Synthesis and Characterization of Fatty Acid Furfuryl Ester Mixtures: Biodiesel from Furfuryl Alcohol

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Abstract

The synthesis of biodiesel fuels from triacylglycerols and common alcohols such as methanol and ethanol has been reported using a variety of methods and catalysts. As part of an effort to explore the properties of biodiesel fuels made from novel feedstocks, furfuryl alcohol is used as the alcohol component in biodiesel synthesis. Commercially-available cooking oils were transesterified using furfuryl alcohol and K_2CO_3 in the presence of a room-temperature ionic liquid catalyst. The resulting product is a fatty acid furfuryl ester (FAFurE) mixture. After purification, the FAFurE product mixtures were analyzed using ^{1}H-NMR spectroscopy. Percentage conversion values were calculated using integration data from the NMR spectra. Percent conversion values ranged from 19 to 75%. The wide range in percent conversion has been attributed to steric interactions between the bulky nucleophile and polyunsaturated fatty acid chains in the oils used. This work represents a proof-of-concept that furfuryl alcohol can serve as an alternative alcohol source for biodiesel fuels or biodiesel additives.

Keywords: Biodiesel, Furfuryl alcohol, Transesterification, 1H-NMR

1. Introduction

The search for an alternative to petroleum-based diesel fuels has inspired much research work in which biodiesel mixtures have been made via transesterification of methanol, ethanol, or other low molecular-weight alcohols using a wide array of triacylglycerol (TAG) sources (Knothe et al., 1997), (Knothe & Van Gerpen, 2005), (Ma & Hanna, 1999). This transesterification process can be done under a variety of conditions including: acid-catalysis (Ataya et al., 2007), base-catalysis (De Oliveira et al., 2005), or enzymatic-catalysis (Lozano et al., 2016). In addition to conventional heat sources, the transesterification reaction can also be performed using microwave heating (Leadbeater & Stencel, 2006). In an effort to explore the properties of biodiesel mixtures made using less-common alcohol sources, furfuryl alcohol (FurOH) was considered as an attractive potential alcohol source.

Furfuryl alcohol is a by-product from biomass such as sugar cane, bagasse, and corn cobs. Surprisingly, furfuryl alcohol is relatively reactive even though it contains an aromatic furanyl moiety. In particular, furfuryl alcohol readily polymerizes in the presence of acids (both Brønsted-Lowry acids and Lewis acids) and strong bases (Choura et al., 1996). The reactivity of furfuryl alcohol has been exploited in polymerization processes for the production of resins, adhesives, and other products (Li et al., 2015). One common use for polymerized furfuryl alcohol is in the production of refractory materials for metal casting (Stancliffe, 2006). In addition, furfuryl alcohol itself is surprisingly acidic; the hydroxylic proton of furfuryl alcohol has been reported to have a pK_a value of +9.55 (Serjeant & Dempsey, 1979). Several previous works have demonstrated that the milder base K_2CO_3 can successfully be used in base-catalyzed synthesis of TAG transesterification (Behina et al., 2011). Moreover, there is some literature precedent in the use of K_2CO_3 to promote transesterification using FurOH with smaller esters (e.g. ethyl acetate and methyl benzoate) (Caulier et al., 1985). In addition, direct esterification of FurOH with palmitic acid under enzyme-catalyzed conditions has been reported (Mistri et al., 2010). More recently, experimental and computational work has been published in which the feasibility of furfuryl esters as potential biofuels was investigated (Antón et al., 2017).

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Additionally, a report of clay-catalyzed etherification of furfuryl alcohol for potential use as biofuels has been published recently (Natsir et al., 2018). Moreover, the work of Lăcătuş et al. has shown that 2,5-bis-(hydroxymethyl) furan can be esterified with free fatty acids under enzyme-catalyzed conditions. The resulting furanyl 2,5-diester species demonstrated significant increases in desirable biofuel properties (e.g. gross calorific value, flash point, and cetane number) when added to commercially-available biodiesel fuel(Lăcătuş et al., 2018). Based on these precedents, the objective of this study was to synthesize FAFurEs via transesterification of TAGs using K_2CO_3 and FurOH.

