

Monitoring of acylglycerides in the biodiesel production process**Monitoramento de acilglicerídeos no processo de produção de biodiesel**

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ABSTRACT

The characteristics of the biodiesel result from the chemical profile present in the raw material (fatty acids) and transformations that occurred in the stages of the production process of this biofuel. In this sense, there must be a wide control of chemical components present in this renewable fuel that directly impact the performance of the finished final product. Thus, with the possession of valuable information about the compounds of interest, it is possible to select the raw materials and suppliers, to better plan the process steps and chemical and physical transformations, in addition to optimizing the production, perfecting the methods used with information of great relevance for the formulation of a high quality and affordable product. Therefore, in this work, the mono, di, tri-glycerol and glycerol signals were identified and

quantified at some points in the biodiesel process. Therefore, in this work, the signs of mono, di, triacylglycerides and free glycerol were identified and quantified at some points in the biodiesel synthesis process. The importance of monitoring these compounds illustrates how $^1\text{H-NMR}$ can be a powerful tool in decision making, making it very informative when combined with the productive sector, in addition to being a simple method that does not require prior treatment and derivatization to perform numerous analyzes.

Keywords: biodiesel, acylglycerides, NMR, monitoring, chemical profile.

RESUMO

As características do biodiesel resultam do perfil químico presente na matéria-prima (ácidos graxos) e transformações ocorridas nas etapas do processo de produção desse biocombustível. Nesse sentido, deve haver um amplo controle dos componentes químicos presentes neste combustível renovável que afetam diretamente o desempenho do produto final acabado. Assim, com a posse de informações valiosas sobre os compostos de interesse, é possível selecionar as matérias-primas e fornecedores, planejar melhor as etapas do processo e as transformações químicas e físicas, além de otimizar a produção, aperfeiçoando os métodos utilizados com as informações. de grande relevância para a formulação de um produto de alta qualidade e preço acessível. Portanto, neste trabalho, os sinais de mono, di, tri-glicerol e glicerol foram identificados e quantificados em alguns pontos do processo do biodiesel. Portanto, neste trabalho, os sinais de mono, di, triacilglicérides e glicerol livre foram identificados e quantificados em alguns momentos do processo de síntese do biodiesel. A importância do monitoramento desses compostos ilustra como o $^1\text{H-RMN}$ pode ser uma ferramenta poderosa na tomada de decisões, tornando-o muito informativo quando combinado com o setor produtivo, além de ser um método simples que não requer tratamento prévio e derivatização para realizar inúmeras análises .

Palavras-chave: biodiesel, acilglicerídeos, RMN, monitoramento, perfil químico.

1 INTRODUCTION

The quality of the biodiesel suffers a great influence in the production process due to the quality of the raw material used, which may bring undesired characteristics.¹ The quality evaluation of the biofuel must be robust and the analyzes carried out must have the purpose of guaranteeing the attendance to aspects technicians.²

The source of animal fat or vegetable oil represents, in a simple way, the composition and nature of the fatty acids present in triglycerides. The type and concentration of fatty acids present have a marked effect on the stability of biodiesel, which will influence its control, storage, and oxidation.³ Thus, it is of great importance to identify the chemical profile and the amount of esters remaining in the process, such as the impurities present in the raw material, the free glycerol content, residual alcohol, unreacted glycerides and water residues; very important aspects that can vary as properties of biodiesel as a whole.⁴ In addition to the

origin of the grease raw material, the mixture between different sources and the methanol profile used can interfere in the synthesis of biodiesel according to the batch and other components present in the mixture. 5 Thereby, the objective of this work was to identify relevant components for the quality control of biodiesel production that meet the indicators pointed out by the National Agency of Petroleum, Natural Gas and Biofuels (ANP).⁶

