Bull. Chem. Soc. Ethiop. **2015**, 29(2), 239-245. ISSN 1011-3924
Printed in Ethiopia

DOI: http://dx.doi.org/10.4314/bcse.v29i2.7

INVESTIGATION OF WASTE BANANA PEELS AND RADISH LEAVES FOR THEIR BIOFUELS POTENTIAL

Abdul Majeed Khan*, Shaista Khaliq and Rabia Sadiq

Department of Chemistry, Federal Urdu University, Gulshan-e-Iqbal Campus,
University Road, Karachi-75300, Pakistan

(Received October 17, 2013; revised January 27, 2015)

ABSTRACT. This article is mainly based on the production of biodiesel and bioethanol from waste banana peels and radish leaves. The oily content from both the samples were converted to biodiesel by acid catalyzed and base catalyzed transesterification using methanol and ethanol. The biodiesel so obtained was subjected to analysis in accordance with the American Standard for Testing Materials (ASTM). The carbohydrates were extracted by distilled water and characterized by physical, chemical and biochemical methods. The carbohydrates were subjected to anaerobic fermentation using *Saccharomyces cerevisiae* to produce bioethanol which was confirmed by the preparation of UV active derivatives namely ethyl benzoate and ethyl salicylate. The highest % yield of fatty acid methyl ester and fatty acid ethyl ester was found to be 75% and 38%, respectively. The yield of bioethanol from banana peels and radish leaves was found to be 1.37% and 1.23%, respectively.

KEY WORDS: Oil, Transesterification, Biodiesel, Carbohydrates, Fermentation, *Saccharomyces cerevisiae*, Bioethanol

INTRODUCTION

Previously, the biodiesel and bioethanol are reported from different bioresources including wheat, maize, sugar beet, potatoes, palm tree, sun flower, fruits and vegetable wastes, and algae [1-4]. The biodiesel is obtained from bioresources that are rich in oily content. The oils are converted to biodiesel by transesterification particularly with methanol or ethanol. Biodiesel and bioethanol are carbon neutral fuels because their renewable sources have an ability to absorb the CO_2 emitted by the combustion of these fuels. Therefore, there is no any significant increase in the CO_2 concentration in the atmosphere. Bioethanol can be obtained from biological resources that contain substantial amount of carbohydrates which can be converted to bioethanol [5, 6]. The industrial and research applications has gradually increased the production of bioethanol [7]. The bioethanol emit lesser amount of toxic and greenhouse gases as compare to petroleum or gasoline. It can be used alone or mixing with gasoline [8].

We report here the production of biofuels from banana peels and radish leaves. The production of biofuels from vegetable oil and other edible resources is not feasible because it can cause food shortage. Therefore, the conversion of waste to energy is a best approach to save the edible resources. In addition, the consumption of waste for energy also reduces the environmental pollution. These features attracted us to use waste banana peels and radish leaves for the production of biofuels. Banana (*Musa paradisiacal*) is a fruit which belongs to the Musacease family. Its outer covering is known as peels and inner part is known as pulp.

The waste banana peels play a significant role to pollute our environment because all the biowastes release toxic gases when they undergo decomposition and biodegradation. To overcome this problem, the best alternate use of banana peels is to consume it for the production of biofuels [9]. Banana peels contain carbohydrates (59.5%), proteins (4.77%), metals and oily contents [10-12]. Production of bioethanol has previously been reported from the banana peels by the process of fermentation in biocontrol fermenter using five different strains of *Saccharomyces cerevisiae* [13].

*Corresponding author. E-mail: dr.abdulmajeedkhan@fuuast.edu.pk

The botanical name of radish leaves is *Raphanus sativus* and belongs to the family Brassicaceae [14]. *Raphanus sativus* grows in temperate climates at height between 190 and 1240 m and it is 30–90 cm tall [15]. It is the rich source of carbohydrates, sugar, dietary fiber, fats, proteins, vitamins, and some metals [16]. Radish leaves has also been used for the production of biogas at a specific temperature of 37 ^{o}C [17]. The literature showed that the production of biodiesel is also reported from radish [14].

