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ORIGINAL ARTICLE

Bioethanol fuel production from date waste as Renewable energy

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ABSTRACT
Reforming of renewable biomass feedstock such as bioethanol is biodegradable, suitable substitute for fossil fuels, and capable to reduce greenhouse gas, CO_2 and NOX, emissions. New feedstock searching is a consequence process of all researchers to enhance the using of bioethanol, suggest the appropriate resources in respect to different geological reason of the world and lead the bioethanol research forward as well. Date is an important subsistence crop in arid and semiarid regions of the world and an obvious feedstock for liquid bioethanol. In this present study, the effects of pH, temperatures, period, substrate concentration, water percent and components of dates on bioethanol production were investigated. From the results, the optimal yield of bioethanol in the parameters such as pH, temperatures, fermentation period, and yeast concentration was found 8.7% having pH 5.8, 28°C, 5 days using 4 g/l, respectively. Viscosity was found under American Society for Testing and Materials (ASTM) standard. The produced bioethanol was analyzed and found that there was no toxic elements and acceptable for transportation fuel and maintained the quality of ASTM standard. The elements mostly contained in the bioethanol samples were Fe, Cu, Mn, P, Ca, Mg and Na. The green house gas emissions such as hydrocarbons, sulfur dioxide, carbon dioxide, and nitrogen oxides were reduced when using the bioethanol, blended with fuel because of the highly oxygenated component of bioethanol fuel. Hence, it is suggested that waste dates can be used as a potential feedstock for bioethanol production and appropriate as fuel for engine use.
Keywords: *bioethanol, fermentation, Saccharomyces cerevisiae, greenhouse gas, renewable energy.*

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INTRODUCTION

The global warming issue is caused by using excessive fossil fuels. Therefore, renewable clean energy, bioresource fuel, is required for replacing fossil fuel to reduce the CO2 emission. Another prominent one is the energy crisis issue and the continuous increase of global petroleum prices has impacts on human life and world politics too [1]. In order to solve these issues, a renewable energy should be developed and introduced as new feedstocks. Bioethanol is a form of renewable energy that has been produced from common agricultural feedstock's such as sugar cane, potato, manioc and maize from the middle of last century. From 2007 to 2008, the share of bioethanol, which produced by fermentation process, has been increased from 3.7% to 5.4% [2]. New feedstock searching is a consequence process of all researchers to enhance the using of bioethanol, suggest the appropriate resources in respect to different geological reason of the world and lead this research forward as well. The financial system of a country would receive a vibrant feedback if the use of bioethanol would be increased day by day continuously. Moreover the use of renewable energy, especially bioethanol would make a better chance to have share of energy from non-fossil energy sources, and it would surely decrease the fossil fuel consumption and increase agriculture base working sector.

In the past few years, the Iran, Iraq, Egypt, Pakistan, Algeria, Saudi Arabia, Sudan, Libya, Morocco and the United States have been the major date producers in the world. The world largest producer of dates is Iran and second position is in Egypt [3]. It was reported that most date (60% of total production) is used for human food, and about 40% is lost as waste in Iran [5]. A 0.36 Tg of the total production of date which is 0.9 Tg is in a waste form. If date production can be efficiently used a 0.129 GL of the date can be converted to bioethanol. In case of Iraq, now-a-days total production of date is 350,000 tonnes per year. Whereas, local consumption is around 150,000 tonnes, and the surplus can't be exported because of low quality [4]. Few of dates are consumed for juice and syrup production. A great deal of dates is, however, thousands tones per year lost during the sorting, the storage and the conditioning [7, 8]. Some are fed to animals, but a lot of dates end up just rotting. The non-use of this date for human food constitutes a real economic loss since it is rich in bioactive compounds and potential feedstock for bioethanol productions which can contribute to national economy to a great extent. In hydrolysis process, chemical reaction, the raw feedstock converts the complex polysaccharides into simple monosaccharide. In the biomass-to-bioethanol process, acids and enzymes are generally used to catalyze this reaction. In anerobic fermentation is a series of chemical reactions that convert monosaccharide into bioethanol. This fermentation reaction is caused by yeast or bacteria, which feed on the sucrose.

In addition, these clean energy sources have attracted the attention of researchers as alternative blending fuel due to their high octane number. Many researchers showed that the blending fuel showed better results in terms of fuel ratio, engine performance and exhaust emissions. This explains as the addition of ethanol to gasoline has two effects on the fuel blend properties: (1) an increase of the octane number, (2) a decrease in the heating value [5]. They also reported that the CO and HC emissions decreased by 46.5% and 24.3% from starch-based feedstocks. The best performance and emissions results were obtained for 20% ethanol with 80% gasoline blend. Therefore date is an obvious feedstock for liquid bioethanol, because it has no acidic component, they are easy to manage, they have high monosaccharide and they can ferment easily. Though, the production of syrup from dates has already been commercially established but innovative studies like bioethanol production by fermentation could bring expansion to new procedure and separation systems. Therefore, the objective of this present study was to determine the impacts of dates on bioethanol yield as a renewable resource optimize the variables and determine the metal elements content.