2 MATERIALS AND METHODS

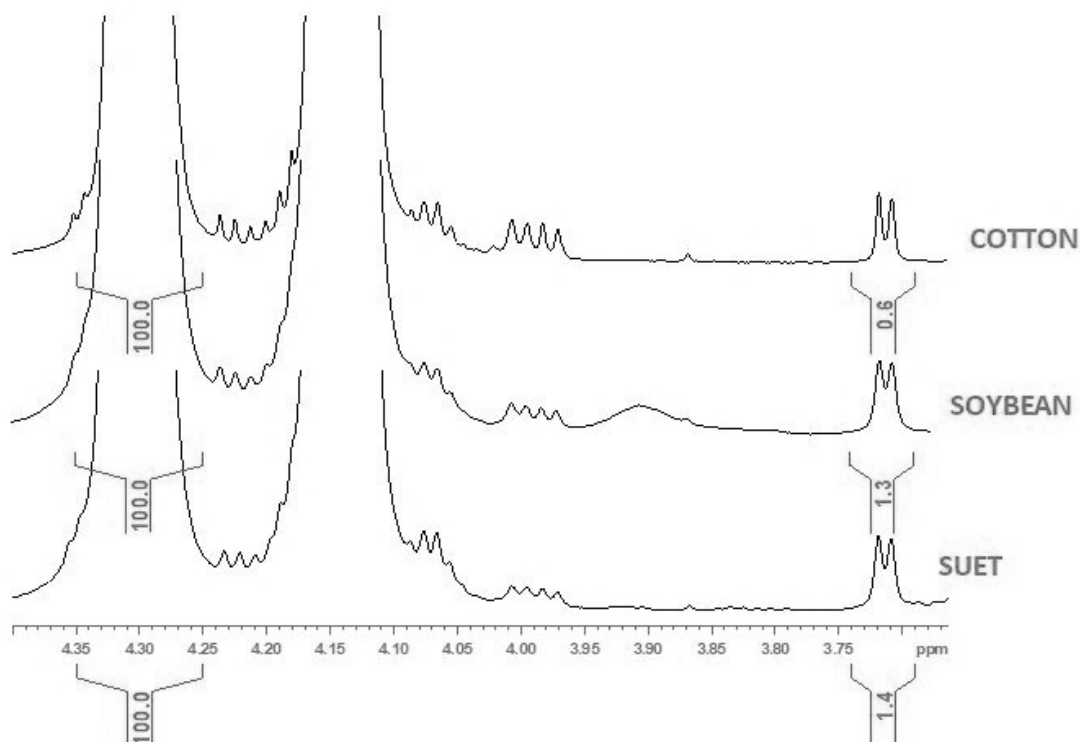
The samples were purchased from a biodiesel company, located in the state of Goiás, Brazil. These samples were analyzed individually with a volume of 200 μL of sample homogenized in 400 μL of CDCl_3 . $^1\text{H-NMR}$ analyzes were performed on a Bruker Avance III 11.75T spectrometer (Billerica –USA), with the multinuclear TBI probe, for a 5 mm diameter tube with reverse detection. The chemical shift was referenced at 0.0 ppm for the internal tetramethylsilane (TMS) reference signal. All spectra were obtained at 28 °C (301 K) with a simple pulse of 90°. Waiting time (3.0 s) and of acquisition time (5.0 s) were used, with a spectral window of 20.0 ppm centered on 4.7 ppm.

spectra were acquired using the number of dots and the 64K data size in an attempt to improve the resolution of the FID. Receiver gain was calculated for each sample with very different characteristics and an exponential multiplication with a factor of 0.3 Hz was used. The $^1\text{H-NMR}$ spectra had the phase and baseline distortions manually corrected in the TopSpin-Bruker program (v 2.1, Bruker Biospin).

