Artigo original *DOI: http://dx.doi.org/105902/2179460X18971*

Ciência e Natura, Santa Maria, v. 37 n. 4 set-dez. 2015, p. 740-746
Revista do Centro de Ciências Naturais e Exatas – UFSM
ISSN impressa: 0100-8307 ISSN on-line: 2179-460X

Controle de qualidade do biodiesel B100 oriundo do processamento de óleo degomado de soja - Nota técnica

Quality control of B100 biodiesel obtained from soy biodiesel processing - Technical note

Cinthia da Costa Berwanger[1], Noeli Júlia Schüssler de Vasconcellos[2], Sandra Cadore Peixoto[3], Alexandre Swarowsky[4,5], Rodrigo Fernando dos Santos Salazar[6]

[1]Tecnóloga Agroindustrial, Campi Cruz Alta, Universidade Estadual do Rio Grande do Sul (Uergs), Cruz Alta, RS, Brasil

[5] Pesquisador, Programa de Pós-Graduação em Engenharia Agrícola, Engenharia Agrícola, Universidade Federal de Santa Maria, Santa Maria, RS, Brasil

[2, 3, 4, 6] Prof. Adj., Conjunto II - Ciências Exatas e Tecnológicas, Centro Universitário Franciscano, Santa Maria, RS, Brasil

Resumo

A crescente demanda por energia e o esgotamento das fontes não renováveis tem gerado a busca por diferentes fontes energéticas, principalmente àquelas que sejam renováveis. Neste contexto o biodiesel apresenta-se como uma das mais interessantes fontes energética da atualidade em virtude do seu caráter renovável e por atingir uma série de setores da sociedade com sua cadeia produtiva diversificada em diferentes localidades. Neste sentido, o objetivo deste trabalho foi o de avaliar as características físico-químicas do biodiesel B100 produzido industrialmente no Rio Grande do Sul ao longo de 2012. Foram determinados a alcalinidade combinada, teor de glicerina livre, teor de glicerina total, índice de acidez e teor de umidade que oscilaram em torno de 0,0002 m_{eq}*/g, 0,024 %m/m, 0,21 %m/m, o,33 mg KOH/g e 343,7 mg/kg, respectivamente. Esses valores encontravam-se em conformidade com a legislação vigente. Deste modo conclui-se que o processo químico de transesterificação foi mantido sob controle durante o período de produção do biodiesel resultante em uma fonte energética confiável.*

Palavras-chave*: Acidez, biodiesel, controle de qualidade, glicerina, umidade.*

Abstract

The growing demand for energy and the depletion of non-renewable sources has generated a search for different energy sources, especially those that are renewable. In this context biodiesel presents itself as one of the most interesting energy source because of its renewable character and achievement of a number of society sectors with its diversified production chain in different locations. In this sense, the objective of this study was to evaluate the physicochemical characteristics of the biodiesel B100 produced industrially in Rio Grande do Sul during 2012 year. We determined the combined alkalinity, free glycerin content, total glycerin content, acid index and moisture content which ranged around 0.0002 m_{eq} */ g, 0.024% w / w, 0.21% w / w to 33 mg KOH / g and 343.7 mg / kg, respectively. These values were in accordance with current legislation. Thus it is concluded that the chemical process of trans-esterification was kept under control during the production period of the resulting biodiesel in a reliable energy source.*

Keywords*: Acidity, biodiesel, glycerin, moisture, quality control.*

1 Introduction

Fuels produced by the esterification process, transesterification or thermal cracking from vegetable or animals raw materials are called biodiesel (Sebrae, 2007). The vegetable raw material most widely used for this purpose is the degummed soybean oil and the animal material used is obtained from beef tallow (BiodieselBR, 2014).

Despite the high cost of production and processing among oilseeds, soy has been chosen for more immediate production of biodiesel, since the price of soybean oil suffered reductions in recent years. The exchange rate had not been favorable for exporters. The tax regime favors soybean production, but not its processing. These facts have contributed to a huge idle crushing capacity. In addition, soybean oil is a byproduct of the production chain of soybean biodiesel and adds value to this abundant supply of by-product in the industry (Prates et al., 2007).