EXPERIMENTAL

Biodiesel production

Banana peels (6.4 kg) were collected from different fruit shops located in Karachi, Pakistan. They were dried under shadow for one week and dried peels were ground into the powder form (855 g). The water content in banana peels was found to be 87%. The oily content from the banana peels was extracted by solvent extraction technique [18, 19]. The peel's powder was soaked in *n*-hexane (2 L) for three days. The *n*-hexane extract was separated by decantation and further by filtration. The soaking process was repeated three times using overall 5 L of *n*-hexane. The *n*-hexane was evaporated on a rotary evaporator (Buchi, Germany) under reduced pressure that yielded 71 g of crude, dark green and gummy oily content. About 8.3% oily content was extracted from banana peels using *n*-hexane as a solvent. Initially, the oily content was subjected to depigmentation with charcoal and column chromatography using silica gel (100-200 mesh size) as stationary phase and *n*-hexane as mobile phase. Through this process, most of the pigments and solid impurities have been removed from the crude oily extract. The oil was again purified by column chromatography using the column of longer length (diameter: 2.5 cm; length: 50 cm) that also removed the other impurities. It yielded semi-pure dark yellow oil (68 g) that was then analyzed by thin layer chromatography (TLC).

Radish leaves (3.13 kg) were collected from the vegetable shops, dried under shadow and then converted into the powder form (0.95 kg). The powder was soaked in *n*-hexane (5 L) for three days. The *n*-hexane extract was separated by decantation and further by filtration. The soaking process was repeated three times using overall 15 L of *n*-hexane. The *n*-hexane was evaporated by rotary evaporator (Buchi, Germany) under reduced pressure that yielded 58 g gummy oily content. The oily content was passed through the process of charcoaling then other impurities were removed by column chromatography that yielded pure oil (56 g).

Characterization of oily contents

The oily contents so obtained from banana peels and radish leaves were characterized in accordance with the ASTM standards including pour point, cloud point, acid value, iodine value, saponification value, density, viscosity, and rancidity (Table 1).

Methanolysis and ethanolysis

The oily contents (1 g from each source) were subjected to transesterification under acidic (conc. HCl, 5 drops) as well as basic (0.2 g NaOH powder) conditions using methanol (4 mL) and ethanol (4 mL) separately. The reaction mixtures were refluxed for 12 hours. The glycerol and soap were separated by hot water whereas the biodiesel was extracted by using *n*-hexane:chloroform (1:1). The biodiesel was purified by column chromatography using silica gel (100-200 mesh size) as stationary phase whereas *n*-hexane:chloroform (9:1) as mobile phase. The purified biodiesel (88%) was characterized by ASTM standards (Table 1).

Bioethanol production

After the extraction of oily contents, the residue (784 g) of banana peels powder was soaked in distilled water (4.5 L) for three days. The water extract that contained carbohydrates was separated by filtration. The same process of soaking was repeated three times that yielded 11 L of water extract. It was evaporated on the water bath at 100 ^{o}C that yielded gummy and blackish water extract (122 g) that contained carbohydrates (Scheme 1).

The residue of radish leaves was soaked in distilled water (15.5 L) for a week. The water extract was separated by using cotton cloth then it was subjected to filtration using Watmann filter paper and the soaking process was repeated three times. After complete extraction process, 15.25 L water extract was obtained. The water was evaporated on water bath at 100 ^{o}C that resulted in the gummy and dark green concentrated water extract (180 g).

