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PRODUCTION OF BIO ETHANOL FROM WHEAT CHAFF USING ALKALINE HYDROLYSIS METHOD

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Abstract : Spent grain, the residue remaining after extracting are major by-products of agriculture. This ligno-cellulose-rich biomass is a source of sugars for fuel ethanol fermentation. In this work, which is basically on the production of Bioethanol from inexpensive raw materials, pretreatment of dried wheat residue was chosen as the suitable method for solubilizing sample before fermentation. Sodium hydroxide was used as the alkaline medium for hydrolysis. Fermentation of hydrolysate was achieved by the use of yeast and the average yield of ethanol per volume of hydrosate was determined to be 18% as opposed to the standard yield of 23% probably due to the presence of yeast inhibitory compounds in wheat chaff.

INTRODUCTION

The production of ethanol or ethyl alcohol from starch or sugar based feedstock is among man's earliest ventures into value added processing. While the basic steps remain the same, the process has been considerably refined in recent years, leading to a very efficient process. Bioethanol is an alcohol made by fermenting sugar components of biomass. In Nigeria, bioenergy is mostly used primitively in cooking and heating, despite the country's potentials in agriculture which serves as a major source of biomass. Apart from food and pharmaceutical uses, ethanol is finding alternative uses such as motor fuel and fuel additive, ethanol as -motor fuel is preferred to fossil fuel in that, it is environmentally friendly, comes from a renewable source and has a higher performance in engine. (Eurasia, 2009)

The aim of this work is to study the production process of ethanol from chaff with emphasis on alkali as the hydrolyzing agent, to improve production processes, to increase ethanol yield with minimal use of agricultural by- product, to produce fuel from a renewable source to compete with crude oil. Also, fermentation was investigated as a way of ethanol production from pure chaff starch.

Ethanol or ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$ its molecular formula is also represented as Et OH, $\text{C}_2\text{H}_5\text{OH}$ and its empirical formula $\text{C}_2\text{H}_6\text{O}$. (Kirk-Orthmer) Its isolation as a relatively pure compound was first achieved by Persian alchemists who developed the art of distillation during the Abbasid caliphate, the most notable of whom was Al-Razi. The writings attributed to Jabir

Keywords : Bio ethanol, wheat chaff, alkaline hydrolysis (NaOH), yeast, yield and Biomass

in Hayyan (Geber) (721-815) mention the flammable vapours of boiling wine. Absolute ethanol was first obtained in 1796 by Johann Tobias Lowitz by filtering distilled ethanol through charcoal. (Roach, 2005) Antoine Lavoisier described alcohol as compound of carbon, hydrogen and oxygen, and in 1808, Nicholas-Theodore Saussure determined ethanol's chemical formula, and fifty years later, in 1858, Archibald Scott Couper published a structural formula for ethanol, this places ethanol among the first chemical compounds to have their chemical structure determined. (Eursia, 2009)

Ethanol was first prepared synthetically in 1826, through the independent effort of Henry Hennel in Great Britain, S.G serullasing France, Michael faraday prepared ethanol by the acid catalyzed hydration of ethylene in 1828, in a process similar to that used in the industrial ethanol production today. (Kirk- Orthmer, 1971) Ethanol can be mass-produced by fermentation of sugars or by hydration of ethylene from petroleum and other sources. (Eursia, 2009)

For most industrial and fuel uses, the ethanol must be purified by removing water, most of the water is removed by distillation, but the purity is limited to 95-96% due to the formation of low-boiling water ethanol azeotrope, the 96% m/m (93%v/v) ethanol, 4% m/m (7%v/v) water mixture may be used as fuel, and it's called hydrated ethyl alcohol fuel. (Eurasia, 2008)

After distillation, ethanol can further be purified by drying it using lime or salt, lime when mixed with water in ethanol will form calcium hydroxide which can then be separated. The ethanol water azeotrope can be broken by the addition of small quantity of benzene, benzene; ethanol and water form a ternary azeotrope with a boiling point of 64.9°C hence this azeotrope can be fractionally distilled out of the ethanol water mixture, extracting essentially, all water in the process. The bottoms from such a distillation is anhydrous ethanol, with several parts per million residue benzene, benzene is toxic to humans, and cyclohexane has largely supplanted benzene in its role as the entrainer in the process. Alternatively, a molecular sieve can be used to selectively absorb the water from the 95.6% ethanol solution. Synthetic zeolite in pellet form can be used, as well as variety of plant derived from absorbents including corn meal, straw and sawdust. (Paul, 2004)