The use of ^{1}H-NMR spectroscopy to quantify percent conversion for transesterified product mixtures in biodiesel synthesis has been reported in the literature (Knothe, 2001), (Gelbard et al., 1995). The ^{1}H-NMR chemical shift values for the furfuroxy methylene protons of furfuryl alcohol (Figure 1a) have been reported in the literature (Dieskau et al., 2011) as have those for the furfuroxy methylene protons in smaller furfuryl esters (e.g. furfuryl acetate) (Figure 1b) (Kadam et al., 2009).
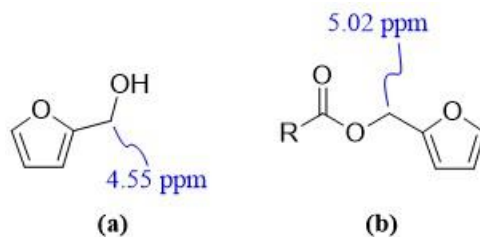

Figure 1. ^{1}H-NMR chemical shift values for the furfuroxy methylene protons of furfuryl alcohol (a) and for the furfuroxy methylene protons of a furfuryl ester (b).

2. Materials and Methods

2.1. Materials

All oils used (canola oil, peanut oil, olive oil, soybean oil, corn oil, and sunflower oil) were purchased commercially at a local grocery store. Furfuryl alcohol, THF, 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$, $CDCl_3$, and TMS were purchased from Sigma-Aldrich. Potassium carbonate was purchased from Fischer Scientific. Alumina gel (chromatography grade) was purchased from Flinn Scientific. A Jeol ECS-400 FT-NMR spectrometer was used for all NMR analyses. NMR data were processed using the SpinWorks freeware program (version 4.2.8), published by the Department of Chemistry of the University of Manitoba, Manitoba, Canada[3]. All NMR spectra were recorded using $CDCl_3$ as solvent with TMS as an internal chemical shift standard.

2.2. Experimental Procedure

A 250-mL round bottom flask was charged with cooking oil, furfuryl alcohol, and K_2CO_3 in a 12:1:1 molar ratio. $[BMIM]^+[BF_4]^-$ (5-7 mol % with respect to K_2CO_3) was added. THF (50-60 mL) was then added so that the flask was approximately halfway full. The mixture was heated at reflux for 3-8 h. After heating, the mixture was allowed to cool to room temperature. Excess base present in the system was neutralized using commercially-purchased white vinegar. The mixture was then washed with aqueous NaCl, followed by washing with deionized H_2O. The organic phase was then separated and dried using anhydrous $MgSO_4$. The organic mixture was then filtered into a 150-mL Erlenmeyer flask. Approximately 1 g of alumina was added to the organic product mixture, which was then stirred for 10 min. The product mixture was then vacuum filtered and stored in a capped vial. A small (~ 0.5 mL) portion of the product mixture was transferred to a 5-mm NMR tube, $CDCl_3$ was added, and the mixture was analyzed using NMR spectroscopy.

2.3. NMR Data Analysis

Percent conversion for the FAFurE products was calculated using ^{1}H-NMR data via a modification of previously-reported methods (Knothe, 2001), (Gelbard et al., 1995). For fatty acid methyl ester mixtures, the percent conversion can be calculated using Equation 1,

$$\% \text{ conversion} = \frac{2\, I_{ME}}{3\, I_{\alpha-CH_2}} \times 100 \qquad \text{(Eq. 1)}$$

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[3]https://home.cc.umanitoba.ca/~wolowiec/spinworks/

Where I_{ME} the integration value for the methoxy peak is, typically observed at 3.6 ppm, and $I_{\alpha-CH_2}$ is the integration value for the α-methylene protons of the fatty acid chain at 2.3 ppm. The coefficients of 3 and 2 in Equation 1 are normalizing factors that take into account the fact that there are three protons giving rise to the methoxy signal at 3.6 ppm, and two α-methylene protons giving rise to the signal at 2.3 ppm. Integration of the α-methylene signal takes into account the presence of any and all fatty acid chains in the sample, whether the fatty acid chain is a part of a transesterified product, part of an unreacted triacylglycerol, or is part of a diacylglycerolor monoacylglycerol species present in the system.

