SULFUR CONTENT IN SELECTED OILS AND FATS AND THEIR CORRESPONDING METHYL ESTERS

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ABSTRACT. *According to Environmental Protection Agency (EPA) regulations, the use of ultra-low sulfur diesel (ULSD) has been mandated for all on-highway transportation diesels since 2006. To comply with the EPA regulations, biodiesel must meet the same ULSD standard for total sulfur which is set at a maximum of 15 ppm. Generally, biodiesel contains lower sulfur than fossil diesel. However, due to the diversity of biodiesel feedstocks, questions have been raised about their sulfur content and the sulfur content of the biodiesel made from them. The objective of this research was to gain basic knowledge about how the sulfur content in biodiesel is affected by the sulfur content of different feedstocks. Sulfur in oilseeds, seed meals, oils and fats, and biodiesel were investigated according to ASTM D5453. Samples of different feedstocks for biodiesel production were investigated. Results showed that sulfur content varies greatly from one source to another. The highest sulfur in seeds and meals was found in rapeseed and mustard, at the level of 9,000 and 15,000 ppm, respectively. Oils from mechanical expeller presses contained very low levels of sulfur, although some were still higher than 15 ppm. Animal fats and waste vegetable oils contained relatively higher sulfur levels and were frequently above 15 ppm. It was observed that sulfur was significantly reduced when the oils and fats were processed into biodiesel. Results showed that most of the biodiesel samples investigated in this study contained less than 15-ppm sulfur. Feedstocks which contain a high percentage of free fatty acids (FFA) must be treated with sulfuric acid to reduce the FFA level before transesterification. In these cases, care is needed during phase separation to exclude sulfur from the fuel layer.*

Keywords. *Biodiesel, Sulfur, Biofuels.*

According to Environmental Protection Agency (EPA) regulations, on-highway diesel fuel must comply nationwide with stringent limitations on sulfur content starting 1 June 2006. The fuel has transitioned from low-sulfur diesel (LSD) with a maximum sulfur level of 500 ppm to ultra-low sulfur diesel (ULSD) at 15 ppm. To ensure that the diesel fuel sold at the pump also meets the standard, diesel refiners have enforced a more stringent criterion to lower sulfur far below 15 ppm, even as low as 3~4 ppm, due to concerns of possible contamination between the refinery gate and retail pumps (National Petrochemical & Refiners Association, 2006). Because it is frequently used as a transportation fuel, biodiesel must meet the same sulfur standard. The ASTM specification for biodiesel has reflected this criterion with the addition of a S15 grade, which corresponds to a sulfur limit of 15 ppm (ASTM Standards, 2007b).

Generally, biodiesel contains less sulfur than fossil diesel. However, the current biodiesel industry has not established the capability, as has been required in petroleum refineries, of refining the fuel to remove sulfur to the level of 15 ppm as specified by the EPA. According to our preliminary study on six feedstocks for biodiesel production, the sulfur content in the raw materials (oils or fats) was typically between 20 and 30 ppm, with the highest being 44 ppm. Although not reported here, after processing, the sulfur content (ppm) in the crude glycerol was generally higher than that in the raw oils (Thompson and He, 2006). This means that sulfur from the feedstock preferentially partitions into the by-product glycerol. The sulfur content in the biodiesel, however, may or may not be lower than 15 ppm. Water-washing of the biodiesel may be a critical step for sulfur removal in biodiesel production, particularly if acid esterification is used as a pretreatment to lower free fatty acids. It was also noticed that the elemental composition of a vegetable oil may vary according to the soil conditions where the oilseed crops grow, which may in turn affect the sulfur content in the seeds and/or in the oils. If animal fats and waste vegetable oils (WVO) are used, the sulfur content is expected to be higher due to the presence of sulfur-containing compounds such as proteins. Also, when high FFA feedstock is processed in a two-step acid-base process and sulfuric acid is used as the catalyst for esterification, the possibility exists that the sulfate may end up in the biodiesel.

There are many important questions which have been raised such as:

- How does the sulfur content in the feedstock affect the sulfur level in biodiesel?
- How does the sulfur content vary among the feedstocks?
- How does the sulfur distribute between the biodiesel and the crude glycerol by-product?
- Is there a correlation between the fatty acid profile and the sulfur content?

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To the authors' knowledge, there has been no information published that systematically addresses these questions. The objective of this research was to gain basic knowledge about how biodiesel is affected by the sulfur content of different feedstocks and how this affects the sulfur distribution in the product streams during processing. This article reports the findings of sulfur determination in feedstocks and biodiesel from selected samples of oils and fats.