Ethanol is increasingly used as an oxygenate additive for standard gasoline, as a replacement for methyl t-butyl ether (MTBE), the latter chemical being difficult to retrieve from groundwater and soil contamination. At 10% mixture, ethanol reduces the likelihood of engine knock, by raising the octane rating. It can be combined with gasoline in any concentration up to pure ethanol (E100). Anhydrous ethanol that is ethanol with at most 1% water can be blended with gasoline in varying quantities to reduce the consumption of petroleum fuels and to reduce air pollution. (Paul, 2004)

Within the tropics, wheat is grown as a high altitude crop, often as part of wheat/dairy farming system. Different varieties are available for different altitude, right up to 2, 800 meters (David and Adam, 2004) The use of relatively inexpensive raw materials like wheat chaff as a source to produce ethanol emits carbon dioxide, a potentially harmful green house gas during fermentation; however, the net effect is offset by the uptake of carbon dioxide gases by the plant grown to produce ethanol, hence, releases less green house gases. (Eurasia, 2008)

Standard distillation leaves over 4% water in the ethanol, so a process called azeotropic distillation was used in all the early commercial ethanol plants to remove the final water from the ethanol. Azeotropic distillation systems tended to be quite expensive, difficult to operate and consumed a significant amount and energy. (Eurasia Bio, 2008)

Synthetic zeolite are known as molecular sieves due to the very precise pore size that enabled them to select and remove one molecule size from a bulk mixture containing molecules with a large size or lower polarity, molecular sieves are used recently to dry ethanol. The basic characteristic of an adsorbent material is a strong affinity for one type of atom or molecule than for the other types in the vapour stream. In the case of molecular sieve ethanol dehydrators an adsorbent was selected with a strong affinity for water and little affinity for ethanol and the other impurities contained in the ethanol feed stream. As the ethanol vapour passes through the bed, the desiccant absorbs the water molecule but not the ethanol molecule. Synthetic zeolite of type 3Å is used in most ethanol dehydrators, because the pores are 3Å in diameter while water molecules are 2.8Å and ethanol molecules are 4.4Å. Therefore water molecules are strongly attracted into the pores but ethanol molecules are excluded. Type 3Å molecular sieve is capable of adsorbing 22% of the weight in water. (Mark, 1995)

EXPERIMENTAL

The grain was milled, sieved and the residue (chaff) was collected and weighed. 500g of the chaff was soaked in 860ml of water for a period of 30 hours after which it was filtered with the aid of the filter cloth. 600ml of the filtrate was collected and made up to 1000ml with boiled water. The mixture was stirred continuously to avoid formation of lumps, it was then allowed to cool and on cooling, a thick-jelly like mass was formed. The gelatinized mixture was then poured into a 2000ml conical flask for hydrolysis. 30ml of 0.5M sodium hydroxide was added to the sample and immersed in the water bath maintained at a temperature of 75°C for 50 minutes. 80ml of ethanoic acid was added to the mixture to terminate the hydrolysis reaction after which the mixture was set aside to cool.

To 4ml of the hydrolyzed sample, few drops of Fehling solution was added in a conical flask, and on heating, produced a brick red precipitate which indicates the presence of simple sugars. 5g, 10g, 15g, 20, of active dry yeast (*Saccharomyces cerevisiae*) were separately added to 100ml of warm water. 2.5g of vitamin B complex was added to each of the mixtures and allowed to stand for some minutes while the yeast was being monitored for growth. The yeast was then added to the sample at growth stage. Each of the mixture was transferred into the fermenter and allowed to ferment for the period of 16 days. At this stage, the enzyme: invertase and zymase contained in the yeast acted on simple sugars degrading them to ethanol and carbon dioxide. After fermentation, the fermentation broth was filtered with a filter cloth and a clear liquid was obtained for distillation. The liquid substance was distilled with the aid of the rotary evaporator to obtain ethanol of about 96% concentration. The density of the ethanol was taken and the yield was determined with respect to each volume of fermented sample. The distillate was further purified by the use of lime (calcium oxide). Lime, a basic oxide was added to the ethanol, an alkaline solution. The calcium hydroxide formed was separated from the ethanol by further distillation which leaves absolute ethanol.

