

Waste Oil and Fat Feedstocks for Biodiesel Production

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Received 21 July 2014; accepted 5 September 2014

Published online 25 September 2014

Abstract

Biodiesel is an alternative for fossil diesel that is produced by transesterification of oils and fats with alcohol. For the sustainable development of this environmental-friendly fuel, feedstock availability is one of the most important issues. Various oils and fats commonly available in China are investigated to clarify their potential as feedstock of biodiesel, in terms of oil yield, characteristics and fatty acid composition. It was found that high potential in feedstock availability can be expected for oils from palm oil. Calculation is made for the amount of waste oils and fats discarded in China. 10 waste oil/fat samples were collected and subjected to the analyses such as acid value, water content, peroxide value, iodine value and fatty acid composition for evaluating as a feedstock of biodiesel. In general, used cooking oil from food service industry and/or households may consist of rapeseed oil and soybean oil according to Chinese dietary habit. China produced 13.74 Mt of waste oil in 2010, including 6.58 Mt of gutter oil, 1.55 Mt of acid oil, and 5.61 Mt of rice bran oil. If all these waste oils and fats were utilized in biodiesel production, nearly 10.84 Mt of biodiesel can be prepared. On the other hand, approximately 146.34 Mt of fossil diesel fuel was on sale annually in China. It was therefore suggested that approximately 7.4% of annual fossil diesel fuel consumption can be replaced by biodiesel derived from wastes.

Key words: Waste oil and fat; Biodiesel; Acid value; Fatty acid composition; Characteristics

Shi, H. L., & Zhang, H. (2014). Waste oil and fat feedstocks for biodiesel production. *Advances in Petroleum Exploration and Development*, 8(1), 31-36. Available from: URL: <http://www.cscanada.net/index.php/aped/article/view/5327>
DOI: <http://dx.doi.org/10.3968/5327>

INTRODUCTION

Biodiesel is an alternative for fossil diesel that is produced by transesterification of oils and fats with alcohol. With increasing concern to the environmental issues such as global warming and air pollution, the use of biodiesel has been recognized and promoted worldwide, especially in EU and US. For the sustainable development of this environmental-friendly fuel, feedstock availability is one of the most important issues.

Now, China is the biggest consumer of oils and fats, the productivity of oils and fats is 56.5 Mt in 2012. However, the domestic productivity cannot meet the requirement, more and more oils and fats are imported since last decade. In 2012, the amount of imported oils and fats, including the production from imported oilseeds, is 9.56 Mt^[1], including 1.83 Mt soybean oil, 1.18 Mt rapeseed oil and 6.34 Mt palm oil. More than half of the oils and fats have disappeared for food purpose for human or animal. Simultaneously, more and more oils and fats are wasted. For the utilization of wastes, the oils and fats can be recycled and converted into biodiesel. Waste oils and fats are collected from households or food service industries and gathered. After pretreatment including filtration, gel removal, water removal, collected waste oils and fats are then converted into biodiesel with alkali-catalyzed method or acid-catalyzed method^[2-7]. Utilization of these waste oils and fats is appreciated because it not only mitigates the risk to return to the dining-table, but also improves process economy by reducing the cost

of raw material. These advantages clearly indicate that biodiesel production from waste oils and fats should be promoted worldwide. China has become the world's top energy consumer and top CO₂ producer. Over 20% of global primary energy supply is now consumed by China, only 8% of China's primary energy supply is provided by renewable energy. Meanwhile, recycled waste oils and fats have shown significant potential being one of the main feedstocks for bioenergy production.

Refined oils and fats consist of triglycerides as the main component and free fatty acids as minor component. However, waste oils and fats often have undergone long-term degradation, thereby being high in free fatty acids and water content due to hydrolysis reaction^[8-9]. Furthermore, degree of the degradation heavily depends on when and where they are disposed of. For example, among various waste oils and fats, the main component of the acid oil is free fatty acids, whereas that of used cooking oil from households is triglycerides^[10].