The use of biodiesel as a fuel has been showing increasing potential worldwide (Mittelbach, 1996; Knothe, et al, 2006; BiodieselBR, 2014). The incentive to production arises of future scenarios that point to the end of oil reserves. The concentration of oil is currently explored in geographical areas of conflict. The new deposits are situate in higher cost location extraction zones and the growing environmental concerns have made the use of biofuels under different aspects needed (Cadó et al., 2014). In the Brazilian scenario, their use can also reduce dependence on imports of oil diesel (Faria, et al., 2007; Cadó et al., 2014).

The commercialization of biodiesel in Brazil is regulated by the National Agency of Petroleum, Natural Gas and Biofuels (ANP) Resolution No. 31 of November 4, 2005, which regulates public auctions where biofuel sale occurred (Brasil 2014). Auctions are organized by ANP, from specific guidelines established by the Ministry of Mines and Energy (MME). The ANP held since 2005, biodiesel sales auctions (Araújo, 2005; BiodieselBR, 2014). In the auctions, refineries buy the biodiesel to mix it to petroleum-based diesel.

The initial purpose of the auction was to generate market and thereby stimulate the production of biodiesel in sufficient quantities to refineries and distributors could comprise a mixture (BX) determined by law (ANP, 2014; Cadó et al., 2015). To be a public event, they are known all trading volumes and their suppliers, as well as the price condition. In addition, the auctions offer equal access for suppliers and do not discriminate the size of the biodiesel producer. Auctions also ensure the participation of family farming. At least 80% of the volume traded in the auctions must be from producers holding the Social Fuel Seal (Faria, et al, 2007; ANP, 2012; BiodieselBR, 2014).

Good quality biodiesel should be produced following strict industry specifications, mainly a monitoring program of all production stages. The establishment of legislation for the definition and characterization of biodiesel quality was a key step to win the market trust, and thereby took a huge step to enter the biodiesel in the Brazilian energy matrix (Brasil, 1993; Brasil, 2011; BiodieselBR, 2014). The resolution that establishes the biodiesel quality and processing specification is contained in the ANP Technical Regulation No 4/2012. (ANP, 2012). The development of the Brazilian market of biofuels takes place at the exact moment when energy becomes a major trading currency in the international market. Consequently there is a growing need to produce large scale and maintain the quality of biodiesel produced by several physicochemical analyses to meet the quality standards required by law and by the market (Brasil, 2011; ANP, 2012; BiodieselBR, 2014; Cadó et al., 2014).

Biodiesel Quality control is very important for commercialization and market acceptance, since the contaminants can lead to operational, economic and environmental problems (Lôbo et al., 2009; Brasil, 2014; Cadó et al., 2014). The process of conversion of fats and oils in methyl or ethyl esters also determines the quality of the fuel. Thus, the production process will determine whether or not the fuel will meet the technical specifications required for marketing. During the process of transesterification, intermediate products are formed, unreacted triglycerides, residual alcohol and catalyst may remain retained in the final product and can lead to contamination. Therefore, problems such as formation of deposits, filter clogging and deterioration of the fuel in engines are formed (Knothe, et al., 2006; Lôbo et al., 2009; Brasil, 2011).

Lôbo and co-workers (2009) state that, from the analytical methods applied in the evaluation of biodiesel quality, information related to selection of raw materials, manufacturing process and storage, as well as the biodiesel performance as fuel and the quality of their emissions can be obtained (Lôbo et al., 2009). The quality of biodiesel can vary depending on the molecular structures of esters. The presence of contaminants in the raw material can lead to a low production process and low quality biodiesel (Araújo, 2005; Knothe, et al., 2006). Under the specifications of various standards, some restrictions are seen for individual contaminants, including free glycerin and total glycerin in order to limit the content of glycerol and glycerides; flash point to limit the residual alcohol content; acid value to limit the content of free fatty acids (FFA), and ash content in order to limit of catalyst residue (Gerpen et al., 2004; Knothe, et al., 2006). In this sense, Araújo (2005) points as critical parameters for quality biodiesel those concentration values of total glycerin, free glycerin, sulfated ash, flash point, acid value, corrosive to copper and water content, confirming the need for controlling the processing steps and biodiesel production (Araújo, 2005; Knothe, et al., 2006; Lôbo et al., 2009; Brasil, 2011).

