Production of Bio-ethanol from Solid Waste Paper Using Biological Activation

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1 Production of Bio-Ethanol from Solid Waste Paper Using Biological Activation

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9 Abstract

Biomass energy is renewable energy source that comes from the material of plants and animals. Forms of biomass energy are bio-ethanol, bio methanol, and biodiesel. Bio-ethanol is one of the most important alternative energy sources that substitute the fossil fuels. The focus of this research is to produce bio-ethanol from waste office paper. Five laboratory experiments were conducted to produce bio-ethanol from wastepaper. The wastepaper was dried in oven and cut in to pieces. Then it passed through dilute acid hydrolysis, fermentation and distillation process respectively. High amount of ethanol was observed at 20 ml/g (liquid to solid ratio) and at the time of 2hr. Cost and economic analysis for ethanol production from wastepaper was performed. Results from the analysis indicated a paper to ethanol plant was feasible from the economic point of view with rate of return (RR) 38.61% and the payback period of 2.2 years.

Keywords: Wastepaper, Hydrolysis, Fermentation, Distillation and Bio-ethanol, Biological Activation.

0 Introduction

Energy is the prosperity that must be transferred to an object in order to perform work on or to the object. It can be classified in to renewable and non-renewable energy resource (Solomon, B. D., et al., 2007). Non -renewable energy is any energy resource that cannot be replaced during the time of a human life span (Stokes H. 2005). It takes thousands of years to form and exist in fixed amount in the earth (Galbe, M. and Zacchi, G. 2007). They need to be conserved before they become depleted (L.C. Meher, D.V. Sagar, S.N. Naik. 2006 Balat H. 2010). Examples of Non-renewable energy resources are nuclear energy and fossil fuels (coal, oil, natural gas). Renewable energy is the term used to cover those energy flows that occur naturally and repeatedly in the environment and can be harnessed for human benefit (Steinbach, V. and F-W. Wellmer 2010). Biomass energy is a renewable energy resource that comes from the material of plants and animals, including their wastes and residues. Forms of biomass energy are bio-ethanol, bio methanol, and biodiesel (M. Molina-Sabio, F. Rodríguez-Reinoso. 2004, Sun, Y. and Cheng, J. 2002).

Bioethanol is one of the most important alternative renewable energy source that substitute the fossil fuels due to its potential to reduce negative environmental impacts such as air pollution and greenhouse gas emission (Hopkins, W.G., 2008, ULRICH G. 1999). Conventionally, bio-ethanol is produced from the fermentation of starchy materials or sucrose-containing feed stocks, such as corn, sugar cane, and honey (Demirbas, A. 2005, Cardona, C. and Sanchez, O. 2007). The yield of bio-ethanol from corn and sugar are high and the techniques are mature, however, it increases the risk of causing global food shortage (Balat M, Balat H, Oz C. 2008). In this context, an alternative to starch and sucrose based bio-fuels has been the production of ethanol from lignocelluloses materials such as weed, grass, saw dust, municipal solid waste, woody biomass, and paper mill waste (Lee D, Owens VN, Boe A, Jeranyama P. 2007).

Wastepaper consists of a considerable share of municipal and industrial waste even though recycling efforts have been strengthened in recent years by legal provisions like the Packaging directive. However, the recycling rate of wastepaper is low and the recycled wastepaper has a low grade paper product because of shorted fiber length (Gaur, K. 2006, Hamelinck, C., van Hooijdonk, G. and Faaij, A. 2003).