3 RESULTS AND DISCUSSION

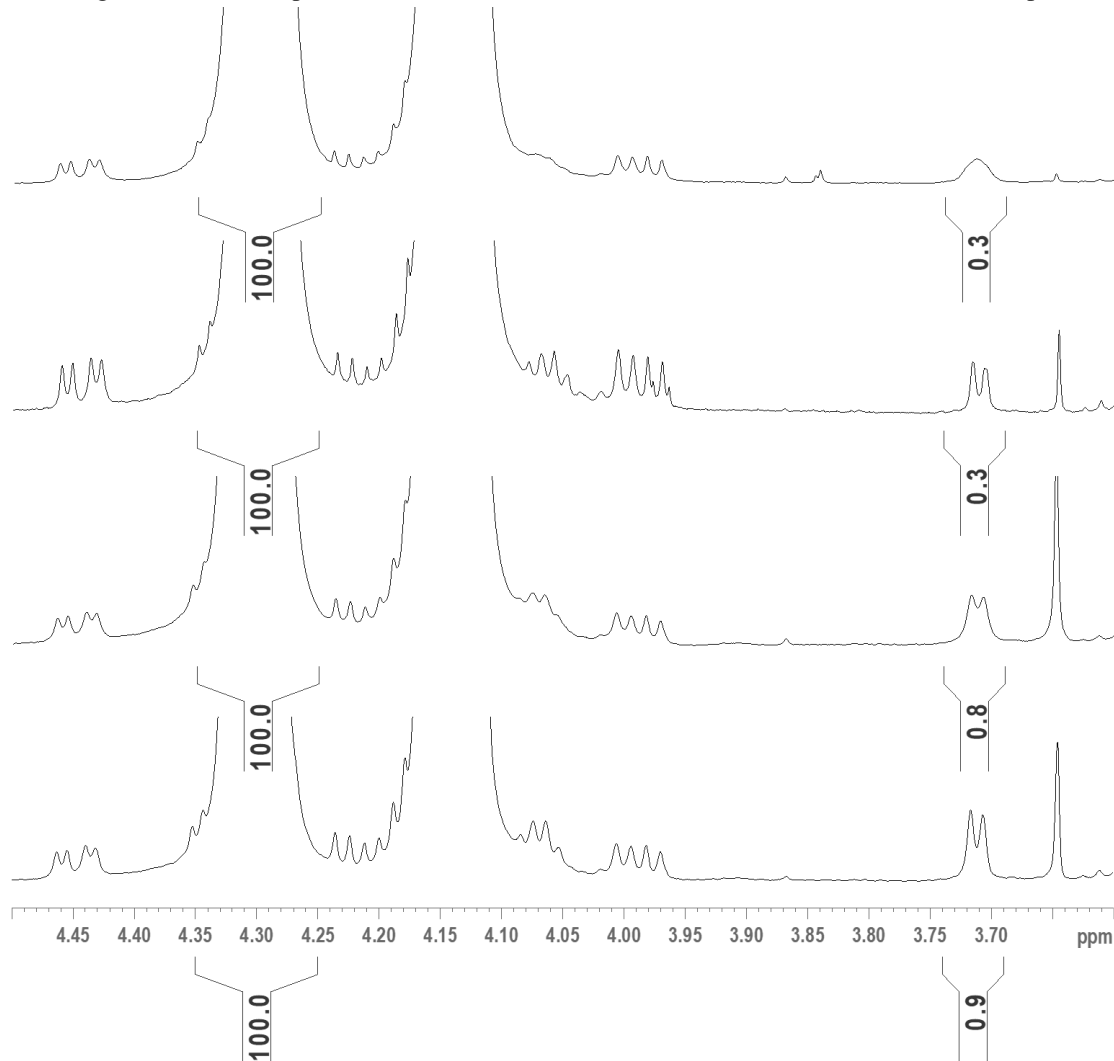
Figure 1 shows the possibility of verifying the proportion between triacylglycerides (TAG) and diacylglycerides (DAG), through the data of $^1\text{H-NMR}$, in each grease raw material, according to its origin. Thus, it can be used to carry out proportions that meet quality parameters, in addition to identifying lots that do not meet the specificities of the process or the resolutions provided for by the ANP.

Figure 1. $^1\text{H-NMR}$ spectra of cotton, soybean and suet grease raw materials with the integration of DAG and TAG signals.