This NMR-based quantification method was modified for analysis of FAFurEs by using the integration value for the furfuroxy ester methylene signal at 5.02 ppm (I_{Fur}) along with the integration value for the signal for the α-methylene protons of the fatty acid chain at 2.3 ppm ($I_{\alpha-CH_2}$). With these factors in mind, Equation 1 can then be used in a modified form to give Equation 2a,

$$\% \text{ conversion} = \frac{2\,I_{Fur}}{2\,I_{\alpha-CH_2}} \times 100 \qquad \text{(Eq. 2a)}$$

where the coefficients of 2 are normalizing factors for I_{Fur} and for $I_{\alpha-CH_2}$ due to the fact that each group consists of two protons. Since both coefficients are identical, Equation 2a simplifies to give Equation 2b.

$$\% \text{ conversion} = \frac{I_{Fur}}{I_{\alpha-CH_2}} \times 100 \qquad \text{(Eq. 2b)}$$

3. Results and Discussion

3.1. Results

In this work, the first synthesis and spectroscopic characterization of fatty acid furfuryl ester (FAFurE) mixtures using FurOH and a variety of common TAGs are reported, as shown in Figure 2.
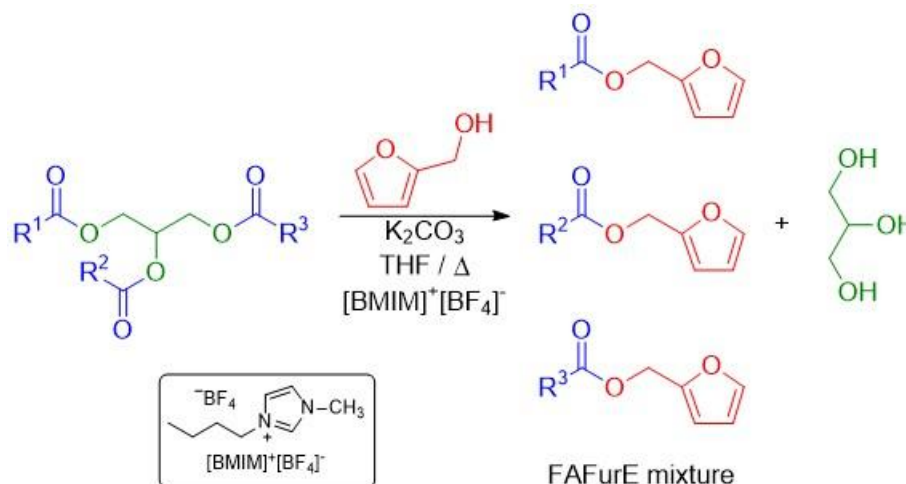

Figure 2. K₂CO₃-promoted transesterification of a triacylglycerol with furfuryl alcohol in refluxing THF with [BMIM]⁺[BF₄]⁻ (5-7 mol % with respect to K₂CO₃).

Based on previous research, canola oil was selected to be used as a test TAG system for transesterification with FurOH. Initial attempts at FAFurE synthesis using canola oil, K₂CO₃, THF, and conventional heating produced very little, if any, detectable FAFurE product. The initial difficulties were attributed to the low solubility of solid K₂CO₃ in the mixture of canola oil and furfuryl alcohol. In an effort to increase the solubility of K₂CO₃ in the reaction mixture, THF was added as a co-solvent. NMR data indicated that these attempts also yielded only small amounts of FAFurE product. Although the addition of THF did allow the reaction to be performed at a lower temperature (~66 ºC), it did not appear that the THF increased the solubility of the K₂CO₃ enough to facilitate transesterification.