Since the shortening of paper fibers decreases the quality of paper, the maximum ratio of paper-to-paper recycling is said to be 65% (Ikeda, Y., Park, E. Y., & Naoyuki, O. 2006, Wayman. M and Parekh. S. R. 1990). This means that a certain fraction of paper would always be sent to disposal. Still, wastepaper is considered as one of the prospective and renewable biomass materials to produce bioethanol (Karuppiyah, R., Peschel, A., Martin, M., Grossmann, I. and Zullo, L. 2007, Kim SH. 2004). The reasons for this include (Lark N, Xia Y, Qin C-G, Gong CS, Tsao GT. 1997). Waste papers are relatively abundant, They are economically competitive with other biomass feed stocks as they are relatively low costs, They contain relatively high levels of carbohydrates that are potential convertible to bioethanol, They are likely to be easily digestible without aggressive physical or chemical pre-treatments, Utilization of waste papers for bio-ethanol production may offer a useful and valuable alternative route to managing these papers in addition to/as a complement to recycling (L.C., Meher, D.V. Sagar, S.N. Naik. 2006, L. Wang et al. 2012). Furthermore, Paper recycling technology itself has limitations, for example, effective deinking technology is needed to produce high quality paper products and recycling to paper is very difficult for wastepaper that has been mixed with other organic waste (kitchen/garden waste etc.) (Lee D, Owens VN, Boe A, Jeranyama P. 2007, Lee D, Owens VN, Boe A, Jeranyama P. 2007). Moreover, this alternative outlet for waste papers could help reduce pressure on other waste management options (i.e. recycling, incineration and landfill) from the increasing waste generation due to rising population (Ikeda, Y., Park, E. Y., & Naoyuki, O. 2006, WWI (WORLD WATCH INSTITUTE. 2006).

MATERIALS AND METHODS

Autoclave, Centrifuge, Digital Balance, Digital PH meter, Flasks of different volumes, Graduated cylinders of different volumes, Incubator, Rotary evaporator and Scissor

Chemicals

5M sodium hydroxide (NaOH) solution, 98% sulfuric acid (H₂SO₄), Distilled water, Dry instant yeast (*saccharomyces cerevisiae*) and Potassium dichromate

Collection of Raw Material

Waste paper was collected from Wolkite University wolkite, Ethiopia

3.2. Methods

3.2.1. Sample Preparation

Waste office papers were collected locally in Wolkite University. The wastepaper was dried in tray dryer (60 °C for 48hr). The sample was cut in to pieces by using scissor. The cut material was kept at desiccator until the next stage of experiment in order to remove contact with the atmosphere. Cutting of the sample wastepaper into pieces increases the surface area of the sample which enhances the contact between hemicelluloses and cellulose with dilute acid (M. Molina-Sabio, F. Rodríguez-Reinoso. 2004).

Figure 1 Sample preparation, (A) Sample on tray dryer, (B) Sample cutting.

3.2.2. Dilute Acid Hydrolysis

The carbohydrate polymers in lignocellulosic materials need to be converted to simple sugars before fermentation, through a process called hydrolysis (Madson, P. and Lococo, D. 2000). Even though there are many types of hydrolysis types, dilute acid hydrolysis is an easy and productive process and the amount of alcohol produced in case of acid hydrolysis is more than that of alkaline hydrolysis (Miles, W. E. et al., eds. 1988. *Pulp and Paper* 1988, McMillan, J. 1994). This process is conducted under high temperature and pressure, and has a reaction time in the range of seconds or minutes, which facilitates continuous processing. The experimental conditions of the different test carried out and the observed hydrolysis time and acid volume in each experiment was shown by table 3.1.

Table 1. Experimental hydrolysis parameters

Test	Liquid to solid ratio(ml/gm)	Time(min)
1	20	60
2	20	120
3	20	180
4	10	120
5	30	120

Acid hydrolysis was done to break down cellulose into glucose units. Experiments were carried out by using different volume of flasks. For that, 10 g of paper was soaked in different amounts of H_2SO_4 (5% weight): 200 and 300 mL [98% sulfuric acid (by volume to water) was diluted to 5% concentration]. The mixture was placed in an autoclave at 121 °C. The influence of time on the process was determined in the range of 60-180 min. After hydrolysis, the samples were filtered and centrifuged to separate the solid particles from the liquid in the hydrolyzed (remove the non-fermentable lignin portion) and to obtain the hydrolyzate product as shown in the figure below. After that, the pH of the obtained product was adjusted at 4.5-5.5 by adding sodium hydroxide solution 5M.

