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Biodiesel Tech Notes

Characterization of Crude Glycerol from Biodiesel Production from Multiple Feedstocks

Biodiesel production worldwide has been on an exponential growth curve over the past several years. The principal by-product of this production is glycerol, also known as glycerin. It occurs in vegetable oils at a level of approximately ten percent by weight. For each gallon of biodiesel produced, approximately 0.35 kg (0.76 lb) of crude glycerol is also produced. This crude glycerol possesses very low value because of its impurities. As the production of biodiesel grows, the quantity of crude glycerol generated will be considerable, and its utilization will become an urgent topic. The make-up of crude glycerol varies depending on the parent feedstock and the biodiesel production process. Before the crude glycerol can be considered for possible value-added products, it is necessary to characterize the crude glycerol for its physical, chemical, and nutritional properties. Most industrial biodiesel processes utilize a 6 to 1 molar ratio of alcohol to oil- which is an excess of 100%, in order to drive the reaction to completion. Most of the excess alcohol (up to 60%) will end up in the glycerol layer after the reaction. Larger scale biodiesel producers refine their crude glycerol and move it to markets in the food, pharmaceutical, and cosmetic industries. It is generally treated and refined through filtration, chemical additions, and fractional vacuum distillation to yield various commercial grades, such as dynamite grade, yellow distilled, and chemically pure as well as grades established by the United States Pharmacopeia (USP). As more and more crude glycerol is generated, researchers are studing economical ways to utilize it, thus further defraying the cost of biodiesel production. This article reports the characterization of crude glycerol obtained when biodiesel was produced from mustard, rapeseed, canola, crambe, soybean, and waste cooking oils.

Analytical tests were conducted on the parent oils and on the crude glycerol as it was recovered after separation from the fuel without further processing. Measurements included fatty acid profile, viscosity, heat of combustion, macro elements, carbon and nitrogen content, and food nutrient analysis. Although not shown here, the fatty acid profile analyses on the vegetable oils showed that each of the oils is dominated by three or four of the fatty acids. Canola, soybean, and WVO oils concentrated more heavily on the shorter chain molecules while the mustard, rapeseed, and crambe oils shift toward the longer, heavier ones, particulary erucic acid. Table 1 shows the analytical results from the macro element screening tests. As expected, the carbon and nitrogen levels in both the oil and the glycerol samples were very homogeneous with the carbon at about 77% in the oil and about 25% in the glycerol, and nitrogen at 0.22% and 0.05% respec-

Feedstocks	IdaGold Mustard	PacGold Mustard	Rapeseed	Canola	Soybean	Crambe	WVO
Measurements on oils							
Calcium, ppm	2.7 +/- 0.2	4.9 +/-0.5	15.7+/- 0.6	7.6+/-0.9	3.1 +/- 0.2	47.7 +/- 0.6	BDL
Potassium, ppm	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Manesium, ppm	0.8+/- 0.0	1.3 +/- 0.1	2.1 +/- 0.1	1.6 +/- 0.0	1.2 +/- 0.1	28.3+/- 2.1	BDL
Phosphorus, ppm	BDL	8.0 +/- 0.9	13.0 +/- 0.9	10.0 +/- 0.8	10.0 +/- 0.9	256.7 +/- 5.8	BDL
Sulfur, ppm	26.0 +/- 2.2	23.0 +/- 1.5	24.0 +/- 1.1	22.0 +/- 1.8	22.0 +/- 0.6	44.0 +/- 1.2	28.0 +/- 2.7
Sodium, %wt	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Carbon,%wt	77.3 +/- 0.58	77.0 +/- 0.00	77.3 +/- 0.58	77.0 +/- 0.00	77.0 +/- 0.00	77.7 +/- 0.58	76.3 +/- 0.58
Nitrogen, %wt	0.22 +/- 0.03	0.21 +/- 0.02	0.17 +/- 0.12	0.22 +/- 0.01	0.22 +/- 0.06	0.22 +/- 0.01	0.25 +/- 0.03
Measurements on Crude Glycerol							
Calcium, ppm	11.7 +/- 2.9	23.0 +/- 1.0	24.0 +/- 1.7	19.7 +/- 1.5	11.0 +/- 0.0	163.3 +/- 11.6	BDL
Potassium, ppm	BDL	BDL	BDL	BDL	BDL	216.7 +/- 15.3	BDL
Magnesium, ppm	3.9 +/- 1.0	6.6 +/- 0.4	4.0 +/- 0.3	5.4 +/- 0.4	6.8 +/- 0.2	126.7 +/- 5.8	0.4 +/- 0.0
Phosporus, ppm	25.3 +/- 1.2	48.0 +/- 2.0	65.0 +/- 2.0	58.7 +/- 6.8	53.0 +/- 4.6	136.7 +/- 57.7	12.0 +/- 1.5
Sulfur, ppm	21.0 +/- 2.9	16.0 +/- 1.4	21.0 +/- 1.0	14.0 +/- 1.5	BDL	128.0 +/- 7.6	19.0 +/- 1.8
Sodium, %wt	1.17 +/- 0.15	1.23 +/- 0.12	1.06 +/- 0.07	1.07 +/- 0.12	1.20 +/- 0.10	1.10 +/- 0.10	1.40 +/- 0.16
Carbon, %wt	24.0 +/- 0.00	24.3 +/- 0.58	25.3 +/- 0.58	26.3 +/- 0.58	26.0 +/- 1.00	24.0 +/- 0.00	37.7 +/- 0.58
Nitrogen, %wt	0.04 +/- 0.02	0.04 +/- 0.01	0.05 +/- 0.01	0.05 +/- 0.01	0.04 +/- 0.03	0.06 +/- 0.02	0.12 +/- 0.01