MATERIALS AND METHODS

Major headings are to be column centered in a bold font without underline. They need be numbered. "2. Headings and Footnotes" at the top of this paragraph is a major heading.

Raw materials

Rotten date fruits (Soccariasp) were obtained from local market, Jeddah, Saudi Arabia. The microorganisms employed were obtained from a commercial supermarket (commercial dry yeast and enzyme) and the ABO Laboratory, Kuala Lumpur, Malaysia.

Sample preparation and fermentation

In order to produce bioethanol there are two methods, which are via chemical synthesis and fermentation pathway. This research, bioethanol production, was focused on via fermentation pathway using yeast, *Saccharomyces cerevisiae*. Pulps were separated from seed and blended by blender. After blending properly the paste sample was taken out to a jar. The 100 ml pulp paste samples were kept in 500 ml schott bottle. The total soluble solid (TSS) of samples was measured before fermentation. The 1, 3, 5 gm/ l yeast was mixed with 15% water and incubated in the water bath at 40 0C for 30 minutes to activate the yeast performance. The pH was adjusted 5.8 using 5 M sodium hydroxide (NaOH) to increase the pH and 1M acid hydrochloride (HCl) to decrease the pH and then shaken well. The fermentation was conducted in the incubator and it was set up at 32^{0}C for 5 days.

Fermentation in different variables

The fermentation method for different variables was same as stated above. Each fermentation was conducted in a 500 ml scott bottle sealed with a rubber stopper to ensure anaerobic conditions. The different variables such as pH (5.6, 5.8 and 6), water level (20, 30, 40, 50 and 60%), yeast amount (2, 3, 4, 5, 7, 10 g/l), dates fruit part (pulp and seed), and temperature (28, 32 and 40^{0}C) were studied separately to assess the optimum value of bioethanol yield. The scott bottle was placed in an incubator for proper fermentation for 5 days while being rotated at 130 rpm on a temperature controlled shaker. Samples were withdrawn aseptically at 1, 3 and 5 days to measure bioethanol yield and asses other parameters.

Bioethanol Synthesis

Bioethanol can be produced from sugar (pulp), cellulose and starch (seed) sources and from different methods of bioethanol production have been practiced by researchers. Bioethanol was produced according to the U.S. Department of Energy as described below:

Biomass was converted to bioethanol by applying two reactions.

a. Hydrolysis is the chemical reaction that converts the complex polysaccharides in the raw feedstock to simple sugars. In the biomass-to-bioethanol process, acids and enzymes are used to catalyze this reaction.

The chemical reactions and involved enzymes in starch hydrolysis (liquefaction) have been shown below:

$2\ nC_6H_{12}O_{11} + n\ H_2O \rightarrow\ n\ C_{12}H_{22}O_{11}$

Starch (*α -amylase*) maltose

$C_{12}H_{22}O_{11} + H_2O \rightarrow 2\ C_6H_{12}O_6$

Maltose (*glucoamylase*) glucose

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

saccharose (invertase) glucose fructose

b. Fermentation is a series of chemical reactions that convert sugars to ethanol. The fermentation reaction is caused by yeast or bacteria, which feed on the sugars.

Ethanol and carbon dioxide are produced as the sugar is consumed. The simplified fermentation reaction equation for the carbon sugar, glucose, is:

$C_6H_{12}O_6 \longrightarrow 2\ CH_3CH_2OH + 2\ CO_2$

glucose ethanol carbon dioxide

Filtration

After 5 days, the samples were taken out from the incubator and filtrated by clean folded cheese cloth. The samples filtrated through the cloth into the beaker and leave the samples approximately about 2 hours until there was nothing comes out from the samples. The glucose content, pH and total soluble solid (TSS) were measured by dichromate colorimetric (DNS) method [6].

Bioethanol analysis and properties testing

Ethanol yield was determined by the measurement of ethanol absorbance at 575 nm after completion the ethanol Assay reagent step using spectrophotometers and compared to the ethanol standard graph and calculated the percentage of bioethanol. In the experimental study, viscosity, acid value and metal content were analyzed by viscometer, acid titration and multi element oil analyzer (MOA II).

Statistical Analysis

Statistical analysis was performed using SPSS software. The one way ANOVA was applied to evaluate the significant difference of the parameters studied in the different treatments. LSD (p=0.05) was calculated using the error mean squares of the analysis of variance.