Literature reports suggested that the use of a room temperature ionic liquid (RTIL) might enhance the solubility of the K_2CO_3 in the organic phase and facilitate transesterification (Hallett & Welton, 2011). Based on this work, the RTIL 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]^+[BF_4]^-$) was used.

The addition of small amounts of $[BMIM]^+[BF_4]^-$ (approximately 5-7 mol % with respect to the amount of K_2CO_3 used) caused significant enhancement of the transesterification reaction. The benefit of adding the $[BMIM]^+[BF_4]^-$ most likely arises from its ability to make the carbonate ion much more soluble in the otherwise low-polarity reaction mixture. The ^{1}H-NMR spectra of product mixtures now showed much larger amounts of the FAFurE product. However, the spectra also showed that a considerable amount of unreacted FurOH remained in the product mixture, as indicated by the presence of a signal for the furfuroxy methylene protons at 4.55 ppm. This problem was a particularly vexing one, as most methods of removing undesirable materials from reaction mixtures often involve the use of acids or bases. The use of such reagents could induce polymerization of the unreacted FurOH and greatly complicate product isolation and analysis. The problem of unreacted FurOH in the product mixture was finally solved by treating the product mixture with alumina (~1 g of alumina per sample of product mixture) in order to remove unreacted FurOH and stirring for 10 min. The alumina was then easily removed from the product using vacuum filtration. The alumina particles most likely adsorbed the unreacted FurOH on their surface. After the product mixture was treated with the alumina, the ^{1}H-NMR spectra of product mixtures showed a singlet for the furfuroxy ester methylene protons at 5.02 ppm. The intensity of the signal for the furfuroxy methylene protons of unreacted FurOH at 4.55 ppm was greatly diminished or not present at all. A portion of the ^{1}H-NMR spectrum from the FAFurE product mixture (after alumina treatment) resulting from reaction of furfuryl alcohol with canola oil, K_2CO_3, THF, and $[BMIM]^+[BF_4]^-$ is shown in Figure 3. The furfuroxy protons of the FAFurE product (Figure 3a), the furfuroxy protons of the furfuryl alcohol starting material (Figure 3b), and the α-methylene protons of the fatty acid groups (Figure 3c) in the sample are highlighted.
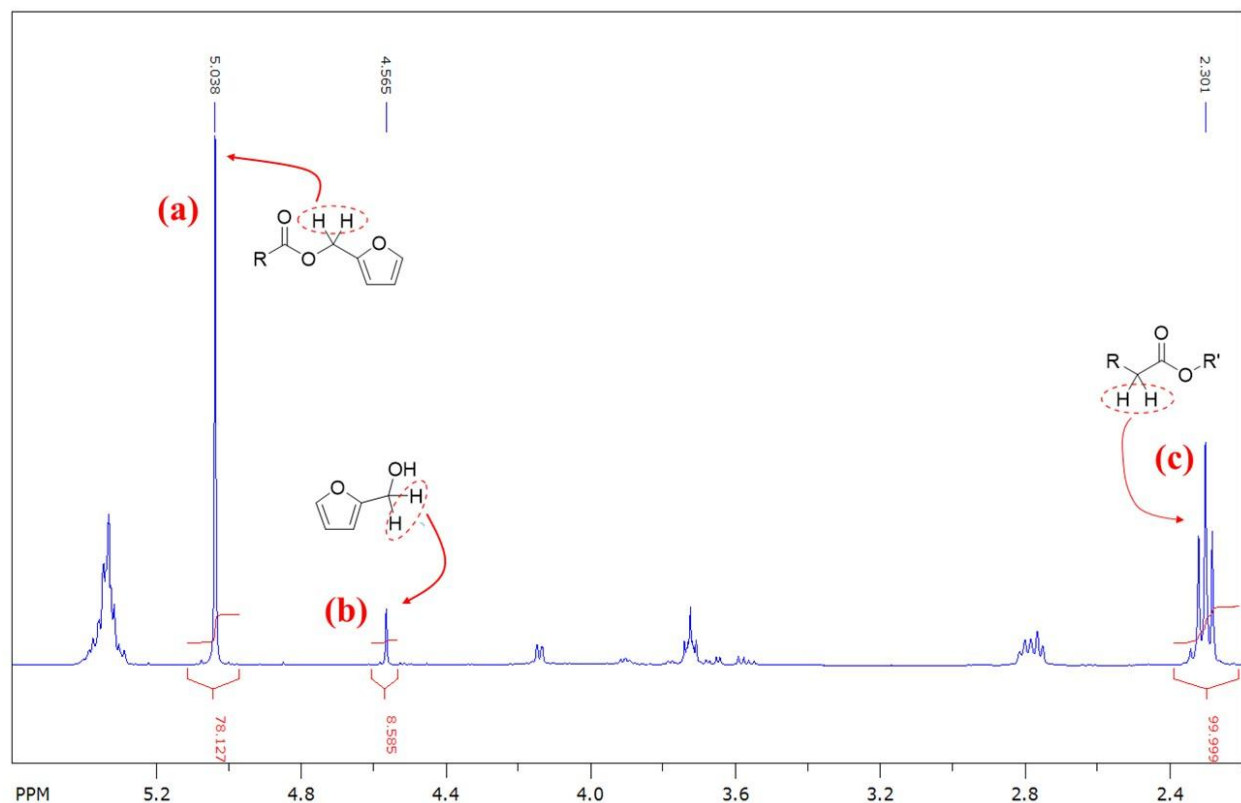

