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^{1}H-NMR Monitoring of the transesterification process of Jatropha oil

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ABSTRACT

Jatropha oil was extracted with hexane from the seeds of a shrub, *Jatropha Curcas*, in high yields, up to 40% by weight. The extracted oil was converted in a laboratory reactor to biodiesel methyl esters by transesterification with methanol using sodium hydroxide as catalyst. Analysis of Jatropha oil and the produced Jatropha biodiesel by ^{1}H nuclear magnetic resonance (^{1}H NMR) showed that Jatropha oil could be readily converted to a biodiesel product through conventional transesterification. ^{1}H NMR spectroscopy was proven to be a useful tool for monitoring the progress of transesterification reaction to convert Jatropha oil to biodiesel.

1. Introduction

Jatropha oil is receiving significant interest as a possible feedstock for alternative fuel (biodiesel) and lubricant basestock [1–4]. Biodiesel is commonly produced by the transesterification of oils with methanol catalyzed by KOH, or NaOH [5–9]. Although many studies have been conducted to investigate the fuel properties of Jatropha biodiesel [10–14], much remains to be learned.

In the current study the progress of the transesterification reaction is monitored by ^{1}H NMR analysis of the Jatropha oil and the transesterification products. In previous studies, ^{1}H NMR has been used effectively to monitor biodiesel production processes [15–18]. Neto, et al. [15] used ^{1}H NMR to quantify the ethanolysis of soybean oil. Knothe [16,17] used near infra-red and ^{1}H NMR for studying the biodiesel production process. This study involves the production of oil from the Jatropha seeds by extraction with hexane in the laboratory, reacting the raw oil with methanol in the presence of a sodium hydroxide (catalyst) to produce biodiesel. To monitor the progress and confirm the completion of the reaction, ^{1}H NMR analysis was used in comparison with results from ASTM specifications [19,20].

2. Experimental

In this study, oil was extracted from Jatropha Curcas seeds using the Soxhlet method and n-hexane as solvent. Fig. 1 shows a photograph of the dry seeds of Jatropha curcas crushed for Soxhlet extraction of the raw oil. From 120 g of crushed Jatropha seeds, up to 41% of oil (49 g) was extracted, and converted into biodiesel using the following procedure. The sample of virgin Jatropha oil was reacted with methanol and sodium hydroxide at a temperature of 55 °C for 60 min to produce fatty acid methyl ester (FAME) biodiesel and glycerol.

The reaction was conducted using the following stoichiometry, 3 mole of alcohol (methanol) reacted with one mole of triglyceride (vegetable oil) to yield 3 mole of methyl ester (methyl ester) and one mole of glycerol. To insure that the reaction does not reverse itself due to water or extra catalyst in the final biodiesel product, two (2) extra moles of methanol were added for a total a five moles

Fig. 1. Jatropha seeds.

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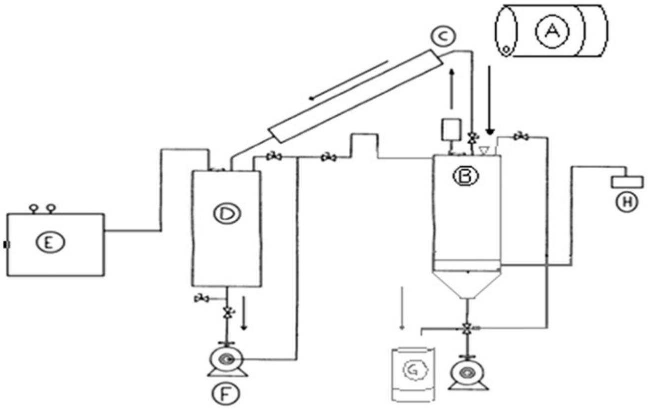

Fig. 2. Biodiesel production flowchart. A: Vegetable Oil. B: Reactor. C: Condenser. D: Methanol Recovery. E: Pressure Gage. F: Recovery Pump. G: Biodiesel + Glycerol Separator Vessel. H: Thermometer (Thermocouple).

of methanol instead of one mole. The reaction occurred in a small size (1 L) reactor equipped with a stirrer and a temperature controller that kept the temperature constant at 55 ± 1 °C throughout the reaction. The glycerol phase was separated from the biodiesel by gravity since glycerol is much denser than biodiesel, and was drawn off the bottom of the settling vessel. Once the glycerin and biodiesel phases have been separated, the excess methanol in the biodiesel phase was removed via an evaporation process. Filtration and purification was conducted via water washing to remove excess contaminants and leftover production chemicals from biodiesel. In this process water was initially sprayed over the sample of biodiesel. The two phase mixture water-biodiesel was gently agitated for 5 min and repeated 3 or 4 four times to allow a maximum of impurities to be removed as the water settles to the bottom vessel. The biodiesel production process is shown in the flowchart presented in Fig. 2. Intermediate reaction products were collected from the reactor during the process to follow the progress of the reaction using ^{1}H NMR.

