FOOD WASTE AS A SOURCE OF BIOFUELS

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ABSTRACT: *The demand for biofuels currently exceeds the supply. This investigation focused on the potential to produce biodiesel from oil extracted from garbage. Several sources of food waste were investigated in the United States and in Vietnam, and the oil content ranged from about 10% to nearly 30% of the dry mass. Conditions were optimized for preparation of biodiesel from the food waste oil. It was also found that the solid residue, after oil extraction, has a caloric value similar to that of brown coal, and thus is a potential source of solid fuel.*

Key words: *Biofuel, biodiesel, food waste oil, solid fuel.*

INTRODUCTION

Concerns over global warming and the rising cost of petroleum derived fuels have led to an increased interest in bio-fuels. Biofuels are carbon neutral, at least in theory. Carbon dioxide absorbed by recently living plants is released into the atmosphere when the plant derived fuel is burned. In recent years, both small and large scale bio-diesel producers have set up manufacturing plants using either virgin vegetable oil or used cooking oil, commonly known in the industry as yellow grease. These commercial operations generally use a base catalyzed transesterification process, and therefore require oil with less than 15% free fatty acid (FFA) content. A recent internet search of large and small scale biodiesel production equipment revealed that nearly all of the mass produced equipment is designed for the base catalyzed process. When using oils with low FFA contents, the base catalyzed process is the most efficient, and batches of bio-diesel can be produced in a few hours. Even more efficient continuous flow processes have been developed [1-3]. Large amounts of FFA increase the amount of catalyst needed, which may cause problems of soap formation and emulsions that are difficult to break. In addition, the resulting excess catalyst and salts must be removed from the biodiesel.

Enzymatic catalyzed processes have also been developed for biodiesel production [4-6].

Although very efficient processes have been developed for using virgin vegetable oil, animal fats, and yellow grease, the supply of those feed stocks remains the limiting factor. All of the yellow grease collected in the United States today, if used for biodiesel, could produce about 100 million gallons (378 million liters) per year [7]. According to the USDA, the price range for yellow grease on April 14, 2011 was between $0.45 and $0.52 per pound ($0.99 to $1.14 per Kg). Depending on the source, yellow grease has a density of between 6.5 and 7 pounds per gallon, making the cost of that starting material between $2.92 and $3.64 per gallon, or $0.77 to 0.96 per liter. Yellow grease can contain significant amounts of FFA and suspended water, both of which make the conversion to bio-diesel fuel less efficient. Thus, even with a sufficient supply of yellow grease, the price of bio-diesel fuel made from that feed stock will likely remain well over $3.00 per gallon or $0.80 per liter.

Although the biodiesel synthesis is more efficient with virgin vegetable oils, the price of those feed stocks can be quite volatile. In March, 2011, the price of soybean oil, a byproduct of soy meal manufacturing, was about $0.51 per pound ($1.12 per Kg). During the 2008 fuel crisis the price reached about $0.64 per pound ($1.41 per Kg), and the largest price spikes occurred during times of peak interest in biodiesel, that is, during periods of high petroleum prices. Rape seed oil, another potential bio-diesel feed stock, was about $0.64 per gallon ($0.17 per liter) in March, 2011. Thus, using those crops to produce biodiesel fuel will likely keep the price well above $3.00 per gallon ($0.80 per liter), with price increases likely to occur coinciding with price spikes in petroleum. Another problem with virgin vegetable oils is that not enough arable land is available to meet a significant portion of America's energy needs, and there is fear that using oil from food crops will increase food prices, particularly in developing countries. There is therefore considerable interest in developing biodiesel production from non-food sources [8-13].

Brown grease refers to lower quality oils and greases, generally containing large amounts of FFA and suspended water. Because of the technical difficulties of making biodiesel from that source of oil, it has received much less attention than virgin or used vegetable oils. Depending on the quality, the use of brown grease requires an acid catalyzed or two-step acid, then base, catalyzed procedure [14]. In spite of those difficulties, we believe the brown grease route is worth pursuing because of its potentially plentiful supply and lower cost. A virtually untapped source of brown grease is garbage, which contains significant amounts of fats and oils from food waste. According to the EPA, the United States produces 34 million tons of food waste per year. A conservative estimate of the oil content is 10% of the dry mass, derived from the results of this work. Thus, 1.7 million

tons of brown grease could potentially be recovered from the municipal waste streams annually and converted to more than 400 million gallons (1,512 million liters) of biodiesel, assuming that the mass of garbage is 50% water. Aside from the reduced dependence on foreign oil, removing that oil from land fills prevents its eventual degradation to methane, a green house gas 21 times as powerful as carbon dioxide. In addition, the organic residue left after extraction of the oil is another possible source of fuel and/or fuel precursor.