Table 1. Analysis results of macro elements, carbon and nitrogen.

Note: BDL indicates values that are below the detection limit for the corresponding analytical method. The detection limits in ppm were as follows: calcium – 2, potassium – 40, Magnesium – 0.20, sodium – 80, phosphorus – 5, sulfur – 15, carbon – 200 and nitrogen – 100. Data shown are in the format of "average +/- standard deviation"

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tively. The only exception to this observation was that the carbon content in the WVO glycerol sample was 50% higher than that of the average. This was probably due to the presence of soaps and dissolved unreacted glycerides and esters. Sodium, which was quantified as an ion, represents the catalyst (sodium methylate, $NaOCH_3$) used in the reaction. It is interesting to note the high levels of elements such as calcium and phosphorus in the crambe glycerol compared to the others. This most likely was due to the soil conditions in North Dakota where the seeds were grown. Additionally, the elements in all of the samples, with the exception of sulfur in the WVO, were concentrated in the glycerol phase. This is a desirable effect, as it would tend to remove the minerals from of the fuel and allow them to be drained off with the glycerol.

From conversations with an animal scientist, it was believed by the researchers that crude glycerol might be used as an animal feed additive or supplement. To investigate this further and to add to the general knowledge about the makeup of crude glycerol, food nutrient analysis was determined on the parent oils and their resulting glycerol the results are shown in Table 2. The efficacy of using crude glycerol as an animal feed supplement is unclear. Currently, there are multiple research activities taking place by several universities and professional research investigators. More detailed findings are expected out soon. As expected, the oils or triglycerides are mostly fat plus a small amount of protein and carbohydrates. The small discrepancies that exist were related to the relative amounts of gums and other impurities in the different crude oils. Nutritional data from the glycerol of the first-use oil samples show that it is mostly carbohydrate and could reasonably be mixed with high protein meal and used as a feed supplement. The WVO glycerol, on the other hand, had a much higher fat content making it more useful as a fat supplement. This data also confirms the presence of higher levels of unreacted glycerides and soaps in the WVO. The ash contained in crude glycerol is mainly sodium from the catalyst.

When refined to a chemically pure substance, glycerol would be a very valuable by-product of the biodiesel production process with hundreds of uses. Purifying it to that stage, however, is costly and generally out of the range of economic feasibility for small to medium-sized plants. Alternative uses for the crude glycerol should be explored to make biodiesel more competitive in the growing global market.

Table 2. Food nutrient analysis for oil and crude glycerol samples.

Feed stocks	Ida Gold Mustard	PacGold Mustard	Rapeseed	Canola	Soybean	Crambe	WVO
Oils							
Fat, %	98.2	99.8	98.9	97.3	97.0	98.7	99.9
Carbohydrates, %	1.36	BDL	1.05	2.36	2.91	1.18	BDL
Protein, %	0.08	0.07	0.06	0.09	0.09	0.10	0.10
Calories, kJ/kg	37.2	37.6	37.4	37.1	37.0	37.4	37.7
Ash, %	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Crude Glycerol							
Fat, %	2.03	1.11	9.74	13.1	7.98	131	7.98
Carbohydrates, %	82.8	83.8	75.5	75.2	76.2	78.6	26.9
Protein, %	0.14	0.18	0.07	0.06	0.05	0.44	0.23
Calories, kJ/kg	14.6	14.5	16.3	17.5	15.8	16.3	27.2
Ash, %	2.80	1.90	0.70	0.65	2.73	0.25	5.50

Note: BDL indicates values that are below the detection limit for the corresponding analytical method.

For details see:
Thompson, J.C. and B. He. 2006. Characterization of crude glycerol from biodiesel production from multiple feedstocks. Applied Eng. Agri. 22(2): 261-265. *This paper can be downloaded from; http://www.uidaho.edu/bioenergy/*

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