On the other hand, biodiesel must satisfy specification standards of EU and US. These standards include not only ester content but also some of the fuel characteristics, such as iodine value, cold flow properties, which are attributed to fatty acid composition of oils and fats. Among them, oxidation stability is one of the important characteristics. For example, highly unsaturated oils and fats such as sunflower oil tend to be susceptible to oxidation. Since biodiesel takes over the characteristics of raw material, it is important to investigate degree of oxidation, which can be evaluated with peroxide value, with respect to waste oils and fats themselves^[11-13].

Based on these backgrounds, in this study, the composition of the oils and fats were analyzed. Various characteristics were analyzed for actual waste oils and fats collected from various sources.

1. EXPERIMENTAL

Waste oils and fats samples were collected from various households and restaurants. Contaminants such as

Table 1
Yield of Oilseeds/Fruits and Oils for Various Oils and Fats Species (a*)

Oils	Oilseeds ^b	Oilseeds yield [ton/ha]	Oil content ^c [%]	Oil yield [ton/ha]
Soybean oil	Soybean	1.8 - 2.3	16 - 22	0.3 - 0.5
Rapeseed oil	Rapeseed	1.4 - 2.5	38 - 45	0.5 - 1.1
Sunflower oil	Sunflowerseed	1.4 - 2.3	28 - 47	0.4 - 1.1
Cottonseed oil	Cottonseed	1.1	15 - 25	0.2
Peanut oil	Peanut	1.0	40 - 50	0.4 - 0.5
Castor oil	Castorseed	0.9 - 1.0	35 - 57	0.3 - 0.6
Palm oil	Empty fruit bunch	20	20	4.0
Palm kernel oil	Palm kernel	0.9	45 - 50	0.4 - 0.5
Coconut oil	Copra	0.5 - 0.6	65 - 75	0.3 - 0.5

Note. a*, the data is collected from reference [8].

For some resources with low oil content, such as soybean and cottonseed, not only mechanical press but also solvent extraction (For example, using hexane) is applied in the extraction, while resources with high oil

insoluble residues were removed by filtration. These samples were then analyzed in terms of acid value, water content, iodine value, peroxide value and fatty acid composition. Acid value, which is a measure of the free fatty acid content, was determined in accordance with GB-T 5530-2005. Iodine value, which indicates the degree of unsaturation, was determined according to the standard method, GB-T 5532-1995. Peroxide value, which suggests hydroperoxide concentration, was measured in accordance with standard methods, GB-T 5538-2005. Water content was measured with Karl Fischer moisture titrator in accordance to ISO 12937. Finally, these oils and fats were derivitized into their methyl esters in sulfuric acid methanol solution and subjected to gas chromatography (GC) for detection of fatty acid composition in accordance with the standard method, , respectively. GC analysis was conducted using Shimadzu GC-14B system equipped with a flame ionization detector (FID) under the following conditions: column, polyethylene glycol, 30 m × 0.25 mm, 0.25 μm DB-WAX (J&W Scientific, Inc., Folsom, CA); oven temperature, 210 °C; detector temperature, 250 °C; carrier gas, helium; injection volume, 1 μL.

2. RESULTS AND DISCUSSION

2.1 Yield of Oils for Commonly Available Oil Resources

Table 1 lists the commonly used oils and their resources in China, which are usually extracted from seed/bean, fruit and kernel depending on the oil crop species; rapeseed oil is extracted from the seeds of rapeseed, whereas palm oil from fresh fruit bunch of oil palm. From Table 1, it is apparent that oil palm is extremely high in oil yield of 4 tons/ha for palm oil compared with that of other resources. Recent wide spread of oil palm plantation is partly attributed to this high viability and suitability for plantation. For its low price, the consumption increased from 0.78 Mt to 5.8 Mt from 1991 to 2011^[14].

contents are sometimes extracted by only mechanical press, indicating that oil recovery is not efficient. It is also noticed that fruit oil such as olive oil and palm oil often contains lipase enzyme after harvested, which eventually

hydrolyzes triglycerides, main component of oils and fats, into fatty acid after long time storage^[15-16]. In order to

get high quality oils and fats free from fatty acids or any impurities, storage condition is quite important^[17-18].

