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Production of Bioethanol from Wate Tissue Paper and Newspaper and Its Characterization

T. Raja*, S. Sivamani
College of Engineering and Technology, University of Technology and Applied Sciences, Salalah
**Corresponding author: raja.t@sct.edu.om*

ABSTRACT:
The world is facing a serious energy crisis due to development in industrial and transportation sectors and population explosion as well. So, in search of an alternative liquid transportation fuels, bioethanol is found to be a renewable energy resource derived from the biomass. In this research, the main aim is to produce ethanol from waste tissue paper and waste newspaper. Waste papers were mixed with 72% sulphuric acid in the mass to volume ratio of 1:5 and the hydrolysis was carried at 80 ℃ for 4 h. Then, hydrolysate was neutralized with 0.7 M potassium hydroxide and proceeded for fermentation with dry yeast (Saccharomyces cerevisiae) at 40 ℃ for 24 h. Finally, fermented broth was subjected to simple distillation to collect bioethanol. The properties of bioethanol like pH, density, refractive index, dynamic and kinematic viscosity. The presence of ethanol was confirmed using Jones and Lucas reagents. The properties of bioethanol reveal that the quality of fuel produced from waste tissue paper is superior than waste newspaper. Hence, it could be concluded that higher cellulose content of 88% in waste tissue paper leads to greater yield of bioethanol.
Keywords: *Waste tissue paper, Waste newspaper, Hydrolysis, Fermentation, Bioethanol*

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I. INTRODUCTION:

The fermentation of sugar into ethanol is one of the earliest biotechnologies employed by humans. The intoxicating effects of ethanol consumption have been known since ancient times. Ethanol has been used by humans since prehistory as the intoxicating ingredient of alcoholic beverages. Dried residue on 9,000-year-old pottery found in China suggests that Neolithic people consumed alcoholic beverages [1].

Although distillation was well known by the early Greeks and Arabs, the first recorded production of alcohol from distilled wine was by the School of Salerno alchemists in the 12th century. The first to mention absolute alcohol, in contrast with alcohol-water mixtures, was Raymond Lull. In 1796, German-Russian chemist Johann Tobias Lowitz obtained pure ethanol by mixing partially purified ethanol (the alcohol-water azeotrope) with an excess of anhydrous alkali and then distilling the mixture over low heat [2]. French chemist Antoine Lavoisier described ethanol as a compound of carbon, hydrogen, and oxygen. In 1807 Nicolas Théodore de Saussure determined ethanol's chemical formula. Fifty years later, Archibald Scott Couper published the structural formula of ethanol [3].

Synthetic ethanol was first prepared first in 1825 by Michael Faraday. He found that sulphuric acid could absorb large volumes of coal gas. He gave the resulting solution to Henry Hennell, a British chemist, who found in 1826 that it contained sulphovinic acid (ethyl hydrogen sulphate). In 1828, Hennell and the French chemist Georges-Simon Sérullas independently discovered that sulphovinic acid could be decomposed into ethanol. Thus, in 1825 Faraday had unwittingly discovered that ethanol could be produced from ethylene (a component of coal gas) by acid-catalysed hydration, a process similar to current industrial ethanol synthesis [4].

Ethanol was used as lamp fuel in the United States as early as 1840, but a tax levied on industrial alcohol during the civil war made this use uneconomical. The tax was repealed in 1906. Use as an automotive fuel dates back to 1908, with the Ford Model T able to run on petrol (gasoline) or ethanol. It fuels some spirit lamps [5]. Ethanol intended for industrial use is often produced from ethylene. Ethanol has widespread use as a solvent of substances intended for human contact or consumption, including scents, flavourings, colourings, and medicines.

In chemistry, it is both a solvent and a feedstock for the synthesis of other products. It has a long history as a fuel for heat and light, and more recently as a fuel for internal combustion engines. To sum up, bioethanol is an alcohol made by fermentation, mostly from carbohydrates produced in sugar or starch crops such as corn, sugarcane, or sweet sorghum. Cellulosic biomass, derived from non-food sources, such as trees and grasses, is also being developed as a feedstock for ethanol production [6]. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil. Current plant design does not provide for converting the lignin portion of plant raw materials to fuel components by fermentation [7].