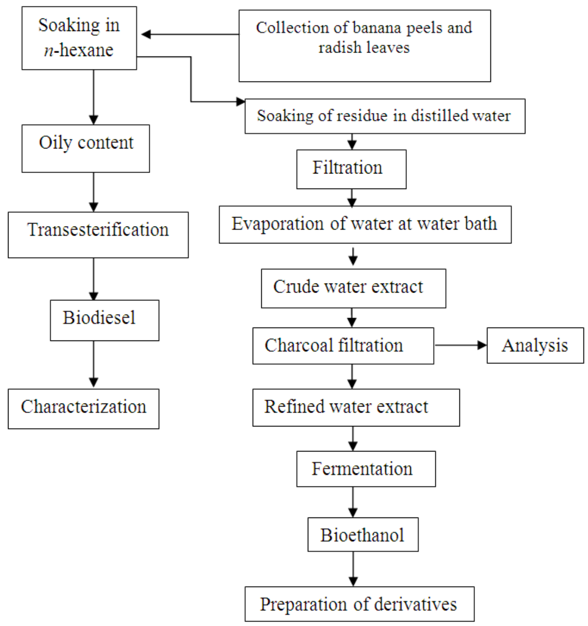
The concentrated water extracts of each sample (20 g each) were again dissolved in distilled water (440 mL) and subjected to column filled with activated charcoal and washed with distilled water. Through this process the unwanted solid impurities and some pigments were removed that resulted in the semi-refined water extract. After pretreatment, the water extracts of both the samples were subjected to biochemical analysis by performing different reported tests including Molisch Test, Fehling's Solution Test and Combur Test [20, 21].

Fermentation

After pretreatment and biochemical analysis of water extracts, they were subjected to partial anaerobic fermentation. Firstly, crude gummy water extract (20 g each) was dissolved in distilled water (440 mL). The pH of water extract of banana peels and radish leaves were found to be 6.9 and 6.0, respectively. Now, partial anaerobic fermentation of water extract that contained carbohydrates was conducted inside the earth's surface (2 feet deep). After fermentation, the pH of the fermented mixture of banana peels and radish leaves was found to be 6.1 and 5.6, respectively. The color of the solution was changed from dark green to the light green for both samples.

Confirmation of bioethanol

The bioethanol is a volatile liquid and it is quite difficult to characterize in its volatile liquid form at laboratory scale, therefore, the bioethanol obtained from banana peels was directly converted into its UV active and non-volatile derivative namely ethyl benzoate whereas the bioethanol from radish leaves converted into ethyl salicylate. For this purpose, fermented mixture (440 mL) containing bioethanol, benzoic acid (1 g) or salicylic acid (1 g) and conc. HCl (0.2 mL for each) were taken in an Erlenmeyer flask and fitted with the water condenser using chiller (Buchi, Germany) separately. The reaction assemblies were placed in the water bath and refluxed at 100 ^{o}C for 12 hours. The product mixtures were allowed to cool down at room temperature. The desired products ethyl benzoate and ethyl salicylate were extracted from the crude mixture by using *n*-hexane:ethyl acetate (100 mL:100 mL). The content of the flask was thoroughly mixed and then allowed to settle down for the separation of the layers. The water layer (lower) and organic solvent layer (upper) were separated by separating funnel, and process of extraction was repeated three times. The water layer was discarded and the organic solvent layers were concentrated using rotary evaporator. The concentrated ethyl benzoate (59.3%) and ethyl salicylate (62.5%) were examined by thin layer chromatography (TLC) using standard ethyl benzoate and ethyl salicylate prepared by the same procedure using known starting materials. *n*-Hexane was used as the solvent system for TLC. The spots were identified by UV lamp at 254 nm. The spots of the sample ethyl benzoate and standard were appeared at the same R_f value (0.76) whereas the spots of sample ethyl salicylate and standard were appeared at 0.74 R_f value.

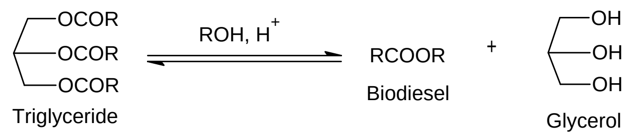


Scheme 1. Production of biodiesel and bioethanol from banana peels and radish leaves.