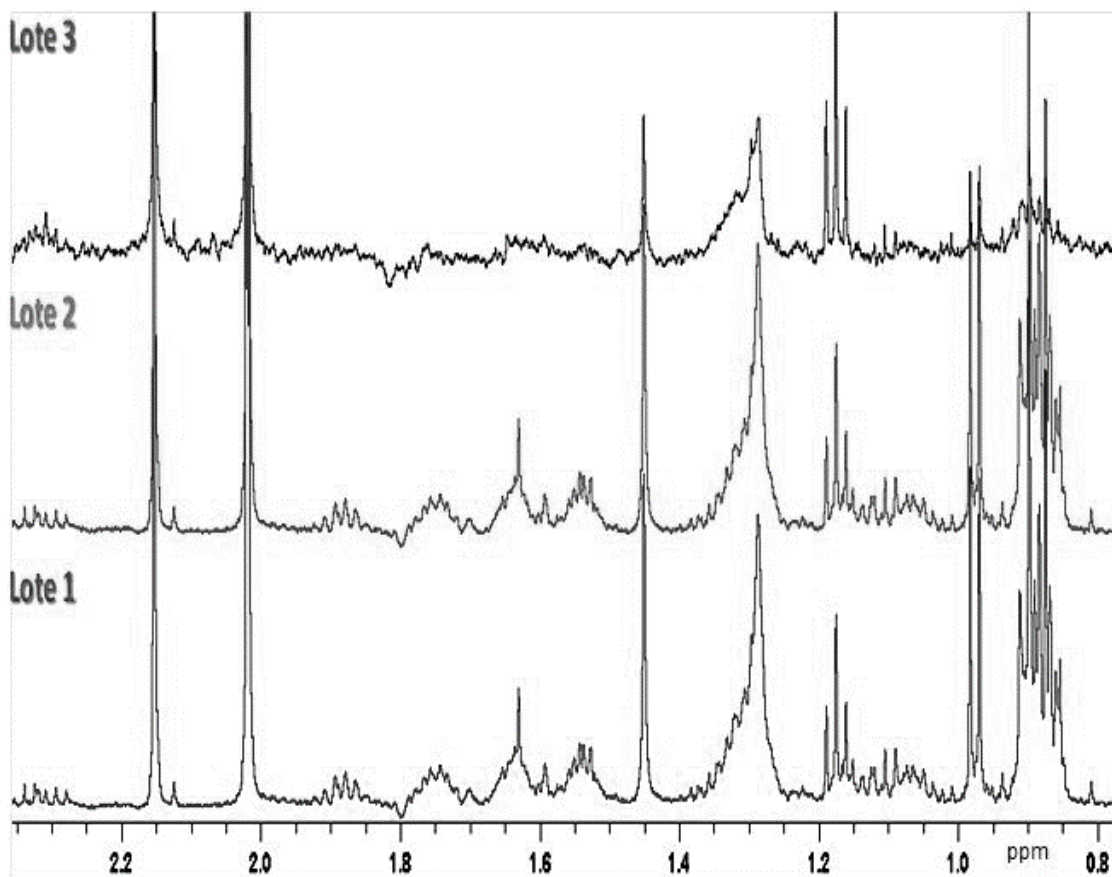
The characteristic of this work was to approach the transformations and main components involved in a semi-quantitative way, proposing to use quantitative estimates, thanks to the care that was attended to in the experiments. Thus, the values of integration of the signals are directly proportional to the concentration of the components and serve to have a dimension of how the components are formed or consumed, regardless of a concentration unit.

It is perceived that this proportion can vary a lot according to the origin of the raw material, in addition, the measurable presence of monoacylglyceride (MAG) has not been identified. Among the oils evaluated, soybean oil had the highest concentration of DAG. The Figure 2 shows the variation in this proportion, now in neutral oils, of different lots of blends between suet, soybeans and cotton. The difference reaches three times the quantity, of lot 1 in relation to lot 4.

Figure 2. $^1\text{H-NMR}$ spectra of different lots of raw materials (lots 1 to 4 from bottom to top).

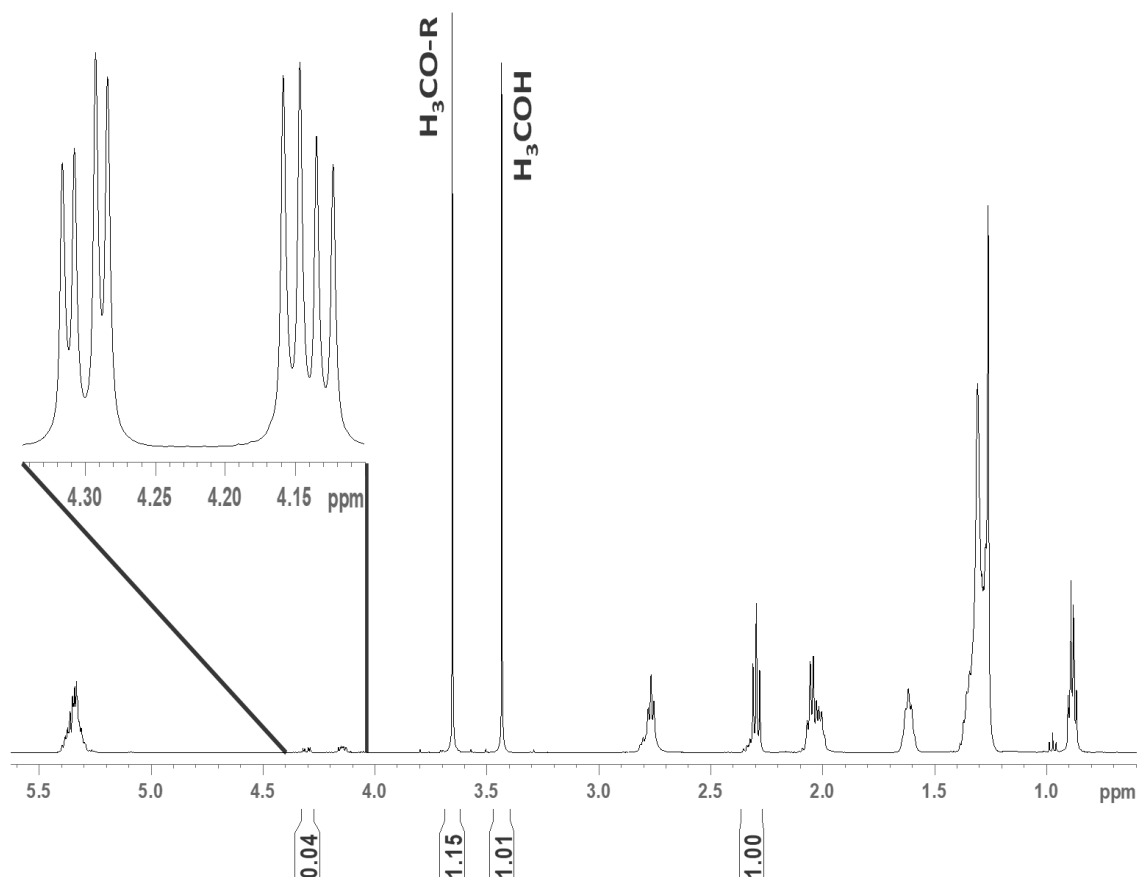
Evaluating different lots of methanol used in the industry (Figure 3), we can see the presence of impurities in the three lots evaluated, with lots 1 and 2 being in greater proportion. It was also possible to identify the presence of water in these raw materials. The biodiesel production process also generates water as a by-product, which may not be completely removed from the final bio fuel.

