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PRODUCTION AND DETERMINATION OF FUEL ETHANOL YIELD USING WASTE PAPER

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ABSTRACT

There is a vested interest in developing alternate sources of fuel to fossil fuel due to lowering stocks, increasing prices and the need for environmentally sustainable energy sources. One major alternative to fossil fuels is bio-ethanol (ethanol from biomass) and waste paper represents a significant source for ethanol production. This work therefore used 3 different types of waste paper (plain white paper, newspaper, office waste paper) to produce ethanol. Each was converted to fermentable sugars using two stage dilute acid hydrolysis method and subsequent fermentation of the sugar was carried out using saccharomyces cerevisae (Baker's yeast) as the fermenting microorganism. Plain white paper gave the best yield of ethanol after distillation with 24 % ethanol yield. Newspaper and office waste paper yielded 12.0 % and 8.4 % ethanol respectively. Factors such as the impurities (inks and pigments) were observed to have significant effect on their yields.

Key Words: Waste Paper, Fuel Ethanol, Production, Hydrolysis, Fermentation.

INTRODUCTION

In recent years, the energy and climate crises have come to the forefront of public awareness. In 2007 the intergovernmental panel on climate change (2007) reported 'unequivocal' evidence of warming of the climate system, and that much of this is 'very likely' owed to anthropogenic greenhouse gas (GHG) emissions (www.ipcc.ch/ipccreports/ar4-syr.htm).
Despite political and scientific advances in environmentally friendly policies and technologies, there still remains much work to be done to make our lifestyles more sustainable and ecologically sensitive. First-generation biofuels – those derived from food crops such as corn ethanol and soy biodiesel – are known to involve multiple environmental and social trade-offs such as net positive GHG emissions from land use change, and threats to global food security, among others (Fargione *et al*, 2008). Second- or third generation biofuels, such as those derived from waste biomass, are widely recognized to be the way forward in biofuels research (Scharlemann and Laurance, 2008), and promise real emissions savings over fossil fuel use (Ragauskas *et al.*, 2006).

Biofuel includes any solid, liquid, or gaseous fuel produced either directly from plants or indirectly from organic industrial, commercial, domestic, or agricultural wastes. In principle, burning biofuel adds less carbon to the environment than burning fossil fuels because the carbon atoms released by burning biofuel already existed as part of the modern carbon cycle. Burning fossil fuels, on the other hand, always adds extra carbon because the carbon they contain comes from a buried source that was not part of the modern carbon cycle (Redmond, 2008). Carbon dioxide is the main greenhouse gas thought to contribute to global warming. Biofuels are seen as one way to reduce the amount of carbon dioxide gas added to the atmosphere. Plants used for biofuels take up the same amount of carbon dioxide as they grow as was released by burning biofuels made from an earlier crop. Biofuels produced and used within the same country are a way to reduce dependence on foreign sources of oil and other fuels, providing energy security and an economic boost for agriculture and industry. Biofuels are also a type of renewable energy resource, unlike fossil fuels, which cannot be grown or created (Redmond, 2008).

During the last few decades, however, the excessive consumption of fossil fuels, particularly in large urban areas, has greatly contributed to generating high levels of pollution. As a step to solve this problem, the addition of ethanol to gasoline, which reduces emission of carbon monoxide and unburned hydrocarbons that form smog (Wyman, 1996), have widely been enforced in recent years. The demand for bioethanol has therefore increased. Mature technologies for ethanol production are crop based, utilizing substrates such as sugar cane juice and corn starch. Since the cost of raw materials can be as high as 40% of the bioethanol cost (Von Sivers *et al*, 1994 and Wyman, 1999), recent efforts have concentrated on utilizing lignocellulose. This natural and potentially cheap and abundant polymer is found as agricultural waste (wheat straw, corn stalks, soybean residues, sugar cane bagasse), industrial waste (pulp and paper industry), forestry residues, municipal solid waste, etc. (Wiselogel *et al*, 1996). It has been estimated that lignocelluloses accounts to about 50 % of the biomass in the world, 10–50 billion tons according to (Claasen *et al*, 1999).

The current food crises is to a large extent been fuelled by the diversion of food resource to biofuel production in a world where crude oil prices reached $147 per barrel. The high oil prices have led to energy crises in both developing and developed countries that are oil dependent. Cassava – a crop crucial for food security, especially in Nigeria – has become an important biofuel crop aside from its traditional role as a food crop (Eneas, 2006). Some experts have raised concerns about the negative consequences of growing crops to provide biofuels. Food prices may rise if a major percentage of grain crops are grown for energy and if areas once used to grow food are converted to energy crops. The price increases could affect impoverished populations in developing countries, Nigeria in particular.