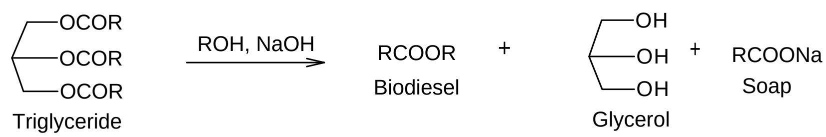
RESULTS AND DISCUSSION

Biodiesel

The global threats like energy crisis, global warming, pollution and biodiversity stimulated us to conduct the research on the alternative, green and environmental friendly biofuels that can overcome the current challenges. In this regards we conducted the research on biowastes including banana peels and radish leaves. The oily contents of both the wastes were characterized by ASTM standards and then subjected to methanolysis and ethanolysis under acidic and basic conditions. The oily contents extracted from banana peels and radish leaves were found to be 8.3% and 5.4%, respectively. Two types of biodiesels namely fatty acid methyl ester (FAME) and fatty acid ethyl ester (FAEE) which were synthesized under acidic as well as basic conditions were characterized by different tests that are necessary for the identification of biodiesel. These tests include TLC examination, acid values, saponification values, iodine values, cloud point, pour point and some others (Table 1). The results of various tests were found to be very close to the ASTM standard values that confirm the presence of biodiesel. The yield of FAME and FAEE was found to be 75% and 37% from banana peels under acidic condition whereas it was found to be 63% and 49% under basic condition respectively. On the other hand, their % yield from radish leaves was found to be 63% and 44% under acidic condition whereas under basic condition it was found to be 45% and 38%, respectively (Table 2). When triglycerides reacted with alcohol under acidic condition then biodiesel and glycerol are formed (Scheme 2) whereas under basic condition biodiesel, glycerol and soap are formed (Scheme 3).



Scheme 2. Conversion of triglyceride to biodiesel and glycerol.



Scheme 3. Conversion of triglyceride to biodiesel, glycerol and soap.

Table 1. The detailed characterization of biodiesel derived from banana peels and radish leaves.

S.No.	Parameters	Oil	FAME*	FAEE**	ASTM standards†
1.	TLC (R_f values, ratio)	0.38	0.56	0.48	-
2.	Acid values (mg/g)	1.58	0.14	0.29	0.8 mg NaOH/g
3.	Saponification values (g)	95	67	65	
4.	Iodine values (g/100 g)	26.0	2.65	4.23	
5.	Moisture content (%)	0.09	0.04	0.01	-
6.	Viscosity (mm^2/s)	35.5	3.4	5.2	1.9 to 6.0 mm^2/s
7.	Refractive index (ratio)	1.41448	1.46560	1.48038	-
8.	Rancidity (pink color)	Negative	Negative	Negative	
9.	Cloud point (°C)	9	11	12	-3 °C to 12 °C
10.	Pour point (°C)	5	3	3	-15 °C to 16 °C
11.	Specific gravity (ratio)	0.9086	0.8934	0.8863	0.875 to 0.9
12.	Absorbance and transmittance (at 701 nm)	0.422 and 36.4	0.457 and 35.5	0.460 and 35.6	-
13.	Density (g/cm^3)	0.91	0.85	0.88	-
14.	Solidification rate (s)	55	85	105	-
15.	pH	6.1	5.3	4.5	-

*FAME: Fatty acid methyl ester; **FAEE: Fatty acid ethyl ester; †[22-24].

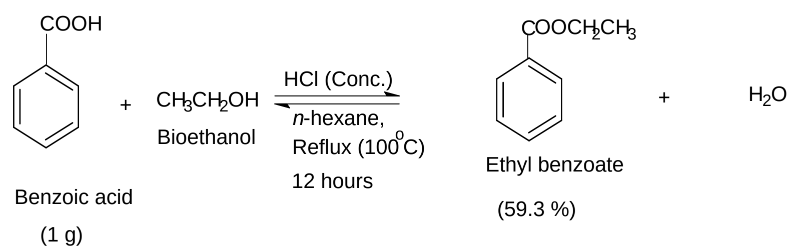
Table 2. Yields (%) of biodiesels, glycerol, soap and bioethanol produced from biowastes.