Recently there has been an increased focus on biofuels due to the impact of fossil fuel consumption on global warming caused by greenhouse gas emissions, the increased energy demand worldwide concomitant with the depletion of fossil fuel reserves. Lignocellulosic biomass is a renewable resource ideal for energy production, as this sustainable feedstock can be converted to bioethanol by biological conversion [8]. 94% of the liquid transportation fuels are derived from petroleum.

First generation bioethanol is commercially established and is produced from crops such as corn and sugarcane. However, it is not sustainable as food crops are used as feedstock. Second generation ethanol is not commercially established but can be produced from sustainable (non-food crop) lignocellulosic biomass that include straw, sugarcane bagasse, energy crops and various forestry and agriculture residues [5]. The major drawback with second generation ethanol is that pretreatment is required to enhance the amenability of the lignocellulosic feedstock for enzymatic hydrolysis.

It has been found that the cost associated with pretreatment could contribute up to 30% of the cost of bioethanol production [9]. However, pretreatment is not required to enhance the amenability of paper sludge for enzymatic hydrolysis, as in the process of paper manufacturing the pulp is extensively chemically treated and as a result paper sludge is a viable feedstock for bioethanol production [10].

The increasing population of South Africa will generate increasing amounts of waste in the future. From an environmental perspective the conversion of waste to products is important as it limits the amount of solid waste produced and leads to increased environmental awareness. Waste paper is a major component of household and industrial solid waste streams, which can be recycled to produce various recycled fibre products such cardboard, roofing materials, newsprint and tissue paper [11]. The manufacturing of recycled fibre products results in the damaging and shortening of pulp fibres. Between 15 and 20% of the pulp feed stock is damaged in the manufacturing process and removed as paper sludge for disposal [12].

Due to the high moisture content of paper sludge, the cost of transport and disposal is high. Paper sludge disposal cost consists out of two parts, namely landfill charges of OMR 3.82 per dry ton and transport costs of OMR 0.94 per dry ton. As a result, paper mills are opting to increase co-product production while minimizing effluent, which is important for a company to market itself as green. The production of bioethanol from paper sludge has the potential to be a cost effective method to reduce transport and disposal costs while providing additional revenue through ethanol sales [13].

Paper sludge typically contains 50% or more carbohydrates with glucan and xylan as the main components, making this material a suitable source for conversion to bioethanol. The benefit of using paper sludge for the production of bioethanol compared to other lingo cellulosic feedstock is the negative feed cost associated with the use of paper sludge [14].

The waste paper is pulped to obtain individual fibres, which undergo various stages of contaminant removal including different screening stages, hydro-cyclone banks, deinking and washing. The cleaned fibres are bleached and sent to the paper machine where tissue paper is produced [15]. The waste effluent obtained from waste water treatment and the rejects obtained from the different contaminant removal processes are combined and dewatered to produce recycled paper sludge.

In recent times there has been an increased focus on the use of paper sludge as a feedstock for the production of second generation ethanol using SSF. Most of this research was conducted on sludge emanating from the Kraft pulping process. There is a lack of information available on the production of second generation ethanol utilizing recycled paper sludge as a feedstock. An economic model is required to assess whether the SSF process is economically viable for the production of bioethanol using paper sludge as a feedstock. To obtain an accurate economic model, information regarding the composition and fermentability of paper sludge as well as the optimum paper sludge and enzyme loadings are required [16].

Fermentation and subsequent purification by distillation, rectification and dehydration are the core process groups [17,18]:

♦ Ethylene hydration:

Ethanol for use as an industrial feedstock or solvent (sometimes referred to as synthetic ethanol) is made from petrochemical feed stocks, primarily by the acid-catalysed hydration of ethylene:

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

In an older process, first practiced on the industrial scale in 1930 by Union Carbide, but now almost entirely obsolete, ethylene was hydrated indirectly by reacting it with concentrated sulphuric acid to produce ethyl sulphate, which was hydrolysed to yield ethanol and regenerate the sulphuric acid:

$$C_2H_4 + H_2SO_4 \rightarrow CH_3CH_2SO_4H$$

$$CH_3CH_2SO_4H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

♦ Separate hydrolysis and fermentation:

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 catalyse this reaction. Acid hydrolysis was used in this study because it is more economical.

$$(C_6H_{10}O_5)n + n\ H_2O \rightarrow n\ C_6H_{12}O_6$$

Fermentation is a series of chemical reactions that converts sugar 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 [4] . The simplified fermentation reaction equation for the 6-carbon sugar, glucose, is:

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

Toxicity of ethanol to yeast limits the ethanol concentration obtainable by brewing; higher concentrations, therefore, are obtained by distillation. To produce ethanol from starchy materials such as cereal grains, the starch must first be converted into sugars. The fermentation for about 24 hours at room temperature. After fermentation all the samples were ready for the distillation.