Figure 2. Acid hydrolysis (A), Sample ready for Dilute Acid Hydrolysis, (B), after filtration and (C) Centrifugation

3.2.3. Adjustment of pH

Before addition of any microorganism to the diluted hydrolyzed sample, pH of these samples had to be adjusted. Otherwise the microorganism will die in hyper acidic or basic state. A pH of around 4.5 - 5.5 was maintained. The hydrolyzed samples were primarily checked for pH using a digital pH meter. The pH then was adjusted to 4.5 - 5.5. If the pH went below 4.5 - 5.5, sodium hydroxide solution was added drop wise to the flask with constant stirring until the pH reaches to a range of 4.5 - 5.5. When the pH went beyond 4.5 - 5.5, concentrated sulfuric was added drop wise to maintain the pH in the range.

Figure 3. PH Adjustment, (A) before PH is adjusted, (B) after PH is adjusted

3.2.4. Fermentation

The yeast *Saccharomyces cerevisiae* was added to the hydrolyzed sample. The fermentation of all the samples was done in the incubator at 30 °C for 72 hours. After 72 hours of fermentation, the sample was taken out and distilled in order to get the bioethanol.

3.2.5. Distillation

All distillation experiments were carried out at a temperature of 90°C and a distillation time of 6 hours by rotary evaporator to separates the bioethanol from water in the liquid mixture.

3.2.6. Identification of Bioethanol

About 5 ml fermented sample was taken and pinch of potassium dichromate and a few drops of H_2SO_4 were added. Color change from orange to green indicated the presence of bio-ethanol.

Figure 4..Identification of bio-ethanol, (A) before adding H_2SO_4 , (B).After adding H_2SO_4 .

Figure 5. process Flow Diagram for Production of Bio-ethanol from waste paper

RESULTS AND DISCUSSION

The focus of this research is to produce bio-ethanol from waste office paper by acid hydrolysis and subsequent fermentation. The Table below shows the value of hydrolysis parameter and the corresponding amount of ethanol of this research.

Table 2. Values of Hydrolysis Parameters and the corresponding result of the research.

Test	Liquid to solid ratio(ml/g)	Time(min)	Amount of ethanol (ml/10g)
1	20	60	1.7
2	20	120	4
3	20	180	2.2
4	10	120	0.8
5	30	120	2

High amount of ethanol was observed at 20 Liquid to solid ratio (ml/g) and at the time of 2hr. By varying time and taking constant liquid to solid ratio (ml/g) the obtained amount of bio- ethanol is described in the Table below.

Table 3. Amount of bio ethanol at constant liquid to volume ratio

Time (min)	Amount of ethanol(ml/10g)
60	1.7
120	4
180	2.2

The graphical representation of the obtained results is shown in the Figure below.

Figure 6. Influence of hydrolysis time on the amount of bioethanol

The results showed that maximum ethanol amount is achieved at 120 min. Therefore, time taken is 120 min for further study. The three experiments were carried out by varying the Liquid to solid ratio (ml/g) and with constant time.

Table 4. Amount of bioethanol at constant time (120 min)

Liquid to solid ratio(ml/g)	Amount of bioethanol(ml/10g)
10	0.8
20	4
30	2

The graphical representation of the obtained results is shown in the Figure below.

Figure 7. Influence of hydrolysis liquid to solid ratio on the amount of bio-ethanol

The data reveal that there was substantial decreases in the amount of bio ethanol when waste office paper was treated with 10 and 30 ml/g. While when treated at 20 ml/g high amount of bio ethanol was obtained.