Sources	Oil (%)	Acidic methanolysis		Acidic ethanolysis		Basic methanolysis			Basic ethanolysis			Fermentation
		FAME (%)	Glycerol (%)	FAEE (%)	Glycerol (%)	FAME (%)	Glycerol (%)	Soap (%)	FAEE (%)	Glycerol (%)	Soap (%)	Bioethanol (%)
Banana peels	8.3	75	7	37	4	63	3.5	21.5	49	5.2	20.0	1.37
Radish leaves	5.4	63	6	43	4.5	45	4.2	23.0	38	3.5	18.5	1.23

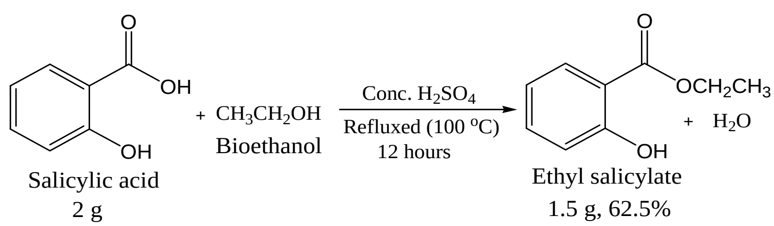
Bioethanol

The carbohydrates and other polar compounds of banana peels and radish leaves were extracted by distilled water. The carbohydrates were further converted to bioethanol fuel by the process of fermentation. The pre-treated water extracts were subjected to different biochemical tests including Molisch Test, Fehling's Solution Test and Combur Test which were found to be significantly positive. The Combur Test showed 1000 mg/dL of glucose and 500 mg/dL of proteins. This test showed the pH level slightly acidic (6.9). The result obtained from Molisch Test and Fehling's Solution Test evidenced that banana peels and radish leaves contain carbohydrates.

After preliminary examination and pre-treatment, the water extracts were treated with yeast (*Saccharomyces cerevisiae*) under partial anaerobic conditions. After seven days of the fermentation process, the pH of the solution was found to be 6.5. It is lower than the pH value before the fermentation (6.9). It showed that the acidic strength of the fermented solution has been increased due to the formation of carboxylic acids. The ethanol is a volatile liquid therefore it is quite difficult to extract it from the product mixture at the laboratory scale experimentation. To overcome this drawback, the bioethanol obtained from banana peels was converted directly into its non-volatile and UV active derivative like ethyl benzoate (Scheme 4) whereas the bioethanol derived from radish leaves was converted into ethyl salicylate (Scheme 5). The percent yields of ethyl benzoate and ethyl salicylate were found to be 59.3% and 62.5% respectively. In addition, the % yield of bioethanol from banana peels and radish leaves was found to be 1.37% and 1.23%, respectively.



Scheme 4. Synthesis of ethyl benzoate from benzoic acid.



Scheme 5. Synthesis of ethyl salicylate from salicylic acid.

CONCLUSION

This article presents the conversion of oily content of banana peels and radish leaves to biodiesel through transesterification as well as carbohydrates of both the wastes to bioethanol through fermentation. The biodiesel was characterized by ASTM standards whereas bioethanol was confirmed by the synthesis of UV active derivatives formation. The transesterification using methanol and ethanol was carried out under acidic as well as basic conditions that produced fatty acid methyl ester and fatty acid ethyl ester with a significant yield. The fermentation of carbohydrates extracted from banana peels and radish leaves produced 1.37% and 1.23% bioethanol, respectively. This significant research can help us to develop the alternative approaches for the conversion of wastes to energy that overcome the energy crisis and help to reduce the environmental pollution.