RESULTS AND DISCUSSIONS

Effect of fermentation period

The samples were kept in anaerobic condition for the period of 5 days. Figure 1 showed that the bioethanol yield gradually increased along with the increase of duration, and reached a maximum stage at the 5th day. The results of the present work show the contribution of selecting the proper variables such as pH, duration and temperature on fermentation progress. These variables can significantly affect the results of the reaction process, and the yield of bioethanol through the hydrolysis and fermentation. The fermentation effectiveness can be described by bioethanol yield [7]. The bioethanol production in fermenting process depends on duration of fermentation, and longer duration increases the ferment-ability of the hydrolyzates. Therefore, almost a linear growth was observed in this present study. After 4 days of fermentation, bioethanol contents reach maximal values for 22.5% [8].

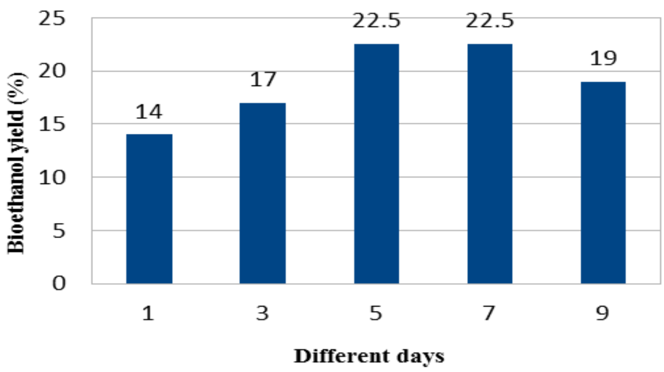

Fig. 1 Bioethanol yield during fermentation

Effect of initial pH

The sample was fermented to evaluate the optimization of pH value and concurrently to obtain maximum yield of bioethanol. The effect of initial pH parameter on bioethanol production is shown in Fig. (2). To evaluate the effect of pH on bioethanol production, the pH ranges from 5.6-6 was selected and other fermentation parameters were kept at constant level. The bioethanol production increased gradually with increasing pH and decreased at pH 6. The effect of pH on ethanol production from mahula flowers was reported, and it has been found that the maximum ethanol concentration, yield and fermentation efficiency were obtained at pH 5.5 [9].

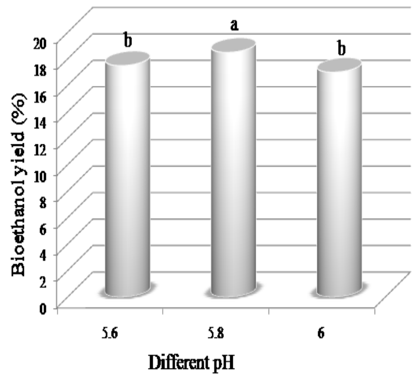

Fig. 2. Bioethanol yield at different pH

Effect of temperature

The optimized medium was selected to study the effect of temperature on bioethanol production by changing the temperature and kept all other fermentation conditions constant. It was meant that the sample was maintained at an optimum pH (5.8) at different temperatures such as 28, 32 and 40 °C. The samples were kept for fermentation period of four days and the fermented solution was filtrated after fifth day. Figure (3) shows that bioethanol production decreased with the increasing of temperature and the maximum were observed at 28 °C. This was probably due to the increase in cell number with the temperature range between 25-30 °C. It has been reported that the bioethanol concentration, bioethanol productivity and fermentation efficiency increased with the increase in fermentation temperature 25-30 °C and decreased gradually between 30 and 35 °C and drastically above 35 °C [10].

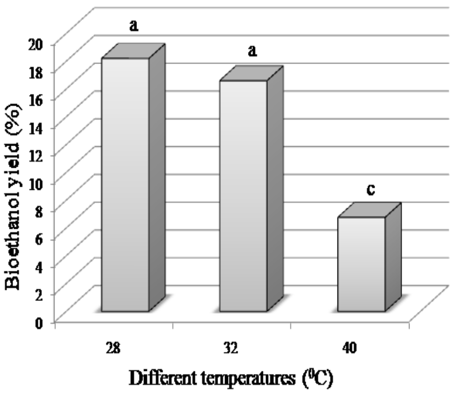

Fig. 3: Bioethanol yield at different temperature

Effect of yeast concentration

Data presented in Fig. (4) Show that as the concentration of yeast increased, the yield of bioethanol increased up to 4 g/L and then decreased. The increase in yeast amount is to certain extent advantageous since the chance of contamination of fermentation is reduced. However, there is a limit of yeast content below which yeast cells may not function to produce ethanol [11]. Another reason might be due to decrease in porosity, lower oxygen interaction and low aeration inside the solution.

