

A Characteristic Analysis of Bio-ethanol produced on Fruit Wastes for Direct Ethanol Fuel Cell (DEFC)

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ABSTRACT

This study is aimed to produce bio-ethanol based on fruit wastes and optimize bio-ethanol and analyze ethanol component. Fruit wastes such as pear, apple and persimmon was used in acid pre-treatment, at temperature 120°C, period of 90min. Hydrolysis rate of pear at concentration 3% is 11.3%(sulfuric acid), 14.1%(nitric acid), 15.5%(hydrochloric acid). For alcohol fermentation, fermentation temperature of 25°C and 30°C, fermentation period of 48 hours were set to alcohol fermentation process. Ethanol concentration was not significantly difference by temperature. After fermentation process was completed, concentration of ethanol produced was 5%. Using the multi column distillation system, more than 95% ethanol was distilled and each component analysis of bio-ethanol was resulted. Comparing ethanol with mixed fuel(bio-ethanol(10%) and ethanol(90%)), the performance of ethanol was higher than that of mixed fuel. The bio-ethanol from this multi column distillation method was corresponded with the international standards of Japan, U. S. A and Brazil. But, In order to use the bio-ethanol on fuel cell, it keep on research how it harmed fuel cell.

Keywords: Fruit waste, Bio-ethanol, Pre-treatment, Fermentation, Component Analysis, Multi column distillation.

1 INTRODUCTION

Energy consumption has increased steadily over the last century as the world population has grown and more countries has become industrialized. Crude oil has been the major resource to meet the increased energy demand. Annual global oil production would decline from the current 25 billion barrels to approximately 5 billion barrels in 2050. Because the economy is the US and many other nations depends on oil, the consequences of inadequate oil availability could be severe. Therefore, there is a great interest in exploring alternative energy source.

Unlike fossil fuels, ethanol is a renewable energy source produced through fermentation of sugars. Ethanol is widely used as a partial gasoline replacement in the US. Fuel ethanol that is produced from corn has been used in gasohol fuels contain up to 10% ethanol by volume. As a result, the US transportation sector now consumes about

4540 million liters of ethanol annually, about 1% of the total consumption of gasoline.[1]

However, the cost of ethanol as an energy source is relatively high compared to fossil fuels. A dramatic increase in ethanol production using the current cornstarch-based technology may not be practical because corn production for ethanol will compete for the limited agricultural land needed for food and feed production. A potential source for low-cost ethanol production is to utilize cellulosic such as fruit waste.

Fruit wastes such as peel of pear, apple and persimmon is disposed of separately. They contains a high concentration of organic matter, but it is necessary to hone the fruit waste to switch to bio-energy.[2] Using fruit waste to produce bio-ethanol, the environmental pollution and waste disposal problems can be solved. In this paper, bio-ethanol production optimization based on fruit waste and component analysis for analyze the characteristics of bio-ethanol is revealed.

2 EXPERIMENT METHOD

2.1 Biomass

Fruit wastes such as pear, apple and persimmon is used as biomass. After it's in air drying process 20 hours, it is investigated for moisture, calorie, protein, crude protein, crude fat, sodium, trans fat, saccharide, saturated fatty acid and cholesterol through Korean Food Standard Codex.

2.2 Pre-treatment

For hydrolysis of fruit wastes, sulfuric acid, nitric acid and hydrochloric acid is utilized in step of pre-treatment. Temperature was set 120°C and pre-treatment time was 90 minutes. Acid concentration was 0.5%, 1.0%, 3.0% and 5.0%, respectively. Hydrolysis was confirmed by the reducing sugar through DNS method. [3]

2.3 Fermentation

Saccharomyces cerevisiae was used in step of fermentation to fruit wastes after pre-treatment. Temperature was set 25°C, 30°C and time was 48 hours. When fermentation was done, it was distilled until 95% alcohol through distillation process. In distillation process,

multi column distillation device was used.(Fig. 1) It was invited to remove moisture and other organic matter. As the distillation, vapours gas(water, ethanol, other organic matters)is keep going to the condenser. But, rising gas was liquefied in middle of tube, relatively heavy molecular dropped to down. Impurities in liquid was distilled by this multi coloumn distillation device.