Figure 3. Magnification of the aliphatic region of the $^1\text{H-NMR}$ spectra of methanol alcohol lots.



In Figure 4, the signs related to the conversion to methyl esters of fatty acids and calculation of the yield of this reaction are highlighted. In this case, the reaction yield was 77.0% and also has a large amount of free methanol in the reaction medium. The excess methyl alcohol is used to ensure an increase in the yield of the biodiesel synthesis reaction.¹ Another parameter that can increase the reaction yield is the control of the quantity of the catalyst.⁴

Figure 4. $^1\text{H-NMR}$ spectra of different lots of raw material with amplification of TAG signals and identification of glycerol signals.



The identification of non-target compounds allows better planning of the synthesis of the biodiesel. Moreover, there is the disappearance of methylenic hydrogens from the glycerol group of the TAG, which suggests the species formed in the conversions. DAG and MAG are intermediates in the biodiesel transesterification reaction and may remain in the final mixture in incompletereactions. Table 1 shows the levels of acylglycerides obtained or remaining from the production process present in the obtained biodiesel. It is noticed that there are preferred MAG and DAG that are formed in greater proportion according to the lot, but only Diglyceride 2 is the major component in any of the evaluated lots.

Table 1. Content of acylglycerides in different lots of biodiesel.

Glyceride	Lot 1	Lot 2	Lot 3	Lot 4
MAG 1	1,098 %	0,074 %	0,063 %	0,206 %
MAG 2	0,475 %	0,452 %	0,485 %	0,637 %
DAG 1	0,210 %	0,114 %	0,076 %	0,166 %
DAG 2	0,442 %	0,527 %	*	0,490 %
TAG	0,225 %	----	0,024 %	0,212 %

-- Absence of the component

* Overlapping signals over component

A possibility desinent from the results is to investigate the influence of these components present in the raw material and whether they are correlated with the transesterification process, interfering in the yield of this reaction, futhermore to their interaction and reaction with the other compounds present in the mixture. In a future study, the research group will simulate reaction conditions to individually evaluate the variables and data obtained in each biofuel synthesis.

4 CONCLUSION

The $^1\text{H-NMR}$ technique shows multiple purposes and different applications in compounds present in complex mixtures, involving the analysis of target and non-target compounds. This provides a broad view of the process and safe decision making, in addition to reducing expenditures and consumable reagents. The possibility of a technique generating several responses quickly, without the need to use high-cost standards and laborious sample preparation protocols, makes the NMR technique viable, since it replaces the use of several other analytical techniques in extremely short time.

The use of modern analytical methodologies presents in universities and a partnership with the private sector can generate several possibilities for development in different areas. Mutual research collaboration can overcome industrial bottlenecks and contribute to scientific and technological advancement.

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⁶ Agência Nacional do Petróleo, Gás natural e Biocombustíveis – ANP; Disponível em: <www.anp.gov.br> Resolução Nr. 45, de 25 de ago. de **2014**.