Ethanol has been produced from waste tissue paper and waste newspaper [15]. But, the conventional process of hydrolysis and fermentation has been attempted in the limited literature [19]. Hence, the present study aims to produce ethanol from waste tissue paper and waste newspaper through separate hydrolysis and fermentation, and to study the properties like pH, density, refractive index, dynamic and kinematic viscosity.

II. MATERIALS AND METHODS:

Materials:

Waste tissue paper and waste newspaper were collected from the University premises. They were screened to remove debris. Dry yeast was procured from the local hypermarket in Salalah. Sulphuric acid, potassium hydroxide, and other reagents were purchased from the native supplier. Glasswares available in the laboratories were used in the experiments.

Preparation of Jones reagent:

Jones reagent is a solution of chromium trioxide in dilute sulfuric acid and acetone. Jones oxidation is an organic reaction for the oxidation of primary and secondary alcohols to carboxylic acids and ketones, respectively. It is named after its discoverer, Sir Ewart Jones. A green color is observed in presence of alcohol.

Preparation of Lucas reagent:

Lucas reagent is a solution of saturated and anhydrous zinc chloride in concentrated hydrochloric acid. This solution is used to classify alcohols of low molecular weight. The reaction is a substitution in which the chloride replaces a hydroxyl group. A positive test is indicated by a change from colorless to turbid. Lucas test in alcohols is a test to differentiate between primary, secondary, and tertiary alcohols.

Preparation of bioethanol from waste tissue paper and waste newspaper:

Waste tissue paper and waste newspaper were cut into small pieces to increase surface area. 50 g each of waste tissue paper and waste newspaper were weighed and takes in beakers. 72% (v/v) H_2SO_4 solution was prepared and mixed with waste papers in the mass to volume ratio of 1:5. The beakers were heated at 80 °C for 4 h. The hydrolysate was separated from the sample by squeezing with spatula. Then, the sample was neutralized with 0.7 M KOH solution. The neutral pH was monitored using pH meter. After neutralization, 5 g of activated dry yeast (*Saccharomyces cerevisiae*) was added to neutralized hydrolysate for fermentation and the beakers were maintained at 40 °C for 24 h. After fermentation, distillation was proceeded to the samples to obtain pure bioethanol (Figure 1). The properties of bioethanol like pH, density, refractive index, dynamic and kinematic viscosity were checked, analysed and compared with the standard ethanol.