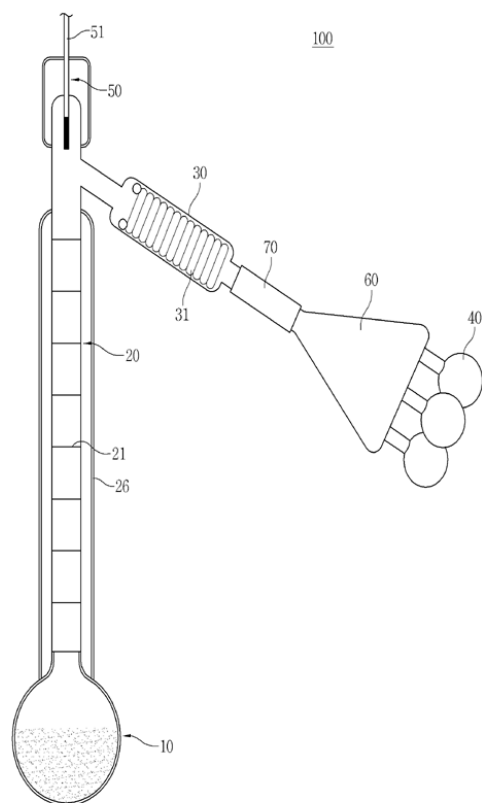


Fig. 1 Schematic of multi coloumn distillation

TABLE 1. PEAR, APPLE AND PERSIMMON NUTRITIVE COMPONENTS

| Nutritive | fruit waste | | |
|------------------------------|-------------|-------|-----------|
| | pear | apple | Persimmon |
| moisture(g/100g) | 4.90 | 4.1 | 5.0 |
| calorie(kcal/100g) | 371 | 356 | 363 |
| carbohydrate(g/100g) | 89.4 | 83.3 | 86.5 |
| crude protein(g/100g) | 2.3 | 2.1 | 3.5 |
| crude fat(g/100g) | 0.5 | 1.7 | 0.3 |
| sodium(mg/100g) | 3.7 | 10.3 | 14.6 |
| trance fat(g/100g) | 0.0036 | 0 | 0 |
| saccharide(g/100g) | 5.3 | 4.6 | 11.7 |
| saturated fatty acid(g/100g) | 0.1 | 0 | 0 |
| cholesterol(mg/100g) | - | - | - |

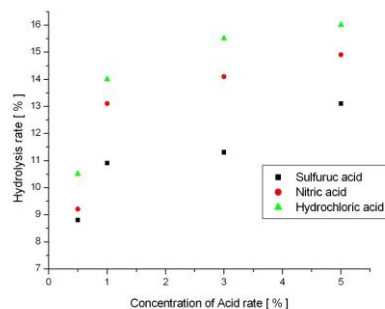


Fig. 2-a) Hydrolysis rate of pear peel

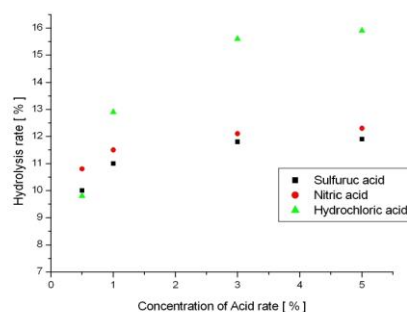


Fig. 2-b) Hydrolysis rate of persimmon peel

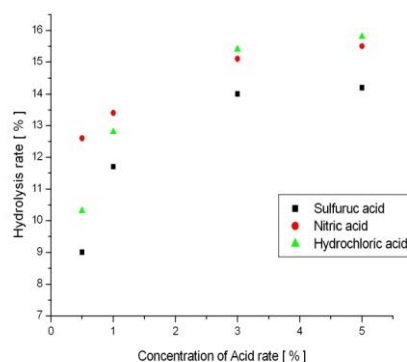


Fig. 2-c) Hydrolysis rate of apple peel

2.4 Component analysis

After Distillation process, bio-ethanol measured components following this ; color, solvent-washed gum, sulfur, aromatic, olefin, methanol and ethanol. Physiochemical components of bio-ethanol was selected based on transport ethanol standard of U. S. A(ASTM D 4806-07) and Japan(JASO M361).