MATERIALS AND METHODS

SULFUR MEASUREMENTS

In order to maintain accuracy and precision, the sulfur measurements in this project were conducted by strictly following the Ultraviolet (UV) Florescence method specified by the ASTM D5453 standard (2007a). All samples were analyzed at the Biofuels Research Laboratory of the Department of Biological and Agricultural Engineering at the University of Idaho. A Mitsubishi TS-100H Sulfur Analyzer (COSA Instrument Corporation, Norwood, N.J.) was used and is capable of measuring sulfur content in both liquid and solid samples. The detection limit is in the ppb (0.001 ppm) range at the lower end and up to 1% (10,000 ppm) at the higher end. The manufacturer's specified relative standard deviation (RSD) is in the range of 0.6% to 2.6% in various applications. During our initial calibration on the machine, the R-values were 0.9997, 0.9993, and 1.000 for low, middle, and high sensitivity levels, respectively. The sample size is in the range of 30 to 50 mg. All samples were measured directly without dilution. Samples reading out of range were rerun using the proper sensitivity. Once the proper burn sequence was established for each type of sample, the time to run a test was about 10 min. The instrument was calibrated using dilutions of Dibenzothiophene to four different sensitivity ranges. The oven temperature was set at 1000°C, the total oxygen flow was set to 600 mL/min and the argon to 400 mL/min. In this method, the sample boat was inserted into the high temperature pyrolytic chamber where the sulfur was oxidized to sulfur dioxide (SO_2) in an oxygen-rich atmosphere. Water produced during the combustion was removed with argon through a special gas permeable dryer tube and the combusted gases were exposed to UV light and the florescence was detected by a photomultiplier tube. The resulting signal was a measure of the sulfur contained in the sample and was converted to ppm through the built-in conversion factors.

Some of the samples, especially the solid samples, contained sulfur levels higher than the machine's upper limit. To gain an understanding of the sulfur levels in these samples, selected samples were also analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy at the Analytical Laboratory of the Holms Research Center at the University of Idaho. The instrument was a Perkin Elmer Optima 3200 RL (Perkin-Elmer Inc., Shelton, Conn.) and utilized a standard plant macro-element screen method. The instrument can measure sulfur content above 10,000 ppm, although the best calibrated range was 60 to 800 ppm. Therefore, the measurements from this method were used for reference purposes only.

SAMPLE PREPARATION

The feedstocks investigated in this study, including oil seeds, meal (the solid product after oil extraction), and oils/fats, were obtained from various sources. The oil seeds were processed in one of two expeller presses, a laboratory scale press or a small capacity industrial press, depending on the quantity of seed available. The laboratory press was a Model E-1SD (Shanq Jer Industries, Taiwan). It features a 120V variable speed reversing 0.4-kW drive motor and a built-in 1-kW temperature control unit that operates two rod heaters located in the casting of the press that surround the cage rings and the worm screw. It has a throughput capacity of 4 to 6 kg/h depending on the type of seed and the feed rate. Seed was fed into the press from a 2-kg hopper that was filled manually. The small industrial press was a Cecoco Hander New Type 52 expeller (Chuo Boeki Goshi Kaisha, Japan). It was powered by a 2.2-kW three-phase single-speed motor. It has an adjustable worm screw and a seed throughput of 30 to 50 kg/h depending on the seed type and temperature, and screw adjustment. The seed input hopper was replaced with a seed heating plenum fabricated from stainless sheet metal with two cones and a silicone blanket heater on each one. The heaters had a wattage density of 7.75 kW/m^2 (5 $W/in.^2$) and were controlled by an Omega CN76000 temperature/process controller (Stamford, Conn.). The seed was fed into the plenum by gravity from a 1,000-kg capacity bin.

Seed, meal, and oil samples were collected during the expelling process. After allowing the oil to settle, biodiesel was produced using a small batch reactor. Sodium methoxide ($NaOCH_3$) was used as the catalyst at 0.6% by weight of the oil. The molar ratio of alcohol to oil was 6:1. The oil was heated to 60°C and 80% of the alcohol/catalyst mixture was added and stirred for 60 min. After removing most of the glycerin, a second reaction was run for an hour using the remaining 20% of the alcohol/catalyst mixture. The fuel was then water-washed and dried. Some of the rendered oils and fats were also made into biodiesel using the same procedure. However, four of the rendered fats were quite high in free fatty acids (FFA) and required an acid pretreatment. For each gram of FFA in the sample, 2.5 grams of methanol and 0.05 grams of sulfuric acid (H_2SO_4) were added and the mixture was stirred for 1 h at 60°C. The resulting product mixture underwent settling, separation of the methanol/water/acid layer, and drying before undergoing a normal base-catalyzed reaction as described above.