Table 2
Characteristics of Refined Oils and Fats Commonly Available in China

Oils and fats	Acid value [mgKOH/g]	Water content [%]	Iodine value [gI ₂ /100g]	Saponified value [mgKOH/g]
Sunflower oil	0.03	≤ 0.01	133.0	191
Soybean oil	0.04	≤ 0.01	132.0	191
Palm oil	0.05	≤ 0.01	57.1	196
Rapeseed oil	0.05	≤ 0.01	110.0	187
Coconut oil	0.05	0.02 ^a	8.6	255
Peanut oil	0.04	≤ 0.01	99.3	191
Cottonseed oil	0.06	0.02	113.0	197
Olive oil	0.88	0.09	81.9	194
Fish oil	0.32	0.04	151.0	184
Beef tallow	3.55	-	49.3	197

Note. a, Karl Fischer titration method (ISO 12937).

Table 2 shows characteristics of oils and fats available in China that can be used for biodiesel production. It can be clearly seen that both acid value and water content are low enough to be used in conventional biodiesel production process for most of the oils and fats. Beef tallow is slightly high in acid value, possibly due to the difference in extraction process; In contrast to vegetable oils and fats, animal fat is generally extracted by rendering, in which fat are heated at 110 °C by steam to elute tallow out. During the process, part of triglycerides may be hydrolyzed into free fatty acids and increased the acid value.

In terms of iodine value, regardless of completeness of the conversion, sunflower, soybean and fish oil give biodiesel that has higher value than specified value (≤ 120 gI₂/100 g) in biodiesel standards of EU and China. It is well known that oils and fats with higher iodine value absorb oxygen faster. From the viewpoint of oxidation stability^[19], these oils are not really suitable feedstock and addition of antioxidant^[20-21] is thus inevitable when utilizing these oils for fuel purpose.

Most of the oils and fats have saponified value around 190 mgKOH/g. In contrast, coconut oil has markedly high saponified value of 255 mgKOH/g. As a definition, saponified value is the minimum amount (mg) of potassium hydroxide required to completely saponify 1g of oils and fats. Therefore, lower saponified value indicates less contamination by impurities when same oil/fat species are compared. On the other hand, incredibly high saponified value can be often seen in the case of coconut oil or palm kernel oil, both of which consist of fatty acids with shorter alkyl chain compared with other oils and fats.

2.2 Estimation of Waste Oils Discarded

Three main kinds of waste oil in could be used for biodiesel production in China: gutter oil, acid oil, and rice bran oil. The China's waste oil potential and feedstock

structure from 2006 to 2010 are listed in Table 3. It is seen that China produced 13.74 Mt of waste oil in 2010, including 6.58 Mt of gutter oil, 1.55 Mt of acid oil, and 5.61 Mt of rice bran oil.

Acid oil is discarded from edible oils/fats refinery. After oils are expelled and extracted from oilseeds, remaining free fatty acids are removed by undergoing neutralization process. The obtained alkali oil sludge, which is a mixture of saponified products, lipids and other minor compounds, is acidified with strong acid such as hydrochloric acid or sulfuric acid to be acid oil (dark oil).

Table 3
China's Waste Oil Potential and Feedstock Structure* (Mt)

Years	Total waste oil ^a	Gutter oil ^b	Acid oil ^b	Rice bran oil ^b
2006	10.42	4.28	0.93	5.21
2007	11.34	5.00	1.01	5.33
2008	11.82	5.20	1.12	5.50
2009	13.08	6.12	1.37	5.59
2010	13.74	6.58	1.55	5.61

Note. a, Total waste oil is equal to the sum of gutter oil, acid oil and rice bran oil.
 b, Domestic production of edible vegetable oil comes from China Industry Economy Statistical Yearbook 2012 table, waster oil, gutter oil, acid oil and rice bran oil are calculated same as in Reference [22].