According to what was presented the aim of this study was to evaluate the quality of B100 biodiesel obtained from soy degummed oil from the determination of free glycerol, total glycerin, combined alkalinity, acidity and moisture content that can compromise the final quality of biodiesel derived from the production.

2 Material and methods

Samples used in the experiment were obtained from a large company that produces biodiesel, located in the Northwest Region of Rio Grande do Sul state. The samples of B100 biodiesel were collected at the end of a crude soybean oil processing batch. Six biodiesel sampling were made along 1st semester of 2012. Each sampling represented three work shifts. Six replicates of each analytical parameter were realized. Considering those three processing work shifts, 180 analytical determination were performed on 36 samples per sampling. Those samples were collected in properly sanitized PVC bottles and subjected to physical and chemical tests in the company's laboratories (ABNT, 1987).

Every solution and reagents used in this work were prepared from stock standard solutions and solids in liquids with reagents and analytical grade (BP). The main reactants used for the determination of biodiesel quality were: distilled water, hydrochloric acid (0.01 mol L^{-1} and 0.1 mol L^{-1}), sulfuric acid (1:3 v/v), neutralized alcohol, 96 ° GL, sodium arsenite, bromophenol blue (1%), sodium bicarbonate, potassium iodide, sodium hydroxide, sodium periodate, Karl Fischer reagent (iodine, sulfur dioxide, pyridine and dry methanol) acetonic solution (98%), phenolphthalein solution (0.1%), and toluene.

The analytical procedures employed for determining the combined alkalinity, free glycerin, total glycerin, acidity and moisture content are described in more detail in the subsections below.

2.1 Determination of combined alkalinity

In this analysis 5.0 g of sample were weighed directly into a 250 mL Erlenmeyer flask. Then was added 20.0 mL of neutralized ethanol and 2 drops of phenol bromine blue indicator (1%). The sample had a greenish hue. The final solution was titrated with hydrochloric acid (HCl - 0.01 mol L^{-1}) until they reached the turning point (yellowish color). The combined alkalinity was determined by equation (1).

$$CA = \frac{V_{HCl} \cdot [HCl]}{M_{sample}} \quad (1)$$

Wherein CA refers to combined alkalinity (mg/g); V_{HCl} is the volume of HCl consumed for the titration (L); [HCl] is the concentration of hydrochloric acid (mg L^{-1}) and "M_{SAMPLE}" refers to the mass of the B100 biodiesel sample (g).

2.2 Free glycerine determination (FG)

Three grams of oil sample were weighed directly into a 125 ml separator funnel. Then 20.0 mL of distilled water was added and 0.50 mL of a solution of sulfuric acid (H_2SO_4, 1:3 v/v) pipetted. A stirring system (funnel + solutions) was applied and left to rest until the separation into two phases was completed. In parallel, 25.0

mL of sodium periodate ($NaIO_4$) were added in a 250 mL Erlenmeyer flask. The higher density phase was discarded. The phase of interest was transferred to the Erlenmeyer flask , which was capped and place to cool in cold water for 10 min. After cooling, a 4.0g of sodium bicarbonate ($NaHCO_3$) was added, resulting in a clear solution with blue tint. Finally, they were added a 1.50 g of potassium iodide (KI). The final solution was titrated with sodium arsenite ($NaAsO_2$) 0.1 mol L^{-1} until it reached the turning point (yellowish). The free glycerin was determined by equation (2).

$$FG = \frac{(V_{NaAsO_2} - V_B)\,.\,[NaAsO_2]}{M_{sample}} \qquad (2)$$

Wherein FG refers to the free glycerol content (mg/g); V_B is the volume of $NaAsO_2$ consumed in the analytical blank (L); $VNaAsO_2$ equivalent to the volume consumed $NaAsO_2$ titration (L); $[NaAsO_2]$ is the concentration of sodium arsenite (mg L^{-1}) and "M_{SAMPLE}" refers to the mass of the B100 biodiesel sample (g).