Table 5. Amount of bioethanol at various time intervals (at 20ml/g and for 120 min)

Time (hr)	Amount of bioethanol(ml/10g)
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2:00	0.8
2:30	1.4
3:00	2.6
3:30	3.1
4:00	3.4
4:30	3.6
5:00	3.8
5:30	3.9
6:00	4
6:30	4

The above table shows the value of evaporation time and the corresponding ethanol amount that was collected in every 30 minutes in rotary evaporator (For the sample in which high amount of bio ethanol was obtained).

The graphical representation of the obtained result is shown in the Figure 4.3 below

Figure 8. Amount of bio-ethanol at various time intervals (20ml/g for 120 min)

High bio ethanol amount was obtained at 20ml/g for 120 min which is 4ml/10g. So, this condition became preferable for the production of bio ethanol from waste paper.

Bioethanol Characterization

Table 6. Characterization of the product

Characteristics	Standard value	Product value
Color	Colorless	Colorless
Odor	Strong odor	Strong odor
Volatility	Volatile	Volatile
Bulk density(g/cm ³)	0.79	0.76

MATERIAL AND ENERGY BALANCE

When we are dealing with chemical engineering, it's mandatory to perform material balance and energy balance on selected areas. Material balances are fundamental to the control of processing, particularly in the control of yields of the products. The first material balances are determined in the exploratory stages of a new process, improved during pilot plant experiments when the process is being planned and tested, checked out when the plant is commissioned

and then refined and maintained as a control instrument as production continues. When any changes occur in the process the material balances need to be determined again.

The increasing cost of energy has caused the industries to examine means of reducing energy consumption in processing. Energy balances are used in the examination of the various stages of a process, over the whole process and even extending over the total production system from the raw material to the finished product. The energy balance determinations are also made to determine the energy requirements of the process, the heating, cooling and power required. In this plant operation it is thought that an energy balance (energy audit) (ministry of Finance and Economic Development (MoFED). 2010) on the plant will show the pattern of energy usage and suggest areas for conservation and savings. In this chapter, description of the basic steps of ethanol production process and detailed mass and energy balance for each unit operations is presented.

5.1. Material Balance

5.1.1. Conservation Of Mass

Material balances are based on a conservation law which is stated generally in the form:

Input + generation – output – consumption = Accumulationeq(1)

Where: Input = enters through system boundaries

Generation = is producing within the system

Output = Exist through system boundaries

Consumption = is a soul within the system

Accumulation is built up within the system

The term that is added in a chemical process is known as generation and the term that is subtracted in a chemical process is known as consumption.

If there is some sort of chemical reaction entire the general equation for material balances,

Input + generation – consumption – output = accumulation

If there is no chemical reaction the process is at steady state (when there is no change) which means there is no generation and consumption. This implies accumulation is zero.

Accumulations are time rates of change of the amount of the entities within the boundary. For example, in the absence of sources and sinks, an accumulation occurs when the input and output rates are different.

Input – output = 0, i.e. input = output [at steady state –accumulation is zero]

Except in nuclear processes, mass is neither generated nor consumed; but if a chemical reaction takes place a particular chemical species may be formed or consumed in the process.

5.1.2. Calculation

The total material balance is written as: Material in = Material out Or $M_i = M_o$ (i = input; o = output).The mass balance calculation starts with wastepaper inputs. The wastepaper to ethanol conversion process can be divided into five basic steps [Sample Preparation (drying), acid hydrolysis, Filtration, centrifugation and Distillation].

Assume Production capacity of 3,000,000 gal/yr of ethanol with plant operation of 300 days/yr.

I. Distillation

➤ If there is no chemical reaction the steady-state balance reduces to

Material in= Material out

$$A = B+C = 1,180,735,273\text{kg/yr} + 2,663,312.65\text{ kg/yr} = 1,183,398,586\text{kg/yr}$$

$$\underline{A=1,183,398,586\text{kg/yr}}$$

II. Centrifugation

Overall material balance

➤ no chemical reaction so, the steady-state balance reduces to: material in= Material out

$$D = E+A$$

$$E=A-D$$

$$E= 3,052,759,309\text{kg/yr} - 1,183,398,586\text{kg/yr}=1,869,360,723\text{kg/yr}$$