MATERIALS AND METHODS

Extraction of oil from food waste

Food waste samples were collected from six sources: The student canteen at the University of Science, a private home in HCM City, the Fisk University cafeteria, the Meharry Medical college cafeteria, Miss Saigon restaurant, and Copper Kettle restaurant in Nashville. The waste samples were dried in an oven or food drier. The dried samples were ground, and the oil was extracted in a Soxhlet apparatus for two hours using ligroin or petroleum ether as the solvent. The solvent was then distilled from the crude waste oil and recycled. The oil was collected and degummed with hot water prior to conversion to biodiesel.

Preparation of biodiesel from waste oil

Because oil from food waste is high in free fatty acids (FFA), an acid catalyzed process was used. The FFA content was estimated by titration and the acid number was found to be between 17 and 19 mg KOH/gram oil. For each preparation, 25 mL of oil was mixed with methanol and a sulfuric acid catalyst, and the mixture was refluxed for periods between 18 and 48 hours. The yield of biodiesel was determined as a function of oil: methanol ratio, amount of catalyst, and reaction time. Upon completion of the reaction, the mixture was allowed to cool, washed with 40 mL water, and the acid catalyst was neutralized by washing with 1 g potassium carbonate in 40 mL water. The biodiesel was then washed with 40 mL portions of water twice or until the wash water was clear. The layers were separated, and the residual water suspended in the biodiesel was removed by heating to break the emulsion.

Product analysis

The acid number (AN) of the BDF produced under each set of conditions was determined by titration, and reported as mg KOH/gram BDF. The titration was performed with a standardized solution of potassium hydroxide at an approximate concentration of 1.0 g KOH/L water, or 0.018 M. The mass of approximately 1 mL of oil was determined, and the oil was dissolved in 10 mL 2-propanol and titrated against the standardized KOH solution with a phenolphthalein indicator. The acid number is determined by: $AN = (V_{eq} - b_{eq})N(56.1/W_{oil})$, where V_{eq} = volume of base at the equivalence point; b_{eq} is the volume of base at the equivalence point in a blank titration of 2-propanol; N is the normality of the standardized base; 56.1 is the molar mass

of KOH; and Woil is the mass of oil or BDF being titrated.

The Fatty Acid Methyl Ester (FAME) distribution was determined on an Agilent model 7890A gas chromatograph with an Agilent 5975C mass sensitive detector and a BD5 column (30m x 0.25 mm, 0.25 Micron thickness). Total and free glycerin from selected samples was determined using ASTM test D 6584-10 by Quatest Laboratories, Ho Chi Minh City, Vietnam. The ash content and caloric values of selected solid samples were also determined by Quatest Laboratories using test procedures TCVN 173:2007 and TCVN 200:2007, respectively.

RESULTS AND DISCUSSION

Oil content of food waste

The oil content of samples of food waste was determined from sources listed above. The results are shown in Table 1. The average oil contents from the student canteen and a private home in Ho Chi Minh City were 10.9 and 14.0% by mass, respectively. Similar oil contents were found in the waste from an American and a Vietnamese restaurant in Nashville, but both the Fisk University and Meharry Medical College cafeterias had much higher oil contents, 25.7 and 29.2%, respectively. These numbers are consistent with the estimate of at least 10% oil content of food waste. The higher values from the Fisk University and Meharry Medical College cafeterias may be more typical of regions of the United States that use large quantities of meat and fat in cooking. The largest sample to sample variations in oil content were from the Fisk cafeteria and the Copper Kettle restaurant, both of which serve food typical of that in the southeastern United States.