^{1}H nuclear magnetic resonance analysis was performed on the different samples of biodiesel in order to study the progress of the transesterification of vegetable oil and identify the intermediates. The principle is to determine the yield of transesterification products using ^{1}H-NMR by identifying positional isomers of diglycerides (dg) and monoglycerides (mgl).

Jatropha biodiesel was produced in Fenske Laboratory at Penn State University using the small size reactor as illustrated in Fig. 2. For ^{1}H NMR studies, two samples of about 5 mL each were taken from the reactor during the processing. The NMR samples were prepared with deuterated chloroform at a ratio of 1:1 by volume and. analyzed in 5 mm ^{1}H-NMR tubes. The chemical shifts were referred indirectly to TMS signal (δ = 0.0 ppm) by assigning the residual signal from mono-protonated CHD_2Cl_3 to 7.26 ppm. ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer operating at 400.13 MHz.

Nuclear Magnetic Resonance allows the identification of individual atoms in a given molecule or functional group. Much like using infrared spectroscopy to identify functional groups, analysis of a ^{1}H-NMR spectrum reveals the atomic environment (for example, methyl proton), and how many of these atoms exist within the sample. Transesterification of vegetable oil is achieved when an alcohol reacts with triglyceride. During the reaction, the triglyceride molecules are broken into two products, FAME and glycerol, as shown in Fig. 6. The glycerol is insoluble in the FAME phase, and separates into the aqueous phase.

A completed transesterification reaction should yield only methyl esters and glycerol. The reaction is reversible and due to many factors, the transesterification process may not reach total completion. The incomplete transesterification would yield monoglycerides, diglycerides, or other related intermediate products and any unreacted triglyceride. Mono and diglycerides resulting from an incomplete reaction are found in the NMR spectra as different isomers depending on the position of the protons in the glyceride. Pure biodiesel (FAME) should not contain any of the three glycerol protons, since the glycerol enters the aqueous phase.

A standard gas chromatography method, ASTM D6751 [21] was used to analyze the biodiesel samples for glycerol and the glycerides, including triglyceride, diglycerides and monoglycerides.

3. Results and discussion

To monitor biodiesel production using ^{1}H NMR, first, the spectrum of Jatropha vegetable oil, which consists essentially of triglycerides, was generated as a base line prior to the reaction. The spectrum showed the typical triglyceride profile as reported in the literature with all the associated compounds as indicated in Fig. 3, [22–24]. The ***a*** and ***b*** labels indicate the protons attached to triglyceride carbons as shown in Fig. 6.

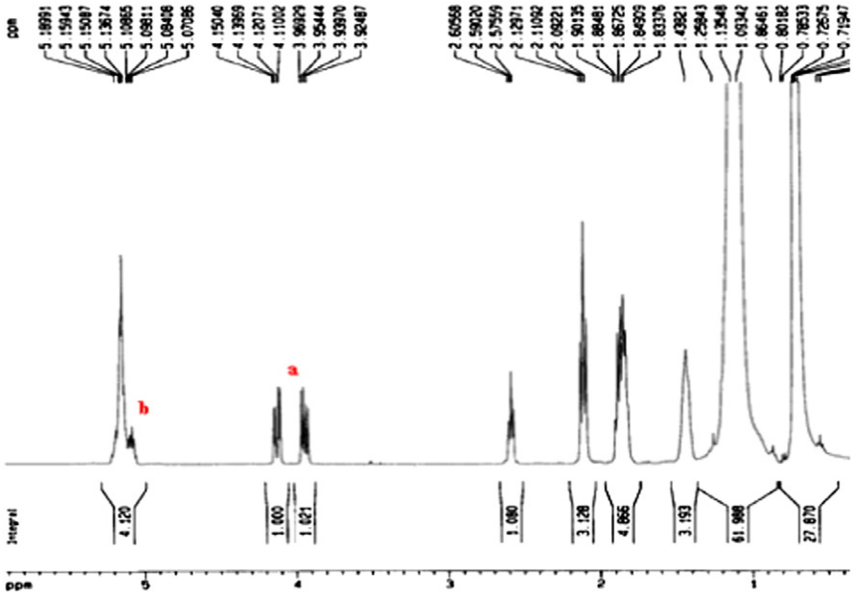

Fig. 3. ^{1}H NMR Spectrum of Jatropha oil.

