

Quantitative Analysis of Chemical Compositions from Various Sources of Crude Glycerine

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ABSTRACT

Crude glycerine is the main by-product of the biodiesel production process. This by-product has high gross energy that can replace some energy nutrition. Nevertheless, the chemical composition of crude glycerine has variables due to sources of oil and production methods which limit its utilization. In this study, glycerine from three biodiesel production scales small, medium and large production were sampled and analyzed for some physical properties and proximate compositions. From the results, pH values of small scale was the highest (8.99) followed by the medium (6.39) and large scale (6.40). The large scale showed the highest kinetic viscosity (99.20 cSt) followed by the small and medium scale (90.28 and 12.51 cSt). In terms of proximate composition, the small scale had 3.93% of moisture, 0.65% of crude protein, 5.05% of crude fat and 7554.61 kcal/kg of heat of combustion, while the medium and large scales had 13.85 and 4.27% of moisture, 0.85 and 0.48% of crude protein, 0.44 and 0.22% of crude fat and 4,387.45 and 4,650.22 kcal/kg of heat of combustion, respectively. For methanol analysis, the medium scale had the highest methanol level (2.87) followed by the small (1.10) and large scale (0.46). Saturated fatty acid was detected only in the small scale (15.95 mg/ml), particularly palmitic acid (C16: 0). In addition, the largest amount of glyceride in this scale consisted of monoglyceride (2.78 mg/ml), diglyceride (0.19 mg/ml), and triglyceride (0.77 mg/ml). For dietary mineral determination, the medium scale had almost the highest.

Key words: Biodiesel, Chemical composition, Dietary minerals

INTRODUCTION

Biodiesel production in Thailand has grown over the past several years, resulting from the rising of world fossil fuel prices. There are many resources that can be used for biodiesel production such as waste vegetable oil, vegetable oil and animal fat. Currently, waste vegetable oil has been widely used in biodiesel production. The main by-product from biodiesel production is crude glycerine that is usually used for various purposes, for instance, fuel, lubricant and animal feeds. Nevertheless, this by-product contains various chemical components from ingredients and reactions (Thompson and He, 2006). Crude glycerine consists of methanol or ethanol, fatty acids, water, and some chemical compounds that derived from tranesterification process (Dasari, 2007). Thus, physical properties and chemical composition of crude glycerine is quite variable depending on the source of oil that used and the method used for biodiesel production (Dasari, 2007; Kerr et al., 2007). Results from physical analysis showed that the viscosity of crude glycerine produced from vegetable oil and waste vegetable oil which are commonly used in biodiesel production was about 8.46 to 8.80 and 26.3 to 26.7 cSt, respectively. The heat of combustion of crude glycerine produced from vegetable oil and waste vegetable oil was about 1.86×10^3 to 20.5×10^3 and 25.2×10^3 kJ, respectively. In addition, analysis of crude glycerine produced from vegetable oil and waste vegetable oil comprised 1 to 13% and 60% crude fat and 75 to 83% and 25% carbohydrate (Thompson and He, 2006).

Biodiesel production in Thailand has been increasing since the year 2005 but up to now there has been lack of information of the utilization of glycerine in animal feeds. Therefore, the aim of

this study is to determine some physical properties and chemical composition of crude glycerine produced from three biodiesel production scales: small, medium and large. Results from this study can provide some basic information for the further use of crude glycerine in animal feeds.

MATERIALS AND METHODS

Crude glycerine samples were collected from three biodiesel plant scales: small scale (from Rattaphum Community's Biodiesel Plant), medium scale (from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University), and large scale (from New Biodiesel Co., Ltd.). Kinetic viscosity of samples was determined according to ASTM D445 (ASTM, 2006) using Cannon-Fenske Routine viscosity Cannon® # 100.s.984 for crude glycerine from small scale, Cannon® # 200 H765 for crude glycerine from medium scale and Cannon® # 350 E696 for crude glycerine from large scale. Proximate composition of crude glycerine samples were analyzed according to AOAC (2000). Minerals contained in samples were analyzed by photometric method for nitrogen, phosphorus and sulfur. Sodium, potassium, calcium and magnesium were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) while titration method was used for analyzing chloride sample. Six replications from each production scale were calculated by mean. Information of three types of crude glycerine is shown in Table 1.