Table 1. Oil content of food waste samples from Ho Chi Minh City, Vietnam; and Nashville, TN

Location	Source	Samples	Average % oil by mass	Standard deviation
HCM City	Student canteen	27	10.9	3.8
HCM City	Private home	4	14.0	3.9
Nashville, TN	Fisk Univ.	5	25.7	12.8
Nashville, TN	Meharry Med.	3	29.2	5.7
Nashville, TN	Copper Kettle	3	13.2	8.1
Nashville, TN	Miss Saigon	3	13.4	1.8

Optimization of the oil to methanol ratio

For each reaction in this experiment, 25 mL of food waste oil was mixed with a fixed volume of methanol and 0.10 mL of sulfuric acid catalyst. The mixture was refluxed for 24 hours, followed by aqueous workup. The percent yield by mass was reported by volume: $(M_{BDF}/M_{oil}) \times 100\%$. Each experiment was performed at least 4 times, and any suspect data points were subjected to the Q test to determine

their validity. In each case, the acid number was determined by titration, and reported in mg KOH/g BDF. The ASTM maximum acid number is 0.5. The results are given in Table 2. The highest yield was obtained with a ratio of 20 mL methanol to 25 mL oil, and the standard deviations reflect the variation between samples of oil. Different oil samples will have variable amounts of triglycerides and free fatty acids, as well as different amounts of oxidation products from unsaturated fats. Depending on the sample, the yield of biodiesel under the optimum conditions will typically range from 85-92% by mass. The slightly lower yields at higher methanol-oil ratios may reflect slightly greater solubility of the oil during the first wash, and thus, greater losses. Since the cost of methanol is a significant portion of the cost of producing biodiesel, lower methanol-oil ratios are desirable, as is efficient methanol recovery.

Table 2. Biodiesel yield as a function of the oil to methanol ratio. 25 mL oil, 0.10 mL H_2SO_4, reflux for 24 hours

Methanol (mL)	Number of trials	Yield of BDF (%)	Standard deviation	Acid number
15	4	77.5	6.9	0.29
20	5	89.5	4.4	0.34
25	4	83.8	7.4	0.37
30	4	80.7	7.9	0.21

Optimization of the amount of catalyst

For each reaction in this experiment, 25 mL of food waste oil was mixed with 20 mL of methanol and a fixed amount of sulfuric acid catalyst, and the mixture was refluxed for 24 hours. The percent yield by mass was determined under each set of conditions, and the results are shown in Table 3. The maximum BDF yield was obtained with 0.10 mL catalyst. Lower amounts were insufficient to catalyze the reaction at a sufficient rate for completion after 24 hours. The drop in yield at higher catalyst ratios may be a consequence of the presence of significant amounts of unsaturated fats, as described below. Protonation of the double bonds will increase the water solubility, resulting in losses during the aqueous workup.

Table 3. Biodiesel yield as a function of amount of catalyst. 25 mL oil, 20 mL methanol, reflux for 24 hours

H_2SO_4 (mL)	Number of trials	Yield of BDF (%)	Standard deviation	Acid number
0.05	4	84.3	0.96	0.47
0.10	4	89.5	4.4	0.34
0.15	4	84.9	1.4	0.38
0.20	4	81.5	0.50	0.34

Optimization of the reaction time

The reaction time will determine the energy cost of biodiesel production, and thus will be an important factor in determining the cost. Too little time will result in incomplete reaction. Too much time will waste energy and possibly result in oxidation or other acid catalyzed side reactions at the double bonds of unsaturated fatty acid chains. The optimum reaction time was determined to be 24 hours, with drop offs in yield at 18 and 48 hours. The results are summarized in Table 4.

Table 4. Biodiesel yield as a function of reaction time. 25 mL oil, 20 mL methanol, 0.10 mL H_2SO_4, reflux for variable reaction times

Reaction time (hrs)	Number of trials	Yield of BDF (%)	Standard deviation	Acid number
18	5	84.0	7.1	0.28
24	4	89.5	4.4	0.34
48	4	83.0	1.4	0.23

The total and free glycerin analysis was performed on the biodiesel samples prepared using 25 mL oil, 0.1 mL H_2SO_4 catalyst, and methanol quantities and reaction times shown in Table 5. In each case, mono-, di-, and/or triglycerides composed the bulk of the free and total glycerin. Increasing the methanol content or the reaction time did not make a significant difference in the total glycerin percentages. The free and total glycerin values indicate the need for some post processing of the biodiesel prior to commercial sales in the United States, in order to meet the ASTM maximum percentages of 0.020 and 0.240, respectively.