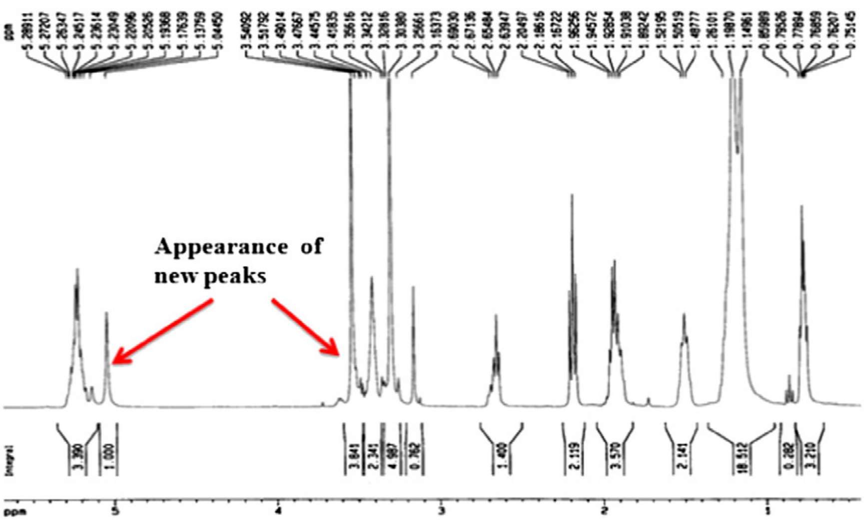

Fig. 4. ^{1}H NMR of intermediate products from transesterification of Jatropha Oil.

Intermediate reaction products are crucial in the process of monitoring the formation of transesterification products. They provide key information, which, if deciphered in the correct manner, would eventually lead to an accurate identification of the reaction products at a specific time. The transesterification reaction removes the glycerol moiety, resulting in the biodiesel product. Intermediate products are the result of incomplete reactions of vegetable oil and can be monitored using ^{1}H NMR spectroscopy at different stages of the biodiesel production process, as illustrated in Fig. 4. This sample was taken from the reactor after 40 min of reaction time.

The spectrum in Fig. 4 characterizes an incomplete transesterification of the Jatropha oil. Several series of spectra could be generated from the analysis of intermediate reaction products to determine the progress of the transesterification reaction towards complete conversion.

The final and most important step in monitoring a transesterification reaction is to analyze the final biodiesel sample (also known as the methyl ester phase). After 60 min of reaction, the spectrum of the final Jatropha product is shown in Fig. 5 and only trace quantities of **a** and **b** are observable. As shown in Fig. 5, the spectrum of the sample is similar to a triglyceride, but missing the peaks from the hydrogen atoms of glycerol. Knothe in a similar task, focused on quantifying the strong singlet peak of the resulting methyl esters to monitor the transesterification of a vegetable oil to methyl esters, [16].

In order to confirm the completion of the reaction as suggested by the proton NMR analysis, a GC analysis was used to quantify the products according to the standard method ASTM D-6751 [21]. The results obtained are shown in Table 1.

Table 1 shows that the concentration of triglyceride and glycerol is equal, or very close, to zero in the final Jatropha biodiesel sample. This is in agreement with the ^{1}H NMR spectroscopy results indicating that at least 99.7% of Jatropha oil was transesterified to B100.

Diglyceride and monoglyceride are similar molecules to triglyceride but missing one and two fatty acid chains, respectively. They can cause problems in a diesel engine when they are more prevalent as a contaminant in biodiesel. The bound glyceride is derived from the ratios of monoglyceride, diglyceride and triglyceride in a sample. The bound glycerin added to the free glycerin turns out to be very low and determines the total glycerin free and bound. The ASTM standard requires 96% or 97% transesterification be reached and still meet the ASTM total glycerin specification of only 0.24 percent. Assignment of ***a*** protons was based on the observation that they integrate to 4 protons and appear further upfield (i.e. lower chemical shift) than the ***b*** proton which integrates to 1 proton at 5.0 ppm. The yields of the reaction can thus be identified using ^{1}H NMR and the appearance of the new proton signals. Several modifications in amplitudes and positions of ***a*** and ***b*** could occur throughout the reaction in addition to the appearance of