Today, paper is made in various types and grades to serve many functions. The major distinction is that between paper and paper board, the latter generally being much heavier, thicker and less flexible than conventional paper. The third broad category sometimes identified separately is construction paper and board. Paper (first category) is comprised of newsprint, fine paper, sanitary tissue and other tissue paper. The second category which is paperboard includes card board lines, corrugating board and other special packaging boards. The last and smallest category comprises construction paper and boards of various kinds including pressed board and paper insulating materials (Casey, 1960).

In this work, waste papers namely; *Plain white paper (PWP] was used.* This is a plain white office paper without inscription or any trace of ink on it; *Newspaper print (NPP).* This type of paper contains different types of ink, pigments etc, Daily Trust Newspaper was used and *Ordinary office waste paper (OWP) This is* common paper with ink writing. These papers which are found littered everywhere with their attendant environmental menace were converted to bio-ethanol. The availability of these waste papers makes them very cheap and thus the bio-ethanol produced could be a good alternative to fossil fuel.

1.0 METHODOLOGY

2.1 Pre treatments.

Three different waste paper samples were used. These include Plain white paper (PWP); Newspaper print (NPP) and Ordinary office waste paper (OWP). Each paper sample was cut into sizes of about 1cm^2 using a pair of scissors. This was soaked in distilled water (in the ratio of 30 g/liter) for about 20 minutes and pulped using a warring blender.

2.2 Two-Stage Dilute acid Hydrolysis.

The aqueous fibrous slurry formed (30 g/liter) was filtered to reduce the excess water for higher solid slurry prior to hydrolysis. The slurry was poured into a 1 liter vessel and 1.0 % H_2SO_4 added and stirred. This was kept in an autoclave for 15 minutes at a temperature of 121 ^oC. The hydrolyzed sample was filtered and transferred into a separate vessel. Water was added to the residual solid to form slurry and the process was repeated the second time. This was to ensure maximum conversion of the slurry to sugar. This was also filtered and the residue discarded. Both filtrates from the first and second hydrolysis were poured into a vessel. After hydrolysis, the sugar solution (hydrolyzate) was allowed to cool to a temperature of about 35 ^oC to 38 ^oC then neutralized by adding 0.5 M of KOH until a pH range of 4.9 to 5.2 was obtained.

2.3 Fermentation/ Distillation.

5g of yeast (saccharomyces cerevisae) was added to the hydrolyzate in a vessel, properly stirred and closed (air tight) for fermentation. The vessel (air tight) was allowed to stand for 72 hours at room temperature. This was followed by distillation in a rotary evaporator set at 78.3^oC to obtain ethanol. The same processes were repeated with each waste paper sample at concentration of 0.8 % and 1.2 % H_2SO_4 respectively. The volume of ethanol obtained in each case was recorded.

2.4 Determination of Glucose Concentration

The Dinitrosalicylic acid (DNS) reagent was used to determine the glucose concentrations in each filtrate (hydrolyzate). 2 ml of DNS Reagent plus 1 ml of distill water were added to 1 ml of each filtrate in separate test-tubes. It was heated in a boiling water bath for 5 minutes. It was allowed to cool and each mixture was made up to 20 ml. The absorbance was taken for each mixture with the aid of a colorimeter. This process was repeated for a prepared standard glucose solution of serial dilutions; 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 mg/ml. A graph of absorbance against the concentration was plotted (standard glucose curve), which was used to determine the concentration in each filtrate (hydrolyzate).

2.5 Determination of Percentage Ethanol yield

The percentage ethanol yield for each fermented sample was determined as follows;

$$\%\ \text{Ethanol Yield} = \frac{Veth}{Vhyd} * 100\% \qquad ..\ 3.1$$

Where

Veth = volume of ethanol formed.

Vhyd = volume of hydrolyzate fermented.

2.6 Determination of some physical properties.

Some physical properties of the ethanol produced were tested and the results obtained were compared with the standard specifications. The properties tested include appearance, flammability; boiling point; flash point; density and percentage purity.

3.0 RESULTS AND DISCUSSION.

This research was performed to determine the potential yield of ethanol from waste paper using two stage dilute acid hydrolysis and fermentation of the hydrolyzate using Saccharomyces Cerevisae (baker's yeast) as the fermenting microorganism. Three types of paper; plain white paper (PWP), newspaper (NPP), office waste paper (OWP) were used as samples. Each sample was cut into sizes of about 1 cm^2 for ease of handling and to reduce homogenization time. 30 g/l of each soaked sample was hydro pulped for effective and homogeneous hydrolysis. Two – stage dilute acid hydrolysis at 121 ^oC was used. This is to avoid sugar degradation and formation of undesirable byproducts which may result in a lower yield of sugar. (Tarhezardeh and Karimi, 2007).