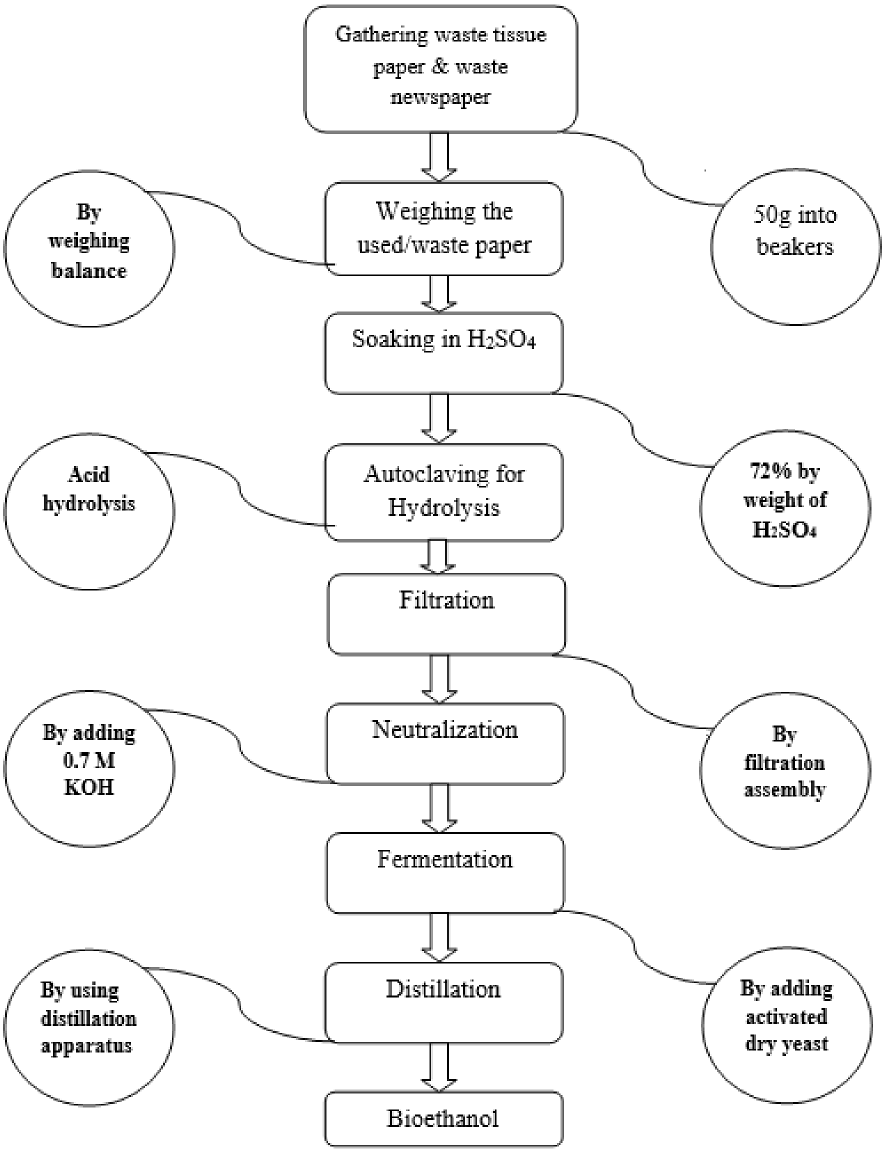

Figure 1. Process flowchart for preparation of bioethanol from waste tissue paper and waste newspaper

Properties of bioethanol:

pH analysis:

The electrode of the pH meter was cleaned using distilled water. The pH of water was checked first whether the pH measurement gives the correct reading or not. After checking the operation of the meter, the pH values of samples were checked and the results were recorded.

Density analysis:

The specific gravity bottles were cleaned and dried from impurities. An empty weight of the specific gravity bottle was measured. The specific gravity bottles were filled with distilled water and their weights were noted to calculate the density. The same procedure was repeated for the standard and samples for calculating the density and the results were recorded.

Refractive index analysis:

The refractometer was switched on and waited until the temperature of the machine stabilize. The refractometer was cleaned from impurities and added few drops of distilled water. The readings of samples were recorded.

Viscosity analysis:

The Ostwald viscometer was cleaned and dried from impurities and air. The viscometer was filled with distilled water until reaches to the top mark of the viscometer using rubber apparatus. A timer was used for recording the time when the distilled water start moving from the top line to the bottom line and write it down. The same procedure was repeated for checking viscosity of the samples.

Analysis of presence of alcohol:
Two reagents were used for checking the presence of alcohol in the experiment samples:

Jones reagent:
One mL of the sample was taken in a test tube. Three drops of the reagent were added into the test tube samples. The changing on the colour of the sample was observed into green colour, which confirms the presence of alcohol in the sample. The procedure was repeated for all obtained samples.

Lucas reagent:
One mL of the sample was taken in a test tube. Five drops of Lucas reagent was added into the test tube samples. The test tube sample were kept in hot water to increase the speed of the reaction and waited for some minutes until the colour change to snowy colour, which confirms the presence of alcohol in the sample. The procedure was repeated for all obtained samples.

III. RESULTS AND DISCUSSION:

Yield of bioethanol:

Table 1. Concentration of bioethanol from waste tissue paper and waste newspaper

Percentage of ethanol (% (v/v))	Density (g/mL)
100	0.798
75	0.847
50	0.921
25	0.967
0	1
86.38 (Waste tissue paper)	0.830
77.33 (Waste newspaper)	0.849

The density of waste tissue paper is 0.830 g/mL while waste paper has the density value of 0.849 g/mL. In bioethanol produced from waste tissue paper, the presence of ethanol is greater than 90% (91.6%). But, the presence of bioethanol produced from waste newspaper is less than 90% (86.4%). Waste tissue paper has more concentration of ethanol than the waste newspaper (Table 1). To identify the extent of bioethanol produced from the research, pH of 7.21 obtained is close to pure ethanol, density value of 0.789 g/cc is close to pure ethanol, refractive index of 1.355 is close to pure ethanol and viscosity of 0.0011 Pa.s is close to pure ethanol at 25 °C.