Biodiesel can be produced from waste oils and fats by transesterification, also called alcoholysis, which has been becoming an ideal approach to use vegetable oil and animal fats on engine without modifications^[23]. For sustainable development of society and energy, biodiesel produced from waste oils and fats has been given more attentions^[24] and commercially used in many countries. If all these waste oils and fats were utilized in biodiesel production, nearly 10.84 Mt of biodiesel can be prepared. On the other hand, approximately 146.34 Mt of fossil diesel fuel was on sale annually in China. It was therefore suggested that approximately 7.4% of annual fossil diesel fuel consumption can be replaced by biodiesel derived from wastes.

Table 4
Penitential of Biodiesel Produced From Waste Oils* (Mt)

Years	Biodiesel from ^a				Fossil diesel usage ^b	Substituted fossil diesel by biodies ^c
	Total waste oil	Gutter oil	Acid oil	Rice bran oil		
2006	9.48	3.89	0.85	4.73	118.35	8.22
2007	10.35	4.54	0.96	4.85	124.97	8.97
2008	10.74	4.72	1.02	5.00	135.33	9.32
2009	11.90	5.56	1.25	5.08	137.57	10.32
2010	12.49	5.98	1.41	5.10	146.34	10.84

Note. a, Biodiesel is equal to the amount of waste oil multiplied by conversion factor of 90.9%^[22].

2.3 Characterization of Various Waste Oils and Fats

In order to know the characterization of waste oils and fats generated in China, 10 waste oil/fat samples are collected from food manufactory industries, restaurants and household. Table 5 shows fatty acid composition of various waste oils and fats. It can be seen that acid oil A, contains highly poly-unsaturated fatty acids such as eicosapentanoic acid (C20:5), docosahexaenoic acid (C22:6). Because high unsaturation results in poor oxidation stability, acid oil A should be decreased in degree of unsaturation before used as a feedstock of biodiesel by hydrogenation or adding antioxidant. However, hydrogenation of oils increases the degree of saturation and production cost, and also deteriorates the cold flow properties. Therefore, waste oils derived from fish oil had better be used as a source of valuable poly-unsaturated fatty acid for other

purpose. Acid oil B, which is derived from rapeseed oil refinery, shows similar fatty acid composition to that of rapeseed oil and high in unsaturated fatty acids, especially oleic acid. Biodiesel produced from rapeseed oil has been commercially used in many counties for its good performance. Acid oil C, from food manufacturing industry, which are derived from palm oil, are high in saturated fatty acid content, namely palmitic acid (C16:0). Consequently, biodiesel from these oils has poor cold flow properties and should be mixed with fossil diesel.

In general, used cooking oil from food service industry and/or households may consist of rapeseed oil and soybean oil according to Chinese dietary habit. Although saturated fatty acid content is relatively higher than that of refined rapeseed oil, cold flow properties are still adequate when converted to biodiesel.

Table 5
Fatty Acid Composition of Various Waste Oils and Fats

Waste oils/fats		Fatty acid composition (wt%)									
		C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}	C _{20:1}	C _{20:5}	C _{22:6}	Others
Acid oil	A	18.7	4.9	5.8	12.5	1.5	2.2	8.1	9.4	12.5	24.4
	B	12.1	-	4.2	49.8	24.2	8.7	-	-	-	1
	C	34.2	0.9	5.8	45	9.7	3.5	-	-	-	0.8
Waste oil from food manufacturing industry	A	42.5	1.2	8.2	43.1		0.2	0.3	-	-	4.5
Used cooking oil from restaurant	A	15.8	1.8	7.9	62.4	0.5	8.4	0	-	-	3.2
	B	4.8	0.5	5.2	48.9	26.5	8.8	5.2	-	-	0.1
	C	14	0.9	4.8	30.8	44.3	3.9	0.4	-	-	0.9
Used cooking oil from household	A	44.5	1.2	5.5	6.5	33.2	5.7	0.9	-	-	2.5
	B	15.5	-	5.6	32.2	25.9	5.4	12.2	-	-	3.2
	C	6.1	1.4	2.9	45.5	26.8	5.6	1.5	-	-	11.2