Table 1 shows the respective volumes (in cm^3) of each sugar solutions (hydrolyzate) at different concentrations of H_2SO_4 after hydrolysis. From the table, it can be observed that the volume of the hydrolyzate increased with increase in acid concentration. The newspaper print (NPP) recorded the highest volume of 265 cm^3 with a concentration of 1.2 %. The office waste paper (OWP) had volume of 255 cm^3 while plane white paper (PWP) had the least volume of 225 cm^3. Also, for each concentration used, PWP had the lowest volume, this can be attributed to low acidity of the PWP hydrolyzate as those of NPP and OWP were higher after hydrolysis which can be attributed to lack of inks and pigments in the PWP. This resulted in the use of more quantity of 0.5 M KOH to neutralize the hydrolyzate solutions of NPP and OWP.

Table 2 shows the absorbance reading from colorimeter for each waste paper hydrolyzate. This was used to determine the glucose concentration of each sample from a prepared standard glucose curve by comparing the absorbance from each sample (Table 2) with those of the prepared standard glucose concentration of different serial dilutions; 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5 mg/ml. From Fig. 1, it can be observed that plain white paper (PWP) gives the best yield of glucose with a yield of 1.5 mg/ml at 1.0 % H_2SO_4 compared to 1.0mg/ml yield from newspaper (NPP) and 0.75 mg/ml yield from office waste paper (OWP). This can be attributed to the presence of impurities such as inks and pigments in the waste paper (NPP and OWP), which are not cellulosic in nature. Thus, tends to hinder the process of hydrolysis and fermentation (Jefferies, 2006, Jeppson *et al*, 2002, Lin and Tanika, 2006).

Fermentation was carried out on the sugar solutions (hydrolyzates) with the highest glucose concentration (1.0 % H_2SO_4) for each of the waste paper substrates. Each sugar solution was allowed stand for 3 days and at room temperature to ferment (Donal, 2000). Fig. 2 shows the results obtained after distillation. Plain white paper had the highest yield of 24 % ethanol, followed by NPP with 12 % ethanol and OWP with 8.4 % ethanol. It was observed that although PWP had the least volume of sugar (hydrolyzate) solution, it yielded the highest volume of ethanol. This therefore implies that the yield of ethanol depends more on the concentration of the sugar and not on the volume. Although the ethanol yield was very low, these were largely as a result of low glucose yield, the inability of yeast (Saccharomyces Cerevisae) to ferment other sugars (such as pentose e.g. xylose) in the hydrolyzates solution and other inhibitory compounds such as furfural and hydroxymethyl furfural (HMF). These tend to hinder the process of fermentation. (Jefferies, 2006, Jeppson *et al*, 2002, Lin and Tanika, 2006).

Considering other factors such as variation in concentrations of the dilute acid used (H_2SO_4), Fig 1 shows an increase in glucose concentration as the concentration of the acid increases though this was not totally true for 1.2 % (H_2SO_4). This may be due to inconsistency of the retention time for the autoclave machine used. Also various physical properties of ethanol such as density, boiling point, flammability and appearance obtained were shown in Table 3. In Comparing with those from literature (http://www.eere.energy.gov/afdc/altfuel/fuel_properties.html), it can be adjudged that the values of the properties, obtained were within standard specification.

Generally, the availability of free raw material (waste paper) and the possibility of using the residue for electricity and heat (Tarhezardeh and Karimi, 2007) make this research viable for industrial scale application.

4.0 CONCLUSION

Waste papers like other lignocelluloses material have the potential to be a major feedstock for ethanol production in the near future. Its abundant availability is an advantage and the utilization will help to alleviate environmental and land fill issues since waste paper is the dominant material in landfills. However, the process of conversion of waste paper is not as easy as the conversion of sugar substances and starchy materials. Dilute acid hydrolysis is a suitable method for conversion of waste papers to fermentable sugars. A suitable reactor design can be applied in other to improve the yield of cellulose conversion by dilute acid hydrolysis and an effective fermentation strategy must be employed for fermenting both pentose and hexose sugars.

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Table 1: Volume of hydrolyzate at different acid concentration obtained from each sample slurry concentration [30 g/liter]

	Volume Of Hydrolyzate (cm^3)		
Samples (30 g/l)	***0.8 % H_2SO_4***	***1.0 % H_2SO_4***	***1.2 % H_2SO_4***
Plain wastepaper	155	200	225
Newspaper	180	250	265
Office waste paper	165	250	255

Table 2: Absorbance readings from Colorimeter for each waste paper hydrolyzate.

Substrates	**Absorbance**		
	0.8 % H_2SO_4	*1.0 % H_2SO_4*	*1.2 % H_2SO_4*
Plain wastepaper	0.05	0.28	0.20
Newspaper	0.11	0.20	0.22
Office waste paper	0.08	0.14	0.11

Table 3: Comparison of Some Characteristic Physical Properties of Ethanol Produced from Different Waste Paper with Characterized Ethanol from the US Department of Energy.

