



## Optimization of cotton seed biodiesel quality (critical properties) through modification of its FAME composition by highly selective homogeneous hydrogenation

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### ABSTRACT

The catalytic (homogeneous) hydrogenation of biodiesel's polyunsaturated fatty acid methyl esters (FAME), synthesized by transesterification of vegetable (cotton seed) oil, selectively to monounsaturated FAME, could upgrade the final quality of biodiesel. The final fuel can be optimized to have a higher cetane number and improved oxidative stability. The low-temperature performance after hydrogenation (CFPP) might be worst, but this, could be further improved through selective wintering and/or blending. The homogeneous hydrogenation of FAMEs of cotton seed biodiesel was catalyzed by the catalyst precursor  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and STPP-TiOA. Four groups of hydrogenation experiments were carried out regarding the effects of pressure, temperature, reaction time and molecular ratio C=C/Rh. Partial hydrogenation of cotton seed FAMEs took place under mild conditions of pressure and temperature and high catalytic activities were observed in very short reaction times, and for high molecular ratios C=C/Rh.

Biodiesel's quality optimization studies, based on existing empirical models of biodiesel properties, were carried out in order to identify optimum FAME compositions and those hydrogenation conditions that could possibly supply them.

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### 1. Introduction

Biodiesel is an alternative diesel fuel made from biological sources, primarily vegetable oils, but also to a lesser extent, frying oils and animal fats. It is produced by the homogenous catalytic transesterification or alcoholysis reaction (usually methanolysis) reaction, the catalyst being either a base or an acid. In alkali (base) catalysis, which is a much more rapid process and thus employed more often, 1 mol of triglyceride, the main constituent of vegetable oils, reacts with three moles of an alcohol (usually methanol) with the presence of sodium or potassium alkoxides acting as catalysts. The produced biodiesel as such, it is mainly consisting of fatty acid methyl esters (FAME) of vegetable oils and it is a renewable, biodegradable, safe (cause of its relatively high flash point), non-toxic, low in sulfur fuel and more importantly it has a negative  $\text{CO}_2$  balance and a low emissions profile (emits less  $\text{CO}$ , hydrocarbons, particulates and smoke). In addition, it is also presents better lubricity characteristics compared with petroleum diesel (Dermibas, 2005; Huber et al., 2006; Knothe, 2005, 2006; Ma and Hanna, 1999).

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In the transport sector it can be used as blended with conventional diesel fuel or in pure methyl esters form. However, biodiesel is still faced with technical challenges, such as its oxidative stability, low-temperature performance and nitrogen oxides ( $\text{NO}_x$ ) emissions (Imahara et al., 2006; Knothe, 2005, 2006; McCormick et al., 2001).

It is evident that biodiesel's final quality, meaning all its critical properties, initially depends on the fatty acid composition of its raw materials (vegetable oils, fats, etc.). However, it is the produced methyl esters qualitative and quantitative composition in biodiesel that virtually defines its properties and its quality in the end. Subsequently, the properties of the various fatty acid methyl esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester. Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn, by the structural features of the various fatty esters are cetane number and ultimately exhaust emissions, cold flow performance, oxidative stability, heat of combustion, viscosity, and lubricity (Knothe, 2005). The strong adverse effects of the degree of saturation of fatty acid methyl esters, on a number of biodiesel quality

properties and particularly those related with oxidative stability and cold flow behavior has been extensively researched (Bouaid et al., 2009; Falk and Meyer-Pittroff, 2004; Knothe, 2005; Ramos et al., 2009). In addition, there are vegetable oils that due to their highly unsaturated content, their FAMES mixture cannot meet basic biodiesel specifications such as iodine value (IV), cetane number (CN) and oxidative stability (OS) as they defined in European standards EN14214 and EN14213. It has been suggested but not quantified, that the selective (partial) hydrogenation of polyunsaturated FAMES to monounsaturated compounds (Fig. 1) may provide substantial solutions to these problems (Bouriazos et al., 2008; Koutsoumba, 2008; Lazaridou, 2008; Moser et al., 2007).

Recently, we reported our investigations for the partial hydrogenation of polyunsaturated methyl esters of sunflower oil (Nikolaou et al., 2009), selectively to monounsaturated fatty esters catalyzed by rhodium sulfonated triphenylphosphite complexes, Rh/STTP, in conventional organic media in order to improve the quality of biodiesel in terms of increased oxidative stability, reduced IV, higher cetane numbers and lower NO<sub>x</sub> emissions. The questions raised then were how much have been affected the critical properties of biodiesel after its partial hydrogenation, which could be an optimum FAME composition and finally at what partial hydrogenation conditions this could be obtained? So, this work mainly intends, among others, to give some answers to these questions.