2.3 Total glycerin determination (TG)

In this procedure, 3.0 g of sample were weighed directly into a flat-bottomed 250 ml flask, which already contained 5.0 mL of 96 ° GL and 3.0 ml of ethanol sodium hydroxide (NaOH, 50% w/v). The sample was kept under heating plate until translucent. Then, it was transfer to a 125 ml separator funnel where 10.0 mL of toluene, 2 drops of phenol bromine blue indicator and 4.0 mL Sulfuric Acid (H_2SO_4) 1:3 were added. The system (funnel + solution) was subjected to stirring and allowed to stand until separation into two phases occurred. In parallel 25.0 mL of sodium periodate ($NaIO_4$) in a 250 mL Erlenmeyer flask were added. Subsequently, the resulting upper phase of the sample decantation was also added to the flask which was then capped and taken to cooling in cold water for 10 min. Soon after cooling, 4.0 g of sodium bicarbonate ($NaHCO_3$) was added, resulting in a clear solution with blue hue. Finally, 1.50 g of potassium iodide (KI) were added. The final solution was titrated with sodium arsenite ($NaAsO_2$ - 0.1 mol L^{-1}) until reaching the turning point (bluish color). The total glycerin was determined by equation (3).

$$TG = \frac{(V_{NaAsO_2} - V_B)\,.\,[NaAsO_2]}{M_{sample}} \qquad (3)$$

Wherein TG refers to the total glycerol content (mg/g); V_B is the volume of $NaAsO_2$ consumed in the analytical blank (L); $VNaAsO_2$ equivalent to the volume consumed $NaAsO_2$ titration (L); $[NaAsO_2]$ is the concentration of sodium arsenite (mg L^{-1}) and "M_{SAMPLE}" refers to the mass of the B100 biodiesel sample (g).

2.4 Determination of the acidity index

Throughout the process the acid index was constantly monitored and controlled, including B100 storage, as changes to this value during storage period indicate the presence of water in biodiesel, which can lead to the formation of soap and enter in the ignite of the engines, promoting the formation of deposits and corrosion, as noted by Mittelbach (1996).

To determine this parameter 5.0 g of sample was weighed directly into a 250 mL Erlenmeyer flask. Next, 25.0 mL of neutralized alcohol (increased by phenolphthalein indicator solution (0.1%)) were added. The final solution was titrated with sodium hydroxide (NaOH - 0.1mol.L^{-1}) until reached the turning point (reddish color). From equation (4), the acid index (AI) was calculated.

$$AI = \frac{(V_{NaOH} - V_B).[NaOH].56{,}11}{M_{sample}} \qquad (4)$$

Wherein (AI) refers to the Acid Index (g/g); V_B refers to the volume consumed NaOH in the analytical blank (L); V_{NaOH} was consumed amount of NaOH for titration of sample (L); [NaOH] is the concentration of sodium hydroxide (mol L^{-1}) and M_{SAMPLE} refers to the weight of sample (g).

2.5 Moisture determination

The moisture was controlled by means of the Karl Fisher method employing a coulometer. This method has been successfully used for measurement of concentration of water in a range from a few parts per million up to relatively high levels. The biodiesel sample was dissolved in anhydrous methanol and titrated with Karl Fisher reagent. Karl-Fischer reagent (RKF) consisted of a mixture of iodine, sulfur dioxide and methanol in pyridine in stoichiometric amounts (Gerpen et al., 2004).

3 Results and discussion

The tolerance values set by the ANP resolutions for different contaminants are: total glycerin, free glycerin, combined alkalinity, acid index and moisture (Knothe, et al., 2006; Lôbo et al., 2009; Brasil, 2014). In this sense, from the physicochemical tests performed, it was possible to verify the quality of the processed biodiesel (Table 1).

Table 1 - Physicochemical characteristics used for the quality control of soybean oil for biodiesel. (n = 6)

Analytical parameters	**Obtained values**	**Reference[1]**	**Tolerance limits (ANP)[2]**
Combined alkalinity (m_{eq}/g)	0,0002 ± 0,0001	≤ 0,0009	--
Free glycerin (%m/m)	0,024 ± 0,001	≤ 0,024	≤ 0,02
Total glycerin (%m/m)	0,21 ± 0,02	≤ 0,25	≤ 0,25
Acid Index (mg KOH/g)	0,33 ± 0,06	≤ 0,50	≤ 0,50
Moisture (mg/kg)	343,7 ± 6,5	≤ 380	≤ 200

[1] Recommendation according to the quality standards established by the company to export the biodiesel B100; [2] ANP Resolution Nº 45, of 08.25.2014 (Brasil, 2014).