Figure 3. A portion of the ^{1}H-NMR spectrum (2.2-5.6 ppm region) of a FAFurE product mixture from transesterification of canola oil with furfuryl alcohol. The singlet for the furfuroxy methylene protons of the FAFurE product is seen at 5.04 ppm (a), the singlet for the furfuroxy methylene protons of unreacted furfuryl alcohol is seen at 4.57 ppm (b), and the triplet for the α-methylene protons of the fatty acid chain is seen at 2.30 ppm (c).

3.2. Discussion

Once the problem of removal of unreacted FurOH had been solved, other common TAG sources were reacted and purified using the same protocol. Percent conversions for transesterification of the oils used are listed in Table 1.

Table 1. Oils used and percent conversion values for FAFurE synthesis.
Oils were purchased commercially. Percent conversion values were calculated from integration data from the ^{1}H-NMR spectra of FAFurE product mixtures.

Oil	Percent Conversion
olive	75.7
peanut	69.9
canola	63.3
corn	53.1
soybean	49.7
sunflower	19.3

The percent conversion values calculated from the NMR spectra are interesting. Olive, peanut, and canola oils showed good conversion (63-75 %) to the FAFurE product. Corn, soybean, and sunflower oils, on the other hand, gave moderate to poor conversion (19-53 %) to the FAFurE product. The range of percent conversions led to the question, "Why did some oils work well when others did not?" The composition of the oils used, in particular, the nature of the fatty acid groups present in the various oils was examined more closely. The presence of larger amounts of polyunsaturated fatty acid (PUFA) groups appears to have affected the results. Oils containing a relatively low amount of PUFAs (e.g. olive oil, canola oil, and peanut oil) gave good percent conversion to FAFurE products. On the other hand, oils with higher amounts of PUFAs (e.g. corn oil, soybean oil, and sunflower oil) gave moderate to poor percent conversions to FAFurE products. The PUFA content (USDA Food Composition Databases, 2018) for the oils used in this study is listed in Figure 4 for comparison. Figure 4 shows that there is an inverse relationship between percent conversion and total PUFA content.