ACKNOWLEDGEMENT

The principal author is greatly thankful to the administration of Federal Urdu University for the provision of financial support for this research work under "*Mini Research Project Program-2012*".

REFERENCES

1. Khan, A.M. *J. Chem. Soc. Pak.* **2010**, 32, 379.
2. Khan, A.M.; Attaullah; Ahmad, I.; Shaheen, A.; Malik, F.; Shahid, H.A. *J. Chem. Soc. Pak.* **2011**, 33, 269.
3. Balat, M. *Energy Expl. Exploit.* **2007**, 25, 195.
4. Schneider, U.A.; Mccarl, B.A. *Environ. Res. Econ*. **2003**, 24, 291.
5. Malça, J.; Freire, F. *Energy Sour*. **2006**, 31, 3362.
6. Peskett, L.; Slater, R.; Stevens, C.; Dufey, A. *Agric. Pov. Red*. **2007**, 107, 1.
7. Dhabekar, A.; Chandak, A. *Asian J. Biotech. Res*. **2010**, 1, 8.
8. Arredondo, V.H.I.; Ruiz, C.A.A.; Colorado, R.A. A.; Junior, O.S. *Energy Renew. Anal. Introd. J. Therm.* **2009**, 12, 155.
9. Krishna, P.R.; Srivastava, A.K.; Ramawamy, N.K.; Suprsanna, P.; Souza, S.F.D. *Ind. J. Biotech.* **2012**, 11, 314.
10. Tartrakoon, T.; Chalearmsan, N.; Vearasilp, T.; Meulen, U. The nutritive value of banana peel (*Musa sapieutum* L.) in growing pigs, Deutscher Tropentag 1999, Berlin. *Proc. Sust. Technol. Dev. Animal Agric.* **1999**.
11. Essien, J.P.; Akpan, E.J.; Essien, E.P. *Biores. Technol.* **2005**, 96, 1451.
12. Shah, A.M.; Qureshi, M.; Memon, Z.N.; Memon, S.N.; Syed, S.K. *Sindh Uni. Res.* **2012**, 44, 71.
13. Manikandan, K.; Saravanan, V.; Viruthagiri, T. *Ind. J. Biotech.* **2008**, **7**, 83.
14. Avila, R.N.D.A.; Sodre, J.R. *Ind. Crop. Prod.* **2012**, 38, 54.
15. Gutierrez, R.M.P.; Perez, R.L. *Sci. World J.* **2004**, 4, 811.
16. Khattak, K.F. *Pak. J. Pharm. Sci.* **2011**, 24, 277.
17. Mandal, T.; Mandal, N.K. *Energy Cons. Manag.* **1997**, 38, 679.
18. Topare, N.S.; Raut, S.J.; Renge, V.C.; Khedkar, S.V.; Chavan, Y.P.; Bhagat, S.L. *Int. J. Chem. Sci.* **2011**, 9, 1746.
19. Ali, M.A.; Saeed, M.A.; Alam, M.S., Yasmin, M.S.; Khan, A.M.; Muhammad, I.I. *Bull. Chem. Soc. Ethiop.* **2012**, 26, 55.
20. Kalaiarasan, A.; John, S.A. *Int. J. Medicobiol. Res*. **2010**, 1, 94.
21. Khan, A.M.; Ali, M.M.; Naz, S.; Sohail, M. *J. Chem. Soc. Pak.* **2010**, 32, 209.
22. Chopade, S.G.; Kulkarni, K.S.; Kulkarni, A.D.; Topare, N.S., *Acta Chim. Pharm. Indica* **2012**, 2, 8.
23. Ofoefule, A.U.; Ibeto, C.N.; Ugwuamoke, I.E. *Int. Res. J. Pure App. Chem.* **2013**, 3, 357.
24. AOCS *Official Methods and Recommended Practices*, Am. Oil. Chem. Soc.: Champaign USA; **1997**.