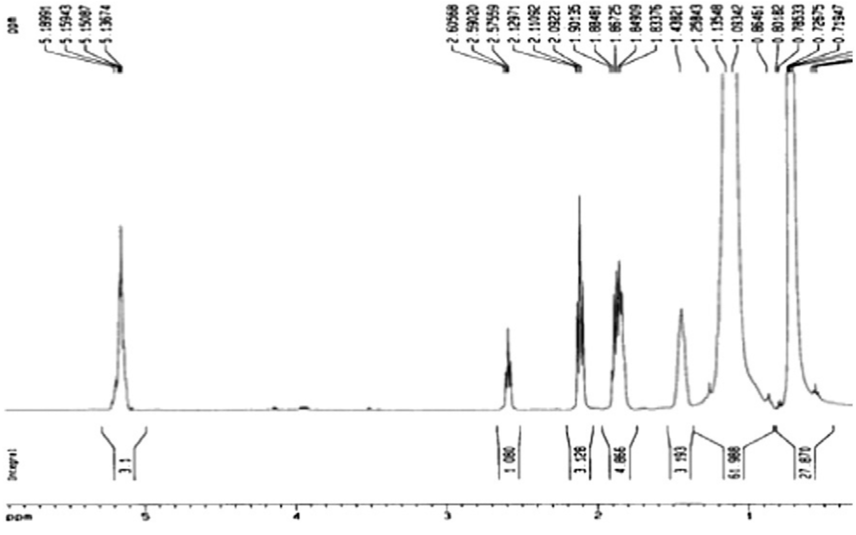

Fig. 5. ^{1}H NMR spectrum of Jatropha biodiesel.

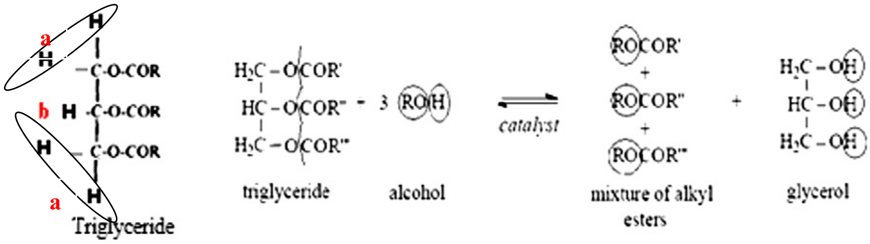

Fig. 6. The labeling of hydrogen atoms in triglyceride and transesterification of triglycerides into alkyl esters and glycerol.

new peaks as shown in Fig. 4. If at a random stage of the reaction, a sample is collected and the spectrum of any of the three hydrogen atoms attached to the glycerol carbon are observable and/or any new peaks are observable, it indicates that the collected sample still contains traces of glycerides, and that the transesterification reaction has not reached completion. These observations could be used to monitor the transesterification reaction of vegetable oil using ^{1}H NMR at different stages. A typical ^{1}H NMR of biodiesel should not feature any of the hydrogen atoms attached to glycerol because pure biodiesel does not contain glycerol. Identification of hydrogen atom sin a biodiesel sample in any case would imply that the transesterification reaction was incomplete.

In summary, the path of transesterification of vegetable oils can be monitored by using NMR to follow the fate of hydrogen attached to the glycerol carbons. ^{1}H-NMR reveals the wide range of intermediate products between the initial vegetable oil and the final yields (biodiesel). ^{1}H-NMR is well established as a useful technique for a variety of quantitative and qualitative analysis of vegetable oils and their corresponding methyl esters [25–26]. Differentiation between vegetable oils can also be achieved via ^{1}H-NMR even without quantification of any components but only by visual inspection of the peak differences in NMR spectra. Similarly to Guillén's approach, the current study shows that differentiation between Jatropha oil, its corresponding methyl esters and intermediate reaction products can be achieved via visual inspection of the differences in NMR spectra a various stages of the transesterification process, [27].

4. Conclusions

The transesterification of vegetable oil yielded two principal phases; a methyl ester and a glycerol phase. The intermediate phase in Fig. 4, confirmed that the reaction was incomplete at the time the sample was collected. The ^{1}H-NMR spectrum showed peaks attributed to ***a*** and ***b*** protons attached to the glycerol carbons (Fig. 3). These peaks determine the fate of transesterification of vegetable oil as their appearance in the final biodiesel product determines whether or not the reaction has gone to completion (Fig. 5) or not as (Fig. 4). The spectrum of Jatropha biodiesel revealed that olefinic hydrogen were left unchanged by the transesterification process of Jatropha oil. Results obtained in this study allow us to conclude that:

1- Glycerol proton identification principle used in this study clearly demonstrated that ^{1}H-NMR could be applied to biodiesel production to monitor and quantify the transesterification reaction of vegetable oil.
2- Experimental results show that the reaction readily goes to completion at 55 °C in the presence of NaOH catalyst.
3- The results of ASTM Method D6751 are in agreement with the NMR spectroscopy analysis and suggest that the transesterification of Jatropha reached completion, with less than 2% of undesired product such as mono and diglycerides in the final biodiesel products.

Table 1
Analysis of final Jatropha biodiesel Sample by Gas Chromatogram, ASTM D 6751.

ASTM Spec. 6751	Jatropha B100
Glycerol	0.028%
Monoglycerides	0.094%
Diglycerides	0.125%
Triglycerides	0%
Biodiesel Esters	99.753%

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