Table 5. Total and free glycerin, % by mass

Methanol (mL)	Reaction time (hrs)	Free glycerin	Total glycerin
20	24	0.036	0.451
20	48	0.062	0.468
30	24	0.019	0.465

Analysis of the distribution FAME

The FAME distribution in 4 different BDF samples was determined by GC-MS. These BDF samples used oil from garbage collected on different days from the University of Science canteen, and they showed only a slight difference in FAME distribution. The major products are shown in Table 6. The primary products are the methyl esters of C16 and C18 saturated and unsaturated fatty acids. Smaller amounts of tetradecanoic acid and dodecanoic acid methyl esters were also found, together

with trace amounts of other products. The quantity of C18:1, C16:0, and C18:2 methyl esters in the garbage oil is comparable to the quantities in palm oil of 37%, 34%, and 8%, respectively [15]. The presence of large

amounts of unsaturated esters is of some concern due to oxidative stability, a problem that can be overcome with antioxidant additives or catalytic hydrogenation of the double bonds.

Table 6. Major FAME products of BDF production from food waste oil

Product	Percentage range
Octadecenoic acid methyl esters, C18:1	33-40
Hexadecanoic acid methyl ester, C16:0	24-30
Octadecadienoic acid methyl esters, C18:2	12-14
Octadecanoic acid methyl ester, C18:0	7-9
Hexadecenoic acid methyl esters, C16:1	2-3
Tetradecanoic acid methyl ester, C14:0	1-3
Dodecanoic acid methyl ester, C12:0	0.4-1

Ash and caloric values of solid residue

Although the food waste produced in the United States and world wide contains enough oil to produce large quantities of biodiesel, between 70 and 90% of the waste dry mass is solid. Since most of that mass is organic material, it is logical to determine whether it has potential as a solid fuel. Numerous solid waste to energy plants already exist in the United States, but they suffer from the drawbacks of odor problems and low caloric values. The latter problem is a consequence of the high water content of raw garbage.

After extracting the oil from the ground garbage, the remaining solids generated considerably less odor than the raw garbage. The residue from several mixed samples was tested for the caloric value, which was found to be 17.0 MJ/kg. By comparison, brown coal has

a caloric value in the 10-20 mJ/kg range. The ash content was determined to be 6.2% by mass, compared to 35% or greater ash contents of coal. Furthermore, since the solid waste was derived from food wastes, the problem of arsenic, mercury, and other toxic heavy metals commonly found in coal ash will not be present to a significant extent in this fuel. Thus, the solid residue is potentially a carbon neutral, environmentally friendly solid fuel.

A sample of the solid residue was converted to biochar by heating to 125 °C in an oil bath for 27 hours in the absence of air. After heating, 93% of the original mass remained as a brown-black solid. The caloric value was slightly higher than the untreated solid at 17.2 MJ/kg, and the ash content was slightly higher at 7.8% by mass. The biochar also had a stronger odor than the untreated solid residue.

CONCLUSION

Oil extracted from food waste was shown to be a viable starting material for production of biodiesel fuel. The optimum ratio of reagents is 25 mL oil, 20 mL methanol, and 0.10 mL sulfuric acid, refluxed for 24 hours. The resulting biodiesel was washed and residual acid was neutralized, and the acid number of the product was below the maximum allowed value of 0.5 mg KOH/g BDF. Some post processing is required prior to commercial sale to remove remaining glycerin and glycerides. The product consisted primarily of methyl esters of C16 and C18 saturated and unsaturated fatty acids. The remaining solid residue was shown to be a potential fuel with a caloric value similar to brown coal, but with much lower ash content.

NGUYÊN LIỆU NHIÊN LIỆU SINH HỌC TỪ CHẤT THẢI THỰC PHẨM

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TÓM TẮT: *Nhu cầu về biofuel hiện nay đã vượt quá khả năng cung cấp. Do đó, nghiên cứu này tập trung vào tiềm năng sản xuất biodiesel từ chất thải. Nguồn chất thải thực phẩm tại một số nơi ở Mỹ và ở Việt Nam được nghiên cứu cho thấy có hàm lượng dầu béo từ 10 đến 30% trọng lượng khô. Những điều kiện cần cho sự điều chế biodiesel từ dầu béo của chất thải thực phẩm đã được tối ưu hóa. Ngoài ra còn nhận thấy rằng chất bả rắn, sau khi ly trích dầu béo, có chứa năng lượng, có thể làm ra than nâu, đó là nguồn tiềm năng về nhiên liệu rắn.*

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