Oil	Total PUFA Content[a]
olive	10.5
peanut	32.0
canola	28.1
corn	54.7
soybean	57.7
sunflower	65.7

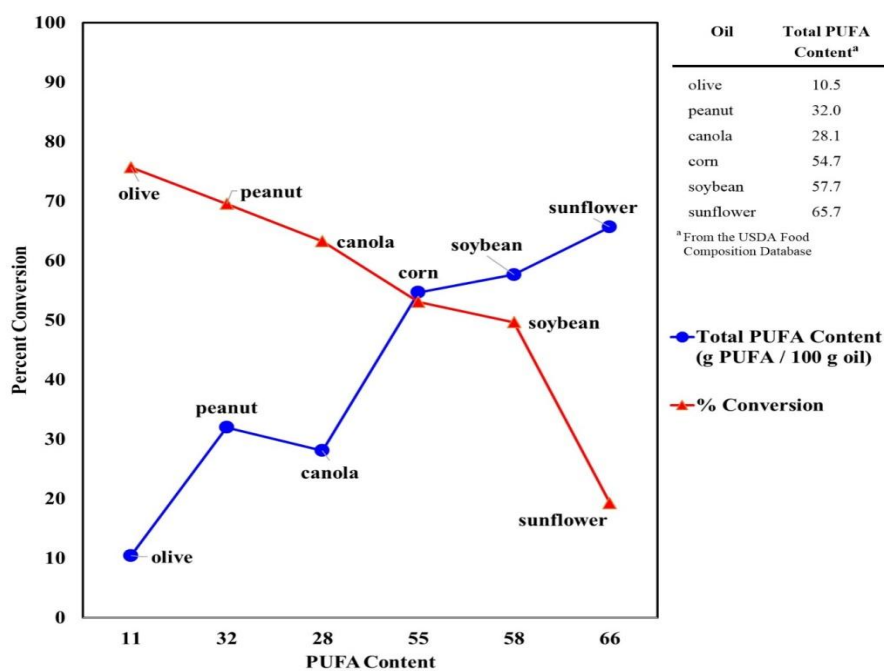[a] From the USDA Food Composition Database

Figure 4. A plot of percent conversion values vs. total PUFA content for the cooking oils used for FAFurE transesterification. Percent conversion data are taken from Table 1. Total PUFA content values are taken from the USDA Food Composition Database.

The reason for this negative correlation might be attributable to steric effects. The active nucleophile in the transesterification reaction is the furfuroxide anion (FurO⁻, the conjugate base of FurOH). When compared to the active nucleophilic species used in typical biodiesel transesterification reactions, e.g. methoxide ion or ethoxide ion, the furfuroxide anion is much larger and much bulkier. The rate of transesterification reactions has been demonstrated to be sensitive to steric effects in the nucleophile (Otera, 2013). The overall rate-determining step in synthesis of biodiesel via base-catalyzed transesterification has been shown to be the conversion of the triacylglycerol into the diacylglycerol (Aransiola et al., 2013). The presence of a large number of PUFA chains in the triacylglycerol could inhibit the approach of the furfuroxide anion when attacking the acyl carbon of the triacylglycerol. This would decrease the rate of reaction and result in diminished percent conversion for the oils having a high PUFA content.

4. Conclusions

This work represents a proof-of-concept that furfuryl alcohol can indeed be considered as a possible alternative alcohol source for the synthesis of biodiesel fuels or biodiesel additives. FAFurE mixtures from a variety of commonly-available cooking oils were successfully synthesized in moderate to good yields using the methodology described above. In addition to refinement and improvement of the reaction and purification protocols,more extensive characterization of the FAFurE product mixtures will be carried out in the future. It will be interesting to see how the properties (e.g. combustion energy, viscosity, cloud point, pour point, etc.) of the FAFurE mixtures compare to those of biodiesel fuels originating from methanol or ethanol. In addition, the scope of oils used will be expanded. In light of the apparent negative correlation between percent conversion and PUFA content, the effects of using oils having a low PUFA content (e.g. coconut oil, palm oil, and ghee) as well as other oils with a high PUFA content (e.g. grapeseed, walnut, and flaxseed oils) will be studied.

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Conflict of Interest: The authors declare that they have no conflict of interest.

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