. The presence of silicon (Si) and boron (B) elements in samples, is due to the corrosion of borosilicate glass that has been used during experiment. NaOH alkaline solution was added to increase the pH that was put in borosilicate glass. The alkaline solution that was NaOH can cause the corrosion of the borosilicate glass, since it only moderate resistance to alkaline solutions. The borosilicate glass has nominal composition of 0.70 SiO_2 , 0.028 B_2O_3 , 0.039 Na_2O , and 0.01 Al_2O_3 (Shrikande et al., 1998). During the studies of Manikandan et al. (1996), they stated that the

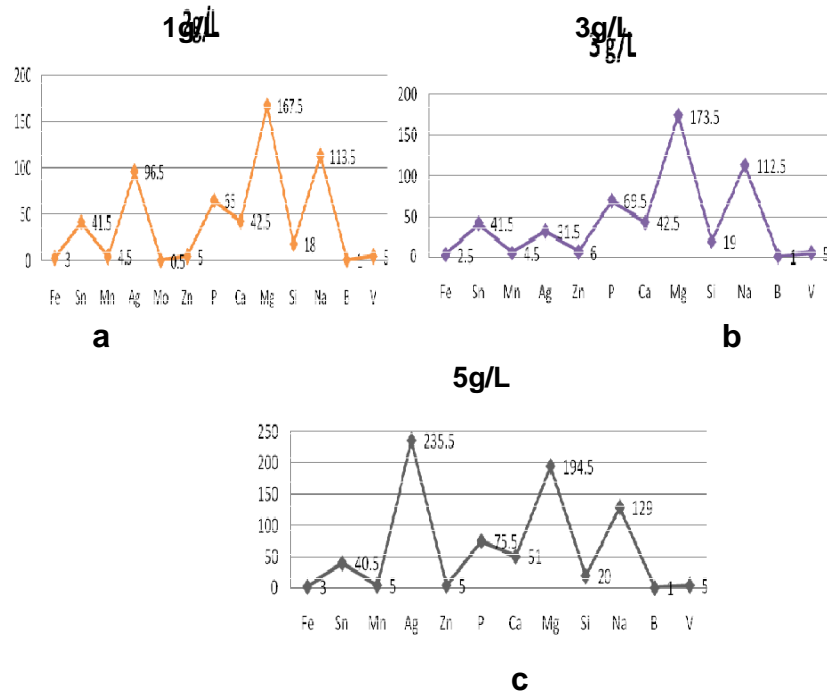


Figure 1. Compositions elements of 2 (a), 3 (b) and 4 (c) g/l of yeast.

degradation (corrosion) occurred when the borosilicate glass is immerse with NaOH solutions in their experiment in 5% NaOH solution at different temperatures for different periods, extending up to 300 h. The results found that, the damage of the glass surfaces was seen under an optical microscope and the corroded surface were identified by electron spectroscopy for chemical analysis (ESCA). These can prove that silicon (Si) and boron (B) elements came from the corrosion of borosilicate glass and split samples.

The presence of molybdenum (Mo) and Vanadium (V) were believed to have come from the samples used in the experiment. It might also come from metals like stain-less steel, spoons and knife made up from vanadium and molybdenum which is to make it more resistant to the corrosion. However, steel is susceptible to pitting corrosion in the presence of chloride ions (Cheramat- Aourasse et al., 2006). This happened when we used stainless steel during preparation of acid hydrochloride (HCL) to increase pH during the experiment. Stainless steels rely on passive film for corrosion resistance, but it is still susceptible to localized corrosion. When there are halogen ions such as HCL present, these can break down the passive film and leads to localized corrosion such as pitting corrosion.

In overall, the anhydrous ethanol samples that have been produced from rotten pineapples wastes are safe to be used as one of the sources of fuel, because they did not contain any dangerous elements and some elements presented at the range of limit acceptance based on the ASTM standard. ASTM D4806 is a standard for anhy-

drous denatured fuel ethanol for blending with gasoline and ASTM D5798 is a standard specification for fuel ethanol (Ed75-Ed85) for automotive spark-ignition engine.

Conclusion

From the experiments, it is proved that the ethanol yield could be produced from rotten pineapples wastes as the substrates. From the experiments, it can be concluded that the optimum bioethanol yield could be produced at 32°C having pH 4 and using 3 g/l yeast. From viscosity analysis, bioethanol yield from rotten pineapples wastes had the values which could be accepted based on American Society for Testing and Materials standard. For concentration of yeast, 1 g/l showed the highest value of viscosity. From the chemical analysis results, the raw ethanol yield from rotten pineapples wastes was in acceptance values based on American Society for Testing and Materials standard and therefore can be recommended to be used safely for petrol engine blending with pure petrol. Bioethanol yield from rotten pineapples wastes were safe to be used in engine cars, as it did not have any dangerous and higher value of element. It also has less environmental impact compared to the other fuels. The ideas for using bioethanol from rotten pineapples wastes could help to clean the environment from wastes and also could overcome the problems of fossil fuel depletion with creation of renewable bioresearch energy, especially bioethanol production.

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