## 2. Methods

### 2.1. Materials

Refined cotton seed oil and purchased from “SOYA HELLAS” factory was used without any further purification. Hydrogen 5.0 N purchased from the company “Aeroskopio Hellas” was used, without further purification, in the hydrogenation reactions. N<sub>2</sub>, Ar, Zero Air, and He 5.0 N from “Aeroskopio Hellas” also were used. RhCl<sub>3</sub>·3H<sub>2</sub>O was purchased from “Acros Organics” and used as catalyst precursor. Methanol extra dry 99.8%, with over molecular sieves (water < 50 ppm), was used as a solvent due to the highest solubility of H<sub>2</sub> in it (Linke and Seidell, 1958), a property of paramount importance in all types of hydrogenation reactions. Selective (partial) hydrogenation of cotton seed biodiesel FAMES reported herein involved the use of a homogeneous Rh catalyst system modified with triisooctylammonium salt of mono-, di- and tri-sulfonated triphenylphosphite (*n*STPP-TiOA) which had been prepared in the Industrial Chemistry Laboratory, Dept. of Chemistry, UOA (Koutsoumba, 2008; Lazaridou, 2008) as shown in Fig. 2.

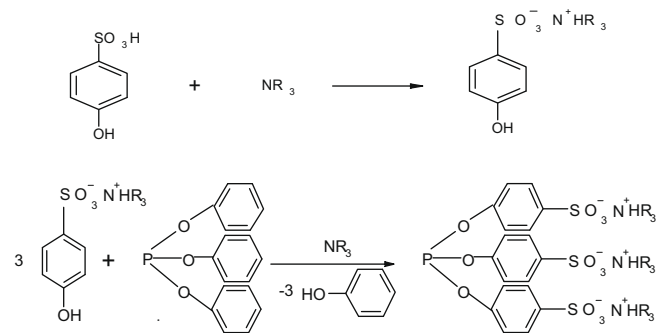


Fig. 2. Synthesis of sulfonated triphenylphosphite (STPP) R = *i*-octyl. When *n* = 3, TSTPP; *n* = 2, DSTPP and *n* = 1, MSTPP.

STPP used herein (Scheme 2) consisted of 56.4% of tri-sulfonated-(TSTPP), 38.6% of disulfonated-(DS) and 5% of monosulfonated-(MS) triphenylphosphite having a Mean Molecular Mass 1400.234 kJ/kg, verified with ACD/ChemSketch v8.0.

### 2.2. Equipment

The transesterification and partial hydrogenation reactions as well as the analysis of the produced FAMES were carried out in the Petroleum Chemistry and Technology and Biodiesel Chemistry and Technology Laboratories, while the modeling and computational work was carried out in the N. Gas Chemistry and Technology (Computational Metrological Analysis and Management) Laboratory, Department of Petroleum and Natural Gas Technology, Kavala Institute of Technology (KIT). The transesterification of cotton seed oil catalyzed by NaOH took place in a 1.000-ml three-necked, round-bottomed flask, equipped with a mechanical stirrer, a thermometer and a condenser.

The reactor used was a batch (AUTOCLAVE ENGINEERS) 100 ml, 316 Lss reactor, with magnetic stirrer in an arrangement as shown in Fig. 3.

### 2.3. Experimental procedure

The fatty acid methyl esters of cotton seed oil (MESCOO) starting material was prepared by a typical transesterification reaction catalyzed by NaOH. Designed to keep the mass ratio NaOH/oil less than 1% and the molar ratio CH<sub>3</sub>OH/oil around 6:1, 3.2 g NaOH dissolved by heating and agitation in excess CH<sub>3</sub>OH (209 g) forming the transesterification catalyst (CH<sub>3</sub>ONa) and then 321 g of cotton

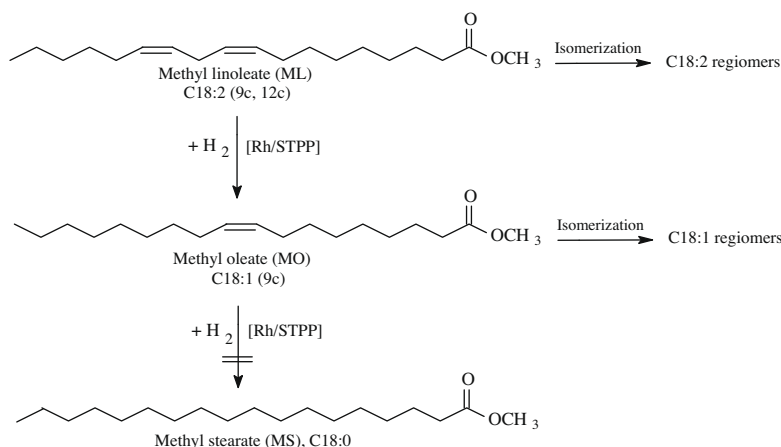


Fig. 1. Rh/STPP catalyzed hydrogenation of MESCOO (methyl esters of cotton seed oil).

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