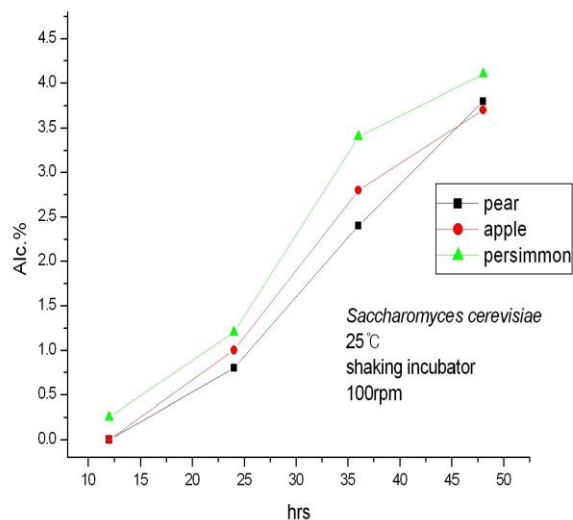


Fig. 3-a) Alcohol concentration(Alc. %) at fermentation temperature 25 °C

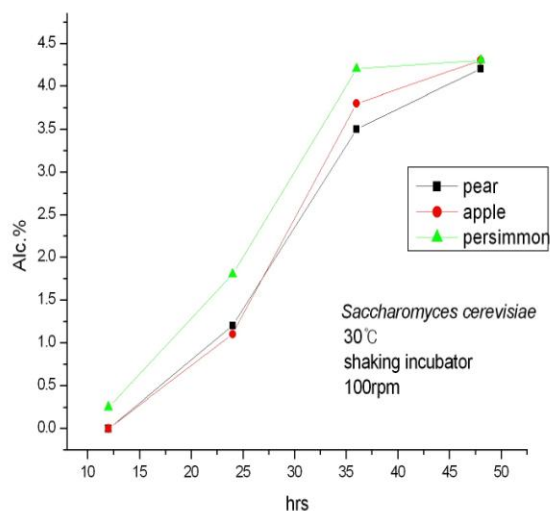


Fig. 3-b) Alcohol concentration(Alc. %) at fermentation temperature 30 °C

2.5 DEFC

Bio-ethanol could be applied as fuel cell whether it was suitable. Direct Ethanol Fuel Cell system schematic is shown in fig. 4. DEFC system consisted of fuel tank(alcohol), air pump, heater and control&monitoring system. Generally, catalysts of DEFC were consisted PtRu or PtSn. Comparing between PtRu and PtSn performance is shown in fig. 5.[4]