RESULTS AND DISCUSSION

Various vegetable oils and animal fats that are used or could potentially be used as feedstocks for biodiesel production were collected. These included soybean and rapeseed oils, the most commonly used biodiesel feedstocks in the United States and Europe, and camelina and jatropha, which are considered to be promising new feedstocks for biodiesel production. The fatty acid (FA) profiles of the vegetable oils, animal fats, and greases were measured (data not shown). There was no evidence that the FA profile, which can be affected by plant variety and the growing conditions, correlates with the sulfur content. This observation is in agreement with reports of crop scientists (Brown, 2008).

Sulfur contents in the oil seeds, their meals, oils, animal fats and greases were determined and are summarized in tables 1 to 3. Tables 1 and 2 show that the sulfur content varies greatly from one source to another. The highest sulfur in the seeds was found in rapeseed and two cultivars of mustard that were at the level of 9,000 ppm. Camelina, canola, and soybean are among the group that contained the second highest sulfur content in their seeds, which was approximately 4,000 to 5,000 ppm. Despite the high sulfur content in the seeds, it was observed that the seed meals contained even higher sulfur content than the parent seeds after oil extraction. For the samples tested, the sulfur increase in the meals was significant, especially for rapeseed (table 1). It is likely that the sulfur-containing compounds remained in the solid structure after the low-sulfur oil was removed, which concentrated the sulfur in the meals. Although no special de-gumming processes were conducted on the oils obtained for this study, some of the gums in the oils settled out to the bottom of the oil containers during storage. It was noted that although the levels of sulfur were different, the gums contained relatively high sulfur content. Therefore, significant sulfur reductions were achieved naturally during the seed processing and natural oil de-gumming during storage, and no specific procedures were adopted for the purpose of sulfur removal. The authors are not certain whether this would be the case for oils obtained via solvent extraction processes of oil seeds. One experiment contained in this study showed that the sulfur contents were 7.0 and 9.5 ppm for mustard oil (cultivar *Pacific Gold*) processed via mechanical extraction versus solvent (hexane) extraction, respectively. This may imply that hexane extracted oils have slightly higher sulfur carry-over.

It can be seen in table 2 that the sulfur content is reduced by 20% to 50% when the oils and fats are converted to biodiesel. The sulfur contained in the oils was believed to partition preferentially into the glycerin layer and may also be lowered during water washing. Limited tests for sulfur were conducted on glycerol produced from animal fats. Results showed high sulfur content in these samples, with ppm levels about 10 times higher than those in the original fats. Similar tests on glycerol from vegetable oils in our previous study did not show as strong a trend in sulfur accumulation in the glycerol as in glycerol from animal fats (Thompson and He, 2006). Table 2 also shows that three of the oils had sulfur levels greater than 15 ppm. Although all of these samples produced biodiesel with sulfur levels below 15 ppm, the corn oil remained very close to 15 ppm. The sample of corn oil was recovered from an ethanol production process and contained high FFA (14%wt). It was converted to biodiesel using the two-step acid-base processing method. Since sulfuric acid was used in the acid-catalyzed step, the residual sulfur was later found to be due to insufficient post-reaction water-washing of the biodiesel.

Table 1. Sulfur contents in selected oil seeds, meals, and oils.

		Sulfur (ppm)			
No.	Sources	Seed	Meal	Gum	Oil
1	Camelina	5,398	5,973	263.2	11.9
2	Candlenut	2,310	3,168	2,468.3	0.6
3	Canola	4,189	5,752	161.0	5.5
4	Croton	-	2,290	1,526.9	3.4
5	Mustard-1[a]	9,464	16,900[b]	5,495.7	2.4
6	Mustard-2[c]	8,950[b]	15,800[b]	5,033.7	4.3
7	Rapeseed	9,260	13,700[b]	5,199.1	11.2
8	Soybean	4,187	4,608	269.9	5.7

[a] Cultivar of IdaGold.
[b] Data were measured by the Analytical Laboratory of the Holms Research Center, University of Idaho by ICP-Atomic Emission Spectroscopy.
[c] Cultivar of Pacific Gold.

Table 2. Sulfur in vegetable oils and reduction after conversion to biodiesel.