It can be inferred, from the results, that the chemical process of transesterification was kept under control during the biodiesel production period. At the same time it can be seen that the raw material used did not affect the analytical parameters to evaluate the quality of biodiesel (Lôbo et al., 2009). However, for market purposes in the country, the processed biodiesel should undergo dehydration to adjust the moisture content of the newly established limits (Brasil, 2014).

During the process of transesterification, intermediate products were formed. Unreacted triglycerides, residual alcohol and catalyst may remain retained in the final product and can lead to contamination. Therefore, problems such as formation of deposits, filter clogging and deterioration of the fuel in engines can happen (Mittelbach, 1996; Gerpen et al., 2004; Knothe, et al., 2006; Lôbo et al., 2009). Additionally, during the biodiesel processing, parallel reactions (basic catalyst) can lead to saponification of the degummed oil. In this sense, the analysis allows the combined alkalinity saponification process to monitor what is happening during processing (Mittelbach, 1996). Due to performed controlling during the transesterification of the process, degummed soybean oil saponification was not observed (Cadó et al., 2014).

A high acid index in the biodiesel, resulted from hydrolysis of natural esters, in particular glycerides of through lipases (Knothe, 2006).

The concentration of residual free glycerin can be reduced by successive biodiesel washes. While it is practically insoluble in biodiesel, glycerin can be dispersed in small sizes. The presence of residual soaps can affect the final quality of biodiesel by increasing the concentration of glycerin in the fuel due to formation of emulsions. The maximum level of free glycerin allowed in biodiesel is 0.02% m/m in Brazil, Europe and the United States (Prates et al., 2007; Brasil, 2014). The combined glycerin, which includes mono-, di- and triglycerides unreacted is the product of an incomplete reaction of glycerides and displays a low conversion rate of biodiesel oil. Thus, this is an important parameter used to evaluate the efficiency of reaction conversion of fats and oils into biodiesel (Knothe, 2006; Prates et al., 2007). According to the concentration in the biodiesel, the unreacted glycerides can cause fuel filter plugging and the formation of deposits on engine parts, as they increase the viscosity of the fuel and thus reduce combustion efficiency (Mittelbach, 1996; Gerpen et al., 2004). The amount of free glycerin with glycerin combination is called as total glycerin. About the total glycerin content, the Brazilian and European standards establish a ceiling of 0.25 %m/m, while in the US the limit is 0.24 %m/m (Lôbo, et al., 2009; Brasil, 2014). For biodiesel evaluated in this study the glycerides levels are within the limits established in the current legislation (Brasil, 2014).

Regarding the oil moisture the ANP Resolution No. 14 of May 11, 2012 admitted the limit of 380 mg kg^{-1}. For monitoring effect on assessments for non-compliance, the moisture content for biodiesel sold in Brazil currently can not exceed 150 mg kg^{-1} for the distributor (Brasil, 2014). However, these limits have been reviewed and it was suggested that there may be elevated levels of tolerance of the storage biodesel. There is a need to consider a range of concentration of water between the producer and the distributor due to hygroscopicity of this fuel that occurs during storage, loading and transport biodiesel (Lôbo et al., 2009; Brasil, 2014; Biodieselbr, 2015). According to ANP Resolution No. 45 (2014), from 2014 onwards, for monitoring effect on assessments for non-compliance, it was established a tolerance range of 50 mg / kg in water content limit in biodiesel for the producer and plus 150 mg kg^{-1} for the distributor (Brasil, 2014).

4 Conclusions

Based on this study it was found that the operating conditions of the transesterification plant employed by the company allow large-scale biodiesel production from crude soybean oil with the required employment quality as an energy source in combustion engines without compromising the mechanical components. From the physicochemical characterization, we conducted, it was found that, most of the time, the biodiesel produced was in line with current legislation. However, because of the fluctuation of moisture levels obtained throughout the study, it is greater in required controlling of B100 dehydration step prior to storage or shipment.