Table 1. Information of crude glycerine collected from 3 production scales.

Items	Small scale ¹	Medium scale ²	Large scale ³
Biodiesel process	Transesterification	Transesterification	Transesterification
Initial source	Animal fat, animal oil	Waste vegetable oil, animal oil	RBD Palm oil ⁴
Organic separate agent	-	H2SO4	-
Reactant	MeOH	MeOH	MeOH
Catalyst agent	NaOH	NaOH	KOH
Crude glycerine neutralizing agent	-	NaOH	NaOH

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³New Biodiesel Co., Ltd., Surat Thani province

⁴Refined bleached deodorised palm oil

RESULTS AND DISCUSSION

Physical properties and proximate composition of crude glycerine from the three sources of production scale is presented in Table 2. From visual evaluation, crude glycerine from the small and medium scales had a dark brown color, and more turbidity than that of the large scale. The pH values of crude glycerine from small, medium and large scales were 8.99, 6.39 and 6.40, respectively. Heat of combustion of crude glycerine from small, medium and large scales was 7,554.61, 4,387.45 and 4,650.22 kcal/kg, respectively. In terms of proximate composition, crude glycerine from small scale contained 3.93% moisture, 0.65% crude protein, 5.05% crude fat, and 0.38% ash whereas the medium and large scales contained 13.85 and 4.27% moisture, 0.85 and 0.48% crude protein, 0.44 and 0.22% crude fat, and 5.62 and 1.44% ash, respectively. The kinetic viscosity of crude glycerine produced from small, medium and large scales was 90.28, 12.52 and 99.20 cSt, respectively.

The higher pH value of crude glycerine collected from the small scale as opposed to both the medium and large scales is related to the incomplete transesterification reaction during biodiesel

Table 2. Physical and chemical characteristics of crude glycerine from 3 scales.

Items	Small scale	Medium scale	Large scale
Physical properties			
Visual evaluation	Dark brown, high turbidity	Dark brown, high turbidity	Light yellow, transparent
Viscosity (cSt/s)	90.28	12.52	99.20
pH	8.99	6.39	6.40
Proximate composition			
Crude fat (%)	5.05	0.44	0.22
Crude protein (%)	0.65	0.85	0.48
Moisture (%)	3.93	13.85	4.27
Ash (%)	10.38	5.62	1.44
Heat of combustion (kcal/kg)	7554.61	4387.45	4650.22
Number of replication	6	6	6

production that resulted in high alkaline compound contamination. The viscosity and heat of combustion of crude glycerine from the small plant scale were higher than those of the medium and large scales due to the additional quantity of trace minerals (such as sodium and potassium) and free fatty acids. Thus, the proximate composition, particularly, crude fat and ash of crude glycerine from the small scale were higher than the others. In addition, the heat of combustion of crude glycerine from the small scale was also higher than the medium and large scales. High level of viscosity and heat of combustion in crude glycerine from the small and large scale were related to the moisture added in during processing period. Therefore, different physical and chemical characteristics of crude glycerine were related to the source of oil and method used for biodiesel production (Dasari, 2007; Kerr et al., 2007; Thompson and He, 2007).

Table 3 illustrates fatty acid composition from the three sources of production. Crude glycerine from the small scale could only be detected for free fatty acids. palmitic acid was the largest amount of fatty acid that was detected (12.6091 mg/ml) followed by stearic acid (2.1895), myristic acid (0.6423), lauric acid (0.3136) and arachidic acid (0.1987), respectively. It could be summarized that initial substances used in the small scale contain a high level of unsaturated free fatty acids from animal fat resulting in their presence in the crude glycerine from small scale production. The high level of unsaturated free fatty acids residue in crude glycerine probably is related to an incomplete transesterification reaction during processing.