RESULTS AND DISCUSSION OF RESULT

Table-4.1 : Raw materials

Raw materials	Wheat chaff
Weight (g)	600
Colour	Light brown

Table-4.2 : Properties of the produced Ethanol

Property	Standard laboratory grade ethanol	Experimentally produced ethanol
Appearance	Clear colourless liquid	Clear colourless liquid
Boiling point	78.32°C	78.4°C
Density	0.789g/cm ³	0.799g/cm ³
Flammability	Flammable	Flammable
Solubility	Highly soluble	Highly soluble

Table-4.3 : Alcohol Yield

Weight of yeast (g)	Volume of hydrolyzed sample (ml)	Alcohol yield (%)	pH
5	100	22.0	4.3
10	200	18.0	4.3
15	300	16.0	4.3
20	400	15.0	4.3

In this work, glucose polymer called starch is being utilized as the source of ethanol from wheat; yeast development was carried out as an ancillary operation to achieve effective fermentation. Premixing was done by mixing the raw material with water in the right proportion to weaken the cellulose structure of the plant so that it can be exposed to reaction. Prior to hydrolysis, the sample was tested for simple sugars using Benedict reagent under the necessary conditions and no colour change was observed, this means that the sugars present in the sample were complex sugars since sugars that do not react are non-reducing sugars. In the fermentation reaction, the microorganisms used were yeast (*Saccharomyces cerevisiae*). Yeast contains some enzymes which do not feed on starch but on simple sugars, therefore, the complex sugars were converted to simple sugars by hydrolysis. Sodium hydroxide was used as the alkali reagent for hydrolysis. The temperatures, concentration and other parameters were carefully monitored to achieve a high degree of starch conversion. After hydrolysis, the hydrolysate was tested for simple sugars by adding few drops of Fehlings solution and on heating, produced brick red precipitate showing the presence of reducing sugars. The yeast was properly developed to make it active for fermentation reaction and the fermentation reaction was completed after a period of 16 days. The fermenting sample was protected from oxygen to avoid oxidation of ethanol to ethanoic acid. Distillation of the fermented product was carried out with the aid of the rotary evaporator, so as to purify the ethanol. This was done by considering the difference in boiling point between ethanol (78.4°C) and water (100°C). The rotary evaporator was maintained at a constant temperature of 78.4°C and the distillate collected contained 95.6% ethanol and 3.4% water. The ethanol yield per volume of hydrolyzed sample and amount of yeast was determined and tabulated. The distillate was further purified to obtain absolute ethanol which is 99.96% ethanol.

Azeotropic distillation can be used for this operation by adding a third solvent (sometimes benzene). Benzene is carcinogenic; Therefore lime was employed for ethanol dehydration lime, when added to the ethanol became mixed with the water in ethanol to form calcium hydroxide which is in the form of ionic compound. Ionic compounds have high boiling points; therefore, the miscible solution was distilled again taking the advantage of the difference in boiling point between ethanol (78.3°C) and calcium hydroxide (172°C) to obtain anhydrous ethanol. From the tabulated results of ethanol yield per volume of hydrolyzed sample, and amount of yeast, it

was observed that, the yield of ethanol decreases with increase in volume of hydrolyzed sample. This implies that, at lower volumes, glucose utilization is higher, hence a higher alcohol yield.

CONCLUSION

Some of the operations involved in laboratory production of bio-ethanol was studied at their various alternatives and compared. These operations include hydrolysis and dehydration of distillate to obtain absolute ethanol, the most safe, high yield, and material available optioned was adopted, therefore, production rate was maximized. The production of bio-ethanol from spent grain was achieved in the laboratory through the controlled combination of various unit operations, hence agricultural by-product can be utilized in this form.

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