Acknowledgments

The authors acknowledge the collaboration of the company to provide samples for this study.

References

ABNT - Associação Brasileira De Normas Técnicas (1987). Preservação e técnicas de amostragem de afluente líquidos e corpos receptores - Procedimento. Rio de Janeiro: ABNT. (ABNT NBR 9898:1987).

ANP – Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (2012). Disponível em: < http://www.anp.gov.br> Acesso em: 2 Maio de 2012.

Araújo, R. M. de (2005). Regulação do Biodiesel-Especificação e Controle de Qualidade. Apresentação feita por Rosângela Moreira de Araújo da ANP no Painel setorial de biodiesel, 29 (11), 2005.

Biodieselbr - O maior portal sobre biodiesel do mundo (2014). **Biodiesel**. Disponível em: <http://www.biodieselbr.com/biodiesel.htm>. Acesso em: 18 nov. 2014.

Brasil. Ministério da Agricultura, Pecuária e Abastecimento (1993). Portaria MAPA Nº 795 de 20/12/1993 (Federal) – Normas de Identidade, Qualidade, Embalagem, Marcação e Apresentação do Óleo de Soja Bruto, do Óleo de Soja Degomado e do Farelo de Soja. Disponível em: <http://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=recuperarTextoAtoTematicaPortal&codigoTematica=1229311>. Acesso em: 05 nov. 2013.

Brasil. Ministério do Meio Ambiente (2011). Conselho Nacional do Meio Ambiente - CONAMA. Resolução Nº 430 de 13/05/2011 (Federal) - Dispõe sobre as condições e padrões de lança mento de efluentes, complementa e altera a Resolução Nº 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente - CONAMA. Disponível em: <http://www.mma.gov.br/port/conama/res/res11/propresol_lanceflue_30e31mar11.pdf>. Acesso em: 11 nov. 2014.

Brasil. Ministério do Minas e Energia (2014). Resolução ANP Nº 45, de 25/8/2014 (Federal) - Dispõe sobre a especificação do biodiesel contida no Regulamento Técnico ANP nº 3/2014 e as obrigações quanto ao controle da qualidade a serem atendidas pelos diversos agentes econômicos que comercializam o produto em todo o território nacional. Diário Oficial da União (DOU) 26.8.2014. Disponível em: http://nxt.anp.gov.br/nxt/gateway.dll/leg/resolucoes_anp/2014/agosto/ranp%2045%20-%202014.xml. Acesso em: 26 jun. 2015.

Cadó, R. G.; Mainardi, L. A.; Vasconcellos, N. J. S.; Salazar, R. F. S. (2014). Gestão de produção de biodiesel e avaliação da coagulação/floculação no tratamento de efluente do processo de fabricação. Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 15, n. 2, p. 159-174, 2014.

Gerpen, J. V.; Shanks, B.; Pruszko, R. (2004). Biodiesel Production Technology: Subcontractor Report. National Renewable Energy Laboratory. Battelle. 110p.

Knothe, G.; Gerpen, J. V.; Krahl, J.; Ramos, L. P. (2006). Manual do Biodiesel. Edgard Blucher, São Paulo, 340p.

Lôbo, I. P.; Ferreira, S. L. C.; Cruz, R. S. (2009). Biodiesel: parâmetros de qualidade e métodos analíticos. Química Nova, 32 (6), 1596-1608.

Mittelbach, M. (1996). Diesel fuel derived from vegetable oils, VI: Specifications and quality control of biodiesel. Bioresource Technology, 56 (1), 7-11.

Prates, C. P. T.; Pierobon, E. C.; Costa, R. C. (2007). Formação do Mercado de Biodiesel no Brasil**.** São Paulo. Disponível em: << http://www.bndes.gov.br/SiteBNDES/export/sites/default/bndes_pt/Galerias/Arquivos/conhecimento/bnset/set2502.pdf >> Acesso em: 16 dez. 2014.

SEBRAE – Serviço Brasileiro de Apoio às Micro e Pequenas Empresas. (2007). Cartilha Biodiesel. Disponível em: <http://www.sebrae.com.br/setor/agroenergia/acesse/biblioteca-on-line/cartilha-biodiesel>. Acesso em: 12 de Junho de 2012.