Property	**Standard Ethanol**	**Ethanol (PWP)**	**Ethanol (NPP)**	**Ethanol (OWP)**
Appearance	Clear Colourless Liquid	Clear Colourless Liquid	Clear Colourless Liquid	Clear Colourless Liquid
Flammability	Flammable	Flammable	Flammable	Flammable
Boiling Point	78.15 ^oC	78.3 ^oC	78.3 ^oC	78.3 ^oC
Flash Point	55 ^oF	55.4 ^oF	56 ^oF	55.7 ^oF
Density	0.789 g/cm^3	0.796 g/cm^3	0.801 g/cm^3	0.799 g/cm^3
Percentage Purity	100 %	99.1 %	98.5 %	98.7 %

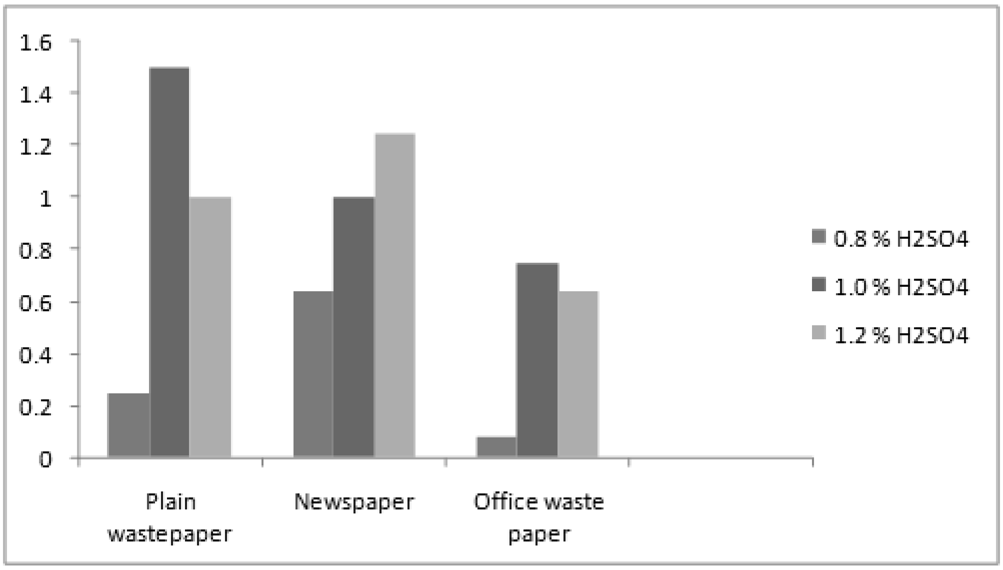

Fig 1: Glucose Concentrations (mg/ml) of each Waste Paper Hydrolyzate from Standard Glucose Curve.

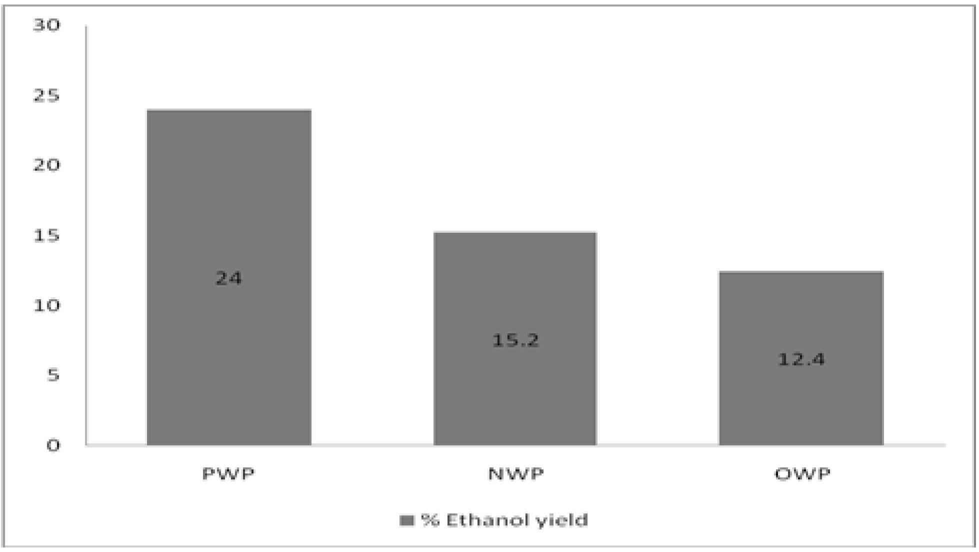

Fig. 2: Percentage Ethanol Yield from Fermentation of 1.0 % H_2SO_4 Waste Paper Hydrolyzate.