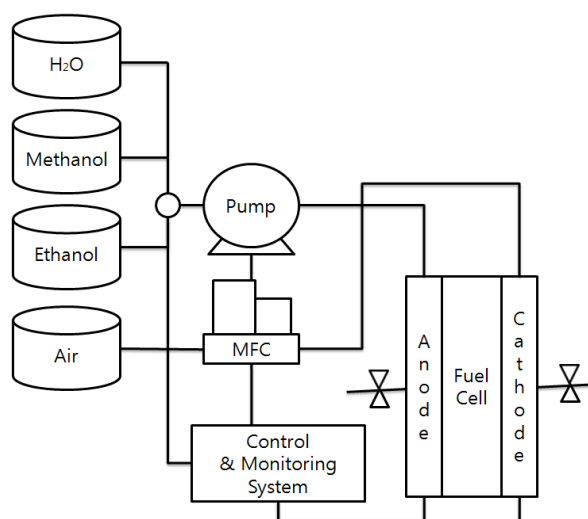


Fig. 4 Diagram of direct ethanol fuel cell

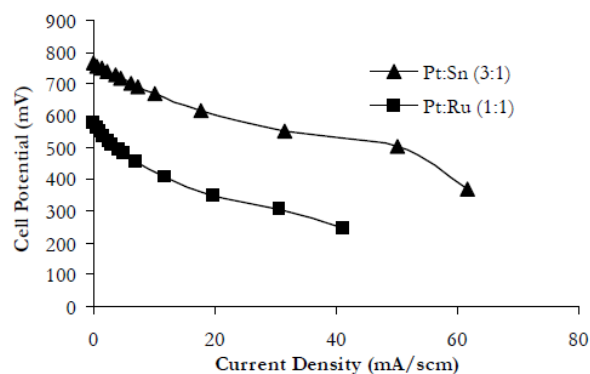


Fig. 5 I-V curve comparing performance by catalysts of Pt:Ru and Pt:Sn

3 RESULTS

3.1 Nutritive components

Results of nutritive components were shown in Table 1. Pear peel calorie is most likely 371kcal. Then persimmon peel was 363kcal, and apple peel was 356kcal. Pear peel carbohydrate was 89.41g/100g, persimmon was 86.5g/100g, apple peel was 83.3g/100g. Apple peel crude protein was 2.1g/100g, pear peel was 2.3g/100g and persimmon peel was 3.5g/100g. Persimmon peel sodium was 14.6mg/100g, apple peel was 10.3mg/100g and pear peel was 3.73mg/100g. Trans fat and saturated fatty acid was not detected in apple peel and persimmon, but trans fat 0.00036g/100g and saturated fatty acid 0.1270g/100g is detected.

Table. 2 Physiochemical components of bio-ethanol that produced this study and transport ethanol standards of Japan, U.S.A and Brazil

| test item | bio-ethanol | Japan (JASO M 361) | U.S.A (ASTM D 4806-07) | Brazil |
|--------------------|-------------|-----------------------|------------------------------|----------------------|
| solvent-washed gum | 2mg/100mL | >5mg/100mL | >5mg/100mL | >5mg/100mL |
| sulfur | 3mg/Kg | - | >30mg/Kg | - |
| color | colorless | colorless or citrine | colorless or citrine | colorless or citrine |
| aromatic | >0.1vol% | >3.0vol% | - | >3.0vol% |
| olefin | 0.2vol% | >3.0vol% | - | >3.0vol% |
| methanol | 0.1wt% | >4.0g/L | >0.5vol% | - |
| ethanol | 99.7wt% | <99.5vol% | <92.1vol% | <99.3wt% |

Saccharide related to bio-ethanol production was 11.7g/100g(persimmon), 5.3g/100g(pear) and 4.6g/100g(apple). There were no cholesterol detection in all fruit wastes.

3.2 Pre-treatment

When acid pre-treatment step, hydrolysis rate was most highest in 5% acid concentration. However, hydrolysis rate compared with 3% acid concentration was almost same hydrolysis 5% acid concentration.(Fig. 2-a, b, c)

3.3 Alcohol fermentation

In alcohol fermentation process, the initial alcohol percent is increased sharply at temperature 25°C and 30°C.(Fig. 3-a, b) After fermentation process was completed, bio-ethanol concentration was 5%. Produced ethanol was carried out a 1st distillation and 2nd distillation process. It was resulted in more than 95% of the alcohol was distilled. Bio-ethanol what distilled until 2nd distillation was injected in multi coloumn distillation device. 95% bio-ethanol was concentrated to 99% bio-ethanol.

3.4 Component analysis

Result of bio-ethanol component analysis is shown in table 2. Color is colorless, sulfur 3mg/kg, solvent-washed gum 2mg/mL, aromatic 0.1vol% less, olefin 0.3vol%, methanol 0.1wt% and ethanol 99.7wt%, respectively. In the result of component analysis, bio-ethanol based on fruit wastes is suitable for ethanol standard of Japan, U. S. A and Brazil.