Table 2. Yield of bioethanol from waste tissue paper and waste newspaper

Percentage of Ethanol	Unit	Waste tissue paper	Waste newspaper
Mass of raw material	g	50	50
Volume of ethanol	mL	25.175	25.175
Density of ethanol	g/mL	0.830	0.849
Concentration of ethanol	% (v/v)	86.38	77.33
Mass of ethanol	g	18.05	16.53
Yield of ethanol	g ethanol/g tissue paper	0.361	0.331

$$Yield\ of\ ethanol\ from\ waste\ paper = \frac{Mass\ of\ ethanol}{Mass\ of\ tissue\ paper}$$

$$= \frac{Concentration\ of\ ethanol\ x\ Volume\ of\ ethanol\ x\ Density\ of\ ethanol}{Mass\ of\ tissue\ paper\ x\ 100}$$

Table 2 shows higher yield of bioethanol for waste tissue paper than waste newspaper due to the fact that higher cellulose content of 88% in waste tissue paper leads to greater yield of bioethanol.

Properties of bioethanol:

Table 3. Physical and chemical properties of bioethanol

Property	Unit	Bioethanol from waste tissue paper	Bioethanol from waste newspaper	Standard ethanol
pH	-	7.21	7.10	7.22
Refractive Index	-	1.354	1.358	1.355
Density	g/mL	0.830	0.849	0.789
Dynamic viscosity	Pa.s	0.0013	0.0016	0.0011
State	-	Liquid	Liquid	Liquid

Flame	-	Flammable	Flammable	Flammable
Colour	-	Colourless	Colourless	Colourless

pH is a measure of how acidic/basic water is. The range goes from 0 - 14, with 7 being neutral. pH less than 7 indicates acidity, whereas a pH of greater than 7 indicates a base. pH is really a measure of the relative amount of free hydrogen and hydroxyl ions in the water and solutions. Table 3 shows the values of pH of the prepared samples and their comparison with the standard ethanol after distillation process. The pH of waste tissue paper is 7.21 while waste paper has the pH value of 7.10, comparing to standard ethanol pH of the waste tissue paper is closer to the pH of standard ethanol is 7.22.

A refractometer is a laboratory or field device for the measurement of an index of refraction (refractometer). The index of refraction is calculated from Snell's law. Table 3 shows the value of refractive index of the prepared samples and their comparison with the standard ethanol after distillation process. The refractive index of waste tissue paper is 1.354 while waste paper has the refractive index value of 1.358, comparing to standard ethanol refractive index of the waste paper is closer to the Refractive Index of standard ethanol is 1.355.

The density, or more precisely, the volumetric mass density, of a substance is its mass per unit volume. The symbol most often used for density is ρ and its SI unit is kg/m^3. Table 3 shows the value of density of the prepared samples and their comparison with the standard ethanol after distillation process. The density of waste tissue paper is 0.769 g/mL while waste paper has the density value of 0.730 g/mL, comparing to standard ethanol density of the waste tissue paper is closer to the Density of standard ethanol is 0.789 g/mL [10].

The dynamic viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of thickness. Table 3 shows the value of viscosity of the prepared samples and their comparison with the standard ethanol after distillation process [19]. The viscosity of waste tissue paper is 0.0013 Pa.s while waste paper has the viscosity value of 0.0016 Pa.s, comparing to standard ethanol viscosity of the Waste Paper is more closer to the Viscosity of standard ethanol is 0.0011 Pa.s.

IV. CONCLUSION:

The present study focusses to produce ethanol from waste tissue paper and waste newspaper. Waste papers were mixed with 72% sulphuric acid in the mass to volume ratio of 1:5 and the hydrolysis was carried at 80 °C for 4 h. Then, hydrolysate was neutralized with 0.7 M potassium hydroxide and proceeded for fermentation with dry yeast (*Saccharomyces cerevisiae*) at 40 °C for 24 h. Finally, fermented broth was subjected to simple distillation to collect bioethanol. The properties of bioethanol like pH, density, refractive index, dynamic and kinematic viscosity. The presence of ethanol was confirmed using Jones and Lucas reagents. The properties of bioethanol reveal that the quality of fuel produced from waste tissue paper is superior than waste newspaper. Hence, it could be concluded that higher cellulose content of 88% in waste tissue paper leads to greater yield of bioethanol.

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