Yeast cell concentration was found to be another factor to continue the fermentation process or effective fermentation. The biomass and yeast ratio have to be suitable in a media. It was reported that a continuous ethanol fermentation system coupled with a membrane unit to retain yeast cells, and the kinetic models for yeast cell growth and ethanol production were correlated with yeast cell concentration [13]. They calculated and obtained the optimum yeast concentrations at which yeast cell growth and ethanol production were absolutely increased. In addition, the impact of yeast cell concentration on ethanol production in a fermentation system similar to that of Baia *et al.* [12]. The relationship between yeast content and bioethanol concentration, using anaerobic fermentation was presented in Fig. (4).The rate of fermentation was increased proportionally as concentration increased but it was eventually decreased at 5 g/l yeast amount.

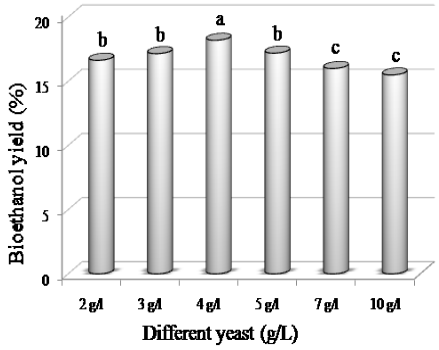

Fig. 4: Bioethanol yield at different yeast concentration

Effect of water level

The difference of bioethanol yield among the different treatments of water percent was presented in Fig. (5). It was found that the production of bioethanol was improved due to the higher amount of water percent. There was no fermentation occurred at all in the case of 20 and 30% water. The linear correlation showed the positive effect.

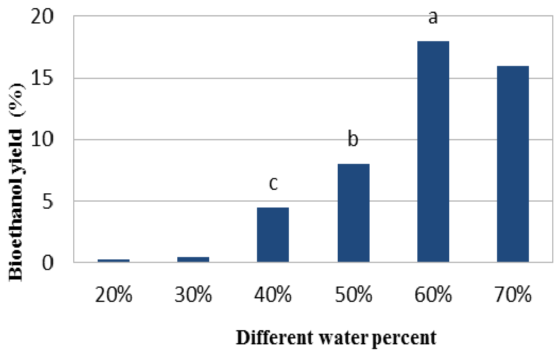

Fig. 5: Optimization of water percent

Table 1: Viscosity and acid value at different days

Properties	Days			ASTM standard of viscosity and acid value
	1	2	3	
Viscosity (cst)	2.1±0.2	2.0±0.4	1.8±0.1	1.9 - 6.0
Acid value(mg KOH/g)	0.5	0.4	0.3	0.0 - 0.5

Table 2. Metal content determination by multielement oil analyzer

Metal content	Days			ASTM standard of Metal content
	1	2	3	
Fe	2.5	1.0	1.9	Usually 0-5 ppm is standard as ASTM 4806
Cu	0.2	0.1	0.2	
Mn	1.0	1.2	1.0	
P	6.0	5.9	5.2	
Ca	5.0	4.2	4.2	
Mg	4.1	4.0	4.0	
Na	3.0	2.9	2.7	
Pb	0.005	0	0	

Presence of trace elements, viscosity and acid value in bioethanol

From the results in Table 2 demonstrated that the samples did not contain the toxic elements based on American Society for Testing and Materials (ASTM) D4806 and ASTM D5709 standards. Table 1 showed the viscosity and acid value at different days. Both the properties maintained ASTM standard as well. The presence of element Ca gave benefit because these compounds provide an alkaline reserve to neutralize acidic by-products of combustion so thus can reduce the formation of insoluble compound and avoid corrosion [14]. The presence of trace elements such as P, Ca, and Mg in bioethanol solution due to feedstock contains these in nature. According to the many researcher experiments, it was stated that the trace metals that contains in fruit juices consist of Pb (0.009 ppm), Mn (15 ppm) [15]. Overall, the anhydrous bioethanol samples that have been produced from date wastes are safe to be used as one of the sources of fuel because they did not contain any toxic metal elements and some elements presence were in the range of limit acceptance based on the ASTM standard. In addition, both the viscosity and acid value at different days were maintained ASTM standard too.

CONCLUSIONS

From the study, it can be concluded that bioethanol can be produced from waste dates as the substrates. The properties of bioethanol seem to be good quality following the ASTM standard. The best bioethanol yield (22.5%) was exhibited in different parameters of 5.8 pH, 28 °C temperatures, 5 days fermentation period and 4 g/l yeast (*S. cerevisiae*) concentration.

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