$$\underline{E=1,869,360,723\text{kg/yr}}$$

III. Filtration

Overall material balance

➤ no chemical reaction so, the steady-state balance reduces to: material in= Material out

$$F = D+G$$

$$G=F-D$$

$$G=4,251,250,000\text{kg/yr} - 3,052,759,309\text{kg/yr} = 1,198,490,691\text{kg/yr}$$

$$\underline{G=1,198,490,691\text{kg/yr}}$$

IV. Acid hydrolysis

Overall material balance

- no chemical reaction so, the steady-state balance reduces to: material in= Material out

$$H+I=F$$

$$F=23,750,000 \text{ kg/yr} + 4,227,500,000\text{kg/yr} = 4,251,250,000\text{kg/yr}$$

$$\underline{F=4,251,250,000\text{kg/yr}}$$

V. Dryer

28,500,000kg/yr waste paper (J)

Overall material balance

- no chemical reaction so, the steady-state balance reduces to: material in= Material out

$$J= K+H$$

$$K=J-H=28,500,000\text{kg/yr} - 23,750,000 \text{ kg/yr} = 4,750,000\text{kg/yr}$$

$$\underline{K=4,750,000\text{kg/yr}}$$

5.2. ENERGY BALANCE

5.2.1. Introduction

As with mass, energy can be considered to be separately conserved in all but nuclear processes.

The conservation of energy, however, differs from that of mass in that energy can be generated (or consumed) in a chemical process.

5.2.2. Conservation Of Energy

As for material a general equation can be written for the conservation of energy:

Accumulation = Energy in + generation — consumption — Energy out

An energy balance can be written for any process step. Chemical reaction will evolve energy (exothermic) or consume energy (endothermic). For steady-state processes the accumulation of both mass and energy will be zero.

So for unit mass of material:

$$U_1 + P_1V_1 + 0.5 U_1^2 + Z_1 g + Q = U_2 + P_2V_2 + 0.5 U_2^2 + Z_2 g + W \dots \dots \dots \text{eq(2)}$$

It is convenient and useful, to take the terms U and PV together; defining the term enthalpy, usually symbol H, as:

$$H = U + PV \dots \dots \dots \text{eq(3)}$$

In chemical processes, the kinetic and potential energy terms are usually small compared with the heat and work terms, and can normally be neglected. So if the kinetic and potential energy terms are neglected equation 2 simplifies to;

$$H_2 - H_1 = Q - W \dots \dots \dots \text{eq(4)}$$

For many processes the work term will be zero, or negligibly small, and equation 2 reduces to the simple heat balance equation:

$$H_2 - H_1 = Q \dots \dots \dots \text{eq (5)}$$

Where heat is generated in the system; for example, in a chemical reactor:

$$Q = Q_p + Q_s \dots \dots \dots \text{eq(6)}$$

Where: Q_s = heat generated in the system

Q_p = process heat added to the system to maintain required system temperature.

If heat is evolved (exothermic processes) Q_s is taken as positive, and if heat is absorbed (endothermic processes) it is taken as negative

I. Dryer

Water = 4,750,000 kg/yr

$$M = 23,750,000 \text{ kg/yr}$$

$$\Delta T = 35 \text{ °C} = 308 \text{ K}$$

$$C_p = 1.4 \text{ J/g} \cdot \text{K}$$

$$Q = M \cdot C_p \cdot \Delta T$$

$$Q = 23,750,000 \text{ kg/yr} \cdot 308 \text{ K} \cdot 1.4 \text{ J/g} \cdot \text{K}$$

$$Q = 1.0241 \cdot 10^{10} \text{ KJ/yr}$$

$$P = Q \cdot T = 1.0241 \cdot 10^{10} \text{ KJ/yr} \cdot (1 \text{ yr} / 300 \text{ day}) \cdot (1 \text{ day} / 16 \text{ hr}) \cdot (1 \text{ hr} / 3600 \text{ s}) = P = 592.65 \text{ KW}$$

$$E = P \cdot T = 592.65 \text{ KW} \cdot 16 \text{ hr} = 9,482.4 \text{ KWh}$$

The quantity of energy required for the dryer per year is: 9,482.4 KWh.