		Sulfur Content (ppm)		Reduced by	
No.	Sample	Oil	Methyl Esters	(ppm)	(%)
1	Avocado	24.8	6.3	18.5	74.6
2	Candlenut	1.1	0.7	0.4	36.4
3	Canola	5.5	3.0	2.5	45.5
4	Corn	18.6	13.8	4.8	25.8
5	Crambe	11.2	7.2	4.0	35.7
6	Croton	3.4	0.5	2.9	85.3
7	Jatropha	4.9	2.4	2.5	51.0
8	Karanja	22.9	10.4	12.5	54.6
9	Mustard-1[a]	2.7	1.4	1.3	48.1
10	Mustard-2[b]	4.3	2.5	1.8	41.9
11	Palm, olean	3.2	2.3	0.9	28.1
12	Palm, crude	9.7	7.5	2.2	22.7
13	Rapeseed	11.2	2.4	8.8	78.6
14	Soybean	5.7	1.1	4.6	80.7

[a] Cultivar of IdaGold.
[b] Cultivar of Pacific Gold.

Rendered oils and fats can have significant amounts of sulfur depending on the way they are processed. Feedstocks that have an FFA level over 5% require either a caustic stripping or an acid pretreatment followed by drying before biodiesel can be made efficiently with a base-catalyzed process. Table 3 summarizes the results of sulfur measurements for the animal fats and WVOs. It is seen that all of the samples achieved a sulfur level below 15 ppm after proper treatment and post-reaction processing even though three-fourths of the oils and fats had initial sulfur levels higher than 15 ppm. This is consistent with the results of vegetable oils where the sulfur content was reduced by the conversion process to biodiesel. Sulfuric acid treatment of the high FFA feedstocks does not carry a significant amount of sulfur over to the finished fuel. Normally, careful operation of regular biodiesel procedures including sufficient water-washing of the biodiesel should ensure the sulfur specification is met. However, insufficient water-washing of the biodiesel from a two-step acid-base process for high FFA feedstock may leave residual sulfate in the biodiesel and throw the final sulfur level out of specification. One case was observed where the sulfur content in the final product exceeded the limit of 15 ppm when a crude tallow was used as feedstock. Further investigation into this case determined that the high sulfur in this specific batch was caused by insufficient water-washing of the biodiesel. Other experiments that used the same procedures all yielded biodiesel fuel that meet ASTM specifications. The sulfuric acid-catalyzed treatment of high FFA feedstocks is the standard practice in the industry. However, recent developments of heterogeneous acid catalysts in the form of ion exchange resins may soon eliminate the need for that procedure (Rohm and Haas, 2008).

Table 3. Sulfur contents in WVO, animal fats and their methyl esters.

No.	Sources	Free Fatty Acid (%)	Acid Treatment	Sulfur (ppm) Oil / Fat	Sulfur (ppm) Methyl Esters	Reduced by (%)
1	WVO, cook line	28.5	Yes	21.4	7.2	66.3
2	WVO, fryer vapor	12.4	Yes	15.7	6.3	59.8
3	Fat, black soldier fly	42.3	Yes	48.3	10.6	78.1
4	Fish oil	3.1	No	18.8	10.8	42.6
5	Render, batch #1	13.0	Yes	1.5	1.1	26.7
6	Render, batch #2	27.5	Yes	5.5	1.1	80.0
7	Render, batch #4	10.5	Yes	9.9	1.3	86.9
8	Render, batch #7	1.5	No	27.8	7.1	74.5
9	Render, batch #11	3.6	No	29.0	8.9	69.3
10	Tallow, Crude	7.0	No	29.4	12.6	57.1

SUMMARY

Sulfur content in vegetable oils, animal fats, and waste vegetable oils varied greatly among the samples tested. Oil seeds can contain sulfur as high as 15,000 ppm. However, the high sulfur content of the seed is not passed to the oil when mechanical extraction is used even without any specially designed sulfur-removing procedures, although some of the mechanically-extracted oils still contain sulfur higher than 15 ppm. The majority of the sulfur-containing compounds remain in the seed meals after pressing. Limited experimental data show solvent extraction might lead to higher sulfur in oils, but more data are needed to confirm this assumption. It was observed that sulfur levels higher than 15 ppm can be reduced when the oils and fats were processed into biodiesel. Results showed that most of the biodiesel samples investigated in this study contained less than 15-ppm sulfur. Special processing was needed for feedstocks which contained a high percentage of free fatty acids such as animal fats and waste vegetable oils. Sufficient post-reaction water-washing of the biodiesel was required to insure minimal sulfur carry-over into the fuel. It is concluded, therefore, that biodiesel with 15-ppm or less sulfur could be achieved from all of the feedstocks investigated in this study as long as proper processing of oil extraction, biodiesel conversion, and post-reaction treatment are practiced.

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