3.5 Ethanol & bio-ethanol performance

Comparing the fuel cell performance of ethanol and mixed ethanol(ethanol(90%)+bio-ethanol(10%)) based on fruit wastes was shown in Fig. 6. In performance test, mixed fuel performance measured about 87% of ethanol fuel performance. It seems to harm fuel cell performance by bio-ethanol impurities such as formic acid and other organic matters.[6] Besides, nafion membrane using in single cell was damaged by swelling and distortion by ethanol.[7]

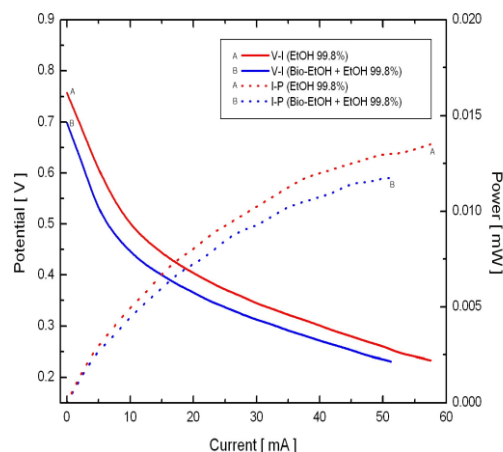


Fig. 6 Compare the performance of ethanol with that of mixed fuel(ethanol 90% + bio-ethanol 10%)

4 CONCLUSION

1)As acid concentraion increased, hydrolysis rate is increased. But, hydrolysis rate compared with 3% acid concentration was almost same hydrolysis 5% acid concentration.

2)Acids of hydrolysis values were best in hydrochloric acid than another acid. Therefore, there was most effective with 3% hydrochloric acid in pre-treatment process.

3)In alcohol fermentation process, the initial alcohol percent is increased sharply at temperature 25°C and 30°C. But, there were no difference in the final alcohol percent. It seems to complete alcohol fermentation within 48 hours because initial saccharide is low. Additional studies are needed to incese the alcohol fermentation efficiency by types of yeast.

4)It was suitable that bio-ethanol based on fruit wates in U. S. A, Japan and Brazil ethanol standards. In order to use the bio-ethanol to fuel cell, it is necessary that ethanol standard for fuel cell is established

5)Comparing ethanol with mixed fuel(bio-ethanol(10%) and ethanol(90%)), the performance of ethanol was higher than that of mixed fuel. Formic acid affected with PEM(Polymer Electrolyte Memebrane). It

has a negative effect on the cathode catalyst layer, specially. It could be adsorption on the electrode surface as well as the formation of reaction byproducts such as CO. Impurity such as acetaldehyde do not significantly affect fuel cell performance.[7]

ACKNOWLEDGMENT

This research was financially supported by Ministry of Education, Science Technology (MEST) and Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Regional Innovation.

This study is supported by Center for organic Agri-Food industrialization (RIC) in Dongshin University Industry&Academy Cooperation Foundation that is Ministry of Knowledge Economy.

REFERENCES

- [1] Ye Sun and Jiayang Cheng, "Hydrolysis of lignocellulosic materials for ethanol production:a review", *Bioresource Technology* 83 1- 11, 2002.
- [2] H. Bouallagui, M. torrijos, J. J. Godon, R. Moletta, R. Ben Cheikh, Y. Touhami, J. P. De;genes, and M. Hamdi, "Two phase anaerobic Digestion of Fruit and Vegetable Wastes:Bioreactors Performance", *Biochem. Eng. J.*, Vol. 21, No. 2, pp. 193-197, 2004
- [3] G. L. Miller, "Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugar", *Anal. Chem.*, Vol. 31, No. 3, pp. 426-428, 1959
- [4] M. Jonathan, M. Scott Daubin, Andrew B. Bocarsly, 'catalysts for direct ethanol fuel cells', *Chen. Soc. Fuel Chem.*, vol. 49, pp 662, 2004
- [5] D.-H. Peck, Y.-C. Park, B.-R. Lee, D.-H. Jung, 'Effect of the impurities in methanol fuel on the performance of MEA for Direct Methanol Fuel Cell', 18th World Hydrogen Energy Conference 2010 – WHEC 2010, Energy & Environment, Vol 78-1, 2010
- [6] T. V. Nguyen, N. Vanderborgh, "The Rate of Isothermal Hydration of Polyperfluorosulfonic Acid Membrane", *J. Membrane. Sci.*, Vol. 143, No. 1-2, 1998, pp. 235-248
- [7] Trent M. Molter, 'Effects on Impurities on Fuel Cell Performance and Durability', FY 2009 Annual Progress Report, Vol. 1, pp. 983-988, 2009