II. Acid hydrolysis

$$M = 4,251,250,000 \text{ kg/yr}$$

$$\Delta T = 96 \text{ °C} = 369 \text{ K}$$

$$C_p = 2.79 \text{ J/g} \cdot \text{K}$$

$$Q = M \cdot C_p \cdot \Delta T$$

$$Q = 4,251,250,000 \text{ kg/yr} \cdot 2.79 \text{ kJ/kg} \cdot \text{K} \cdot 369 \text{ K}$$

$$Q = 4.37 \cdot 10^{12} \text{ KJ/Kg}$$

$$P = Q \cdot T = 4.37 \cdot 10^{12} \text{ KJ /Kg} \cdot (1 \text{ yr}/300 \text{ day}) \cdot (1 \text{ day}/16 \text{ hr}) \cdot (1 \text{ hr}/3600 \text{ s}) = 253,281 \text{ KW}$$

$$E = P \cdot T = 253,281 \text{ KW} \cdot 16 \text{ hr} = 4,052,504 \text{ KWh}$$

The quantity of energy required for the hydrolysis per year is: 4,052,504 KWh

III. Distillation

$$M = 1,180,735,273 \text{ kg/yr}$$

$$\Delta T = 65 \text{ °C} = 338 \text{ K}$$

$$C_p = 4.18 \text{ J/g} \cdot \text{K}$$

$$Q = M \cdot C_p \cdot \Delta T$$

$$Q = 1,180,735,273 \text{ kg/yr} \cdot 4.18 \text{ J/g} \cdot \text{K} \cdot 338 \text{ K}$$

$$Q = 1.67 \cdot 10^{12} \text{ KJ/Kg}$$

$$P = Q \cdot T = 1.67 \cdot 10^{12} \text{ KJ/Kg} \cdot (1 \text{ yr}/300 \text{ day}) \cdot (1 \text{ day}/16 \text{ hr}) \cdot (1 \text{ hr}/3600 \text{ s}) = 96,539 \text{ KW}$$

$$E = P \cdot T = 96,539 \text{ KW} \cdot 16 \text{ hr} = 1,544,620 \text{ KWh}$$

The quantity of energy required for the distillation per year is: 1,544,620 KWh

CONCLUSION

The bio-ethanol production from solid waste paper was successful. The best conditions for acid hydrolysis of 10 g of raw material were 200 mL of 5% sulfuric acid and 120 min of reaction time at 121 °C. After fermentation with *Saccharomyces cerevisiae*, 0.4 mL of bio-ethanol/g was obtained. Finally, some properties were measured according to the standards and the obtained bio-ethanol conforms to the set limit. Based on the obtained results, it can be concluded that waste paper is a suitable raw material for bio-ethanol production. It was found that a paper to ethanol plant was feasible from the economic point of view. It makes a significant annual multi-million birr profit, with payback time being less than three years. Therefore, Ethanol production from wastepaper is doubtlessly an attractive business from economic and environmental point of view. This technology can be used as an alternative solution for sustainable waste management and material / energy recovery.

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Authors' contributions

Zeynu Shamil contributed to the proposal writing, experiment design, fieldwork, data collection, data analysis and interpretation using and writing the manuscript. Rezika Tofike. Her assisted in the proposal writing, experiment

333 design fieldwork, data collection, data analysis and interpretation using and writing the manuscript. Both the authors
334 read and approved the final manuscript.

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338 We declare that the data and materials used in this manuscript can be made available as per the editorial policy of
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340 **Declarations**

341 **Ethics approval and consent to participate**

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345 **Competing interests**

346 The authors declared that there is no competing interest.

347 **Reference**

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