The glyceride analytic profiles are given in Table 4. Monoglyceride (2.78), diglyceride (0.19) and triglyceride (0.77) have been found only in the small scale production. Normally, alkaline catalyzed transesterification of triglyceride proceeds by of exchanging ester group with fatty acids while in this study, initial substances from small scale had high level free fatty acids that even made the soaps formation in transesterification reaction and dissolved unreacted glycerides in the both of methyl ester and crude glycerine.

Table 3. Fatty acids composition variable from 3 scales.

Items	Small scale	Medium scale	Large scale
Caprylic acid (C8 : 0) (mg/ml)	ND	ND	ND
Capric acid (C10 : 0) (mg/ml)	ND	ND	ND
Lauric acid (C12 : 0) (mg/ml)	0.3136	ND	ND
Myristic acid (C14 : 0) (mg/ml)	0.6423	ND	ND
Palmitic acid (C16 : 0) (mg/ml)	12.6091	ND	ND
Stearic acid (C18 : 0) (mg/ml)	2.1895	ND	ND
Arachidic acid (C20 : 0) (mg/ml)	0.1987	ND	ND
Behenic acid (C22 : 0) (mg/ml)	ND	ND	ND
Linolenic acid (C22 : 0) (mg/ml)	ND	ND	ND
Total saturated fatty acid (mg/ml)	15.9502	ND	ND

*ND indicates values that are below the detection limit for corresponding analytical method.

Table 4. Glyceride analytic profile from 3 scales.

Items	Small scale	Medium scale	Large scale
Monoglyceride (g/ml)	2.78	ND	ND
Diglyceride (g/ml)	0.19	ND	ND
Triglyceride (g/ml)	0.77	ND	ND

In terms of methanol residue in crude glycerine, Medium scale contained the highest level of methanol (2.87%) followed by the small (1.10%) and large scales (0.46%), respectively. The high methanol residue content was related to the high account of fatty acids contained in an initial substance. The high level of methanol residue is probably related to the transesterification reaction being superseded by the saponification reaction. In addition, some of methanol derived from incomplete transesterification reaction may remain in crude glycerine.

Macro-minerals and nitrogen from the three production scales are presented in Table 5. Inorganic contaminant from the medium scale was the highest level of calcium (783.84 ppm), phosphorus (212.82 ppm), sulfur (3.70 ppm) and nitrogen (0.20 %wt), respectively. This was due to the composition of wasted vegetable oil and used animal fat derived from the cooking routine that brings mineral compositions residue and impurity (Table 1). Sulfur residue from sulfuric acid (H₂SO₄) that was used for organic content separation before processing can be detected in the final product. The large scale has the highest content of sodium contaminant (172.69 ppm) followed by the medium (116.13 ppm) and small scales (6.76 ppm), respectively. The existing sodium residue was related to the relative amounts of crude glycerine neutralizing agent for neutralized crude glycerine that will be contained in the final product of crude glycerine.

Table 5. Analysis result of macro mineral and nitrogen found in crude glycerine from 3 scales.

Items	Small scale	Medium scale	Large scale
Calcium (ppm)	634.98	783.84	723.62
Phosphorus (ppm)	106.17	212.82	7.99
Sulfur (ppm)	2.895	3.70	2.39
Sodium (ppm)	6.76	116.13	172.69
Chloride (% wt)	0.30	0.25	0.30
Potassium (%wt)	2.40	0.32	0.03
Magnesium (%wt)	0.20	0.09	0.20
Nitrogen (%wt)	0.12	0.20	0.13

CONCLUSION

Crude glycerine from different sources of oil and processes used for biodiesel production illustrated different physical properties and chemical composition of crude glycerine. Heat of combustion, crude fat, pH value, free fatty acids, glyceride and methanol residue of crude glycerine from the small scale were higher than those of the medium and large scales. However, the medium scale had higher crude protein, moisture and mineral contents than the others. This is related to the initial substances and chemical agents. However, before using crude glycerine in animal feed (monogastrics), the amount of methanol that contained should not exceed than 150 ppm. In addition, free fatty acid, water and mineral contents should be considered.

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