Table 6 shows some key characteristics including water content, acid value, peroxide value and iodine value of collected waste oil/fat samples. It is clearly seen that all acid oils show notably high acid value in the range from 69 - 160 mgKOH/g, suggesting that acid oil usually contains 65% - 95% of free fatty acids. In addition, these acid oils were high in water content up to nearly 8.5%. It is known that alkali-catalyzed method must use the feedstocks with low water content and low acid value. Free fatty acid is converted to the saponified product with alkyl catalyst^[10]. This saponification causes not only decrease in the yield of fatty acid methyl ester, but also formation of emulsion during washing process, which makes separation of water and biodiesel difficult.

Moreover, water should be removed before the reaction since it hinders the catalytic activity for both acid- and alkali-catalyzed methods. Therefore, this kind of feedstock must be pretreated to remove the water and esterified to decrease the fatty acid content^[25-27].

Waste oil from food manufacturing industry is found to be low in both acid value and water content as shown in Table 6. Therefore, this waste oil seems to have promising qualities for successful conversion as well as refined oils and fats.

In terms of used cooking oils from food service industry and households, acid value and peroxide value of the former is relatively higher than that of the latter. This might be attributed to the used frequency of before

disposal. From the results of acid value, both used cooking oils have a good quality to be converted into biodiesel by alkali-catalyzed method. From the viewpoint of recovery,

it is suggested that cooking oil from both restaurant and household are converted into biodiesel for its large quality.

Table 6
Characterization of Various Waste Oils and Fats

Waste oils and fats		Water content	Acid value	Peroxide value	Iodine value
		(%)	mgKOH/g	meq/kg	gI ₂ /100g
Acid oil	A	8.5	150	-	118
	B	2.5	189	-	158
	C	4.2	165	-	69
Waste oil from food manufacturing industry	A	0.55	0.66	< 0.50	69
	A	0.65	8.2	0.75	25
Used cooking oil from restaurant	B	0.05	6.8	27	158
	C	0.09	6.4	< 0.50	114
	A	0.02	0.54	2.8	125
Used cooking oil from household	B	0.88	0.58	1.9	164
	C	0.92	2.5	5.1	121

PROSPECTIVE

Various oils and fats are examined as feedstock of biodiesel including edible and waste ones. The refined oils and fats from seed/bean and fruit are mainly consumed in China. The refined oils and fats would have enough fuel properties after conversion of biodiesel. It is apparent that oil palm is extremely high in oil yield. Recent wide spread of oil palm plantation is partly attributed to this high viability and suitability for plantation. For its low price, it is a good candidate as biodiesel feedstock. A lot of oils and fats are wasted in China, if all these waste oils and fats were utilized in biodiesel production, nearly 10.84 Mt of biodiesel can be produced, approximately 7.4% of annual fossil diesel fuel consumption can be replaced by biodiesel derived from wastes.

Various waste oil/fat samples are collected from food manufactory industries, restaurants and household and their characteristics are analyzed. Due to the small scale of waste cooking oil, it is not easy to maintain the uniform quality of waste oils and fats at constant supply. For the constant quality of biodiesel production, however, feedstocks should be constant in quality and quantity. In addition, efficient collection system of feedstock is a prerequisite in any commercially viable process. When these conditions are taken into consideration, acid oil appears to be an appropriate candidate, constant supply can be expected at reasonable price.

Furthermore, it is important in the future to find feedstocks from non edible resources including soapnut, jatropha^[28] and algae^[29] and low price oil seed. For example, production of palm oil from oil palm has been increasing recently to become the mostly produced oil followed by soybean oil, which had been the most largely produced vegetable oil worldwide. From these lines of information, it was found that for the promotion of biodiesel production, not only effective utilization of waste oils and fats discarded but also collection of oils and fats resources in the area that not suitable for crops.

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