



## Research paper

## Fatty acid methyl ester production via ferric sulfate catalyzed interesterification



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## ABSTRACT

While biodiesel production is on the rise, so too is the production of the low-value product, glycerol. Interesterification is an alternative reaction that produces fatty acid methyl esters (FAME) and avoids the production of glycerol. In this work, ferric sulfate is used as a potential heterogeneous catalyst for interesterification of model triglyceride, triolein, using methyl acetate. Reaction conditions were optimized by varying reaction temperature, methyl acetate to oil mole ratio (MAOMR), catalyst loading, as well as FAME as co-solvents. Additionally, this work also evaluated the effect of typical triglyceride feedstock contaminants, water and free fatty acids (FFA). The optimal reaction conditions were found to be 120 °C, 20:1 MAOMR and a mass loading of 7.5% ferric sulfate with yields up to 83%. The addition of FAME and water in the system is shown to have potential benefits on reaction rate and yield while FFA addition had mildly negative impacts on initial reaction rate. The results in this work show relatively high yields at mild temperatures and reagents loadings and could be a promising means of alternative FAME production.

## 1. Introduction

In the United States over 5.5 hm<sup>3</sup> of biodiesel were produced in 2016 [1], and growth of this renewable alternative to petroleum-based diesel fuel is expected to continue. Current biodiesel is typically produced via transesterification of triglycerides with methanol to produce fatty acid methyl esters (FAME) and glycerol as a by-product (Fig. 1). This reaction is commonly catalyzed by a strong base, homogeneously blended with the oil/alcohol mixture [2]. The use of homogeneous catalysis and the formation of the glycerol by-product lead to the requirement for neutralization and separations in order to prevent contamination of the fuel product and recovery of glycerol [3]. These steps are energy and resource intensive, decreasing the efficiency and adding costs to production. Furthermore, this process is susceptible to by-product formation via saponification with common triglyceride feedstock contaminants, free fatty acids (FFA) and water [4]. Previous research has suggested that suitable feedstocks for a base-catalyzed process requires FFA < 1% and preferably < 0.05%, and that the feedstock must be dry (< 0.5% moisture) [5], limiting the types of feedstocks that may be used or requiring upstream processing to remove impurities. As such improved biodiesel production systems would seek to avoid the production of glycerol while maintaining high yields with marginal feedstocks over heterogeneous catalysts.

Replacing the alcohol with an alkyl acetate as the acyl acceptor

group substitutes the production of glycerol with a short chain triglyceride via interesterification [6]. For instance, the use of methyl acetate yields triacetin instead of glycerol as the terminal product of the interesterification during the formation of FAME [7] (Fig. 1). The production of triacetin instead of glycerol is favorable as it has value as a solvent and plasticizer [8]. Furthermore, in fuel applications, triacetin may be left in the product mixture as a fuel component that would improve several biodiesel properties (such as oxidative stability and cold flow) and effectively improve fuel yield [9,10]. The energy intensity of this process has been shown to be comparable to that of transesterification in certain scenarios [11], however the analyses done so far have not comprehensively evaluated the effect of reaction conditions and downstream separations on reaction energy use and cost.

Compared to transesterification with methanol, interesterification of triglyceride feedstocks with methyl acetate typically has slower kinetics which may affect the energy consumption during the process (Table 1). Reaction conditions (temperature, pressure) and reaction time as well as other variables such as alkyl acetate to oil mole ratio and catalyst type/loading can be optimized in order to improve yields and kinetics. Furthermore, basic, acidic, and biological catalysts as well as catalyst-free conditions have been evaluated for interesterification with trade-offs associated with each (Table 1). Using basic catalysts typically results in faster reaction kinetics however, is susceptible to feedstock contaminants, free fatty acids and water, which lead to saponification

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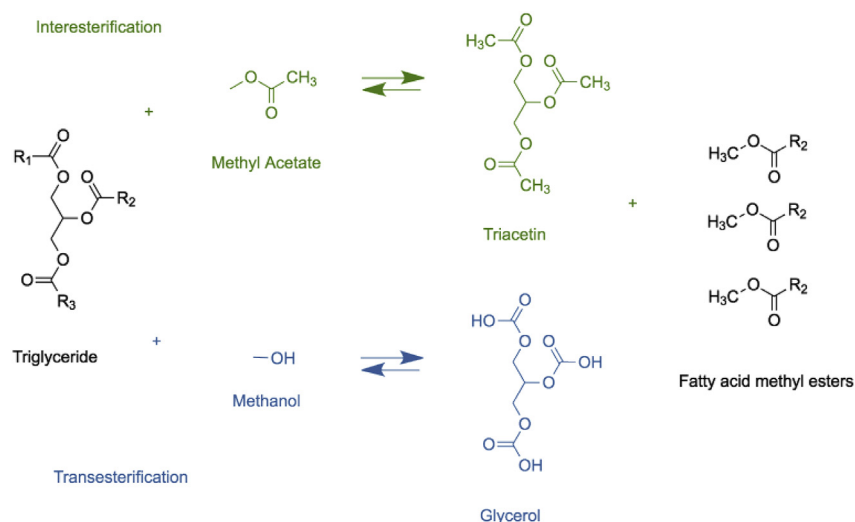


Fig. 1. Reaction schematic for the conversion of triglycerides to fatty acid methyl esters via interesterification (top) and transesterification (bottom).

**Table 1**  
Summary of previous methyl acetate interesterification reaction conditions and yield.

Type	Temp (°C)	Pressure (MPa)	Time (h)	MAOMR	Catalyst	Yield	Ref.
Homog. Base	Boiling	ambient	1	36	Sodium methoxide	75%	[11]
Homog. Base/Methanol-enhanced	50	ambient	mins.	48	MethanolicPotassium methoxide	77%	[8]
Homog. Basic/Ultrasound-assisted	40	ambient	0.5	12	Potassium methoxide	90%	[12]
Lipase	40	ambient	10	12	Novozym-435	92%	[13]
Lipase	40	ambient	24	12	Lipase	90%	[14]
Lipase/Ultrasound-assisted	40	ambient	3	9	Lipase	96%	[14]
No catalyst/Supercritical	350	17.8	0.75	42	None	90%	[15]
Homog. Acidic/Supercritical	300	20	0.75	42	Acetic Acid	97%	[16]
Heterog. acid	210	ambient	20	40	Tin Octoate	61%	[17]

[9,12,13]. Enzymes (lipases) have also been shown to be effective and recalcitrant to reaction contaminants though enzymes are relatively expensive and have slower reaction kinetics [14,15]. The use of supercritical conditions for interesterification can eliminate the need for a catalyst, yet these reactions require high pressures and temperatures which may require significant input energy and can lead to product degradation [16,17]. Current research on acidic catalysts in this system is limited but indicates slow reaction kinetics with high methyl acetate to oil mole ratio (MAOMR) [18]. Low cost acidic catalysts should be further pursued in order to evaluate their ability to interesterify feedstocks contaminated with free fatty acids or water at moderate reaction conditions.

The choice of a homogeneous versus heterogeneous catalyst also can influence the reaction yield and required process energy. For example, the use of basic homogeneous catalysts in this reaction has reported yields of 77% in the timeframe of minutes [6,19,20] however, the energy required for catalyst separations may comprise a large fraction of processing energy due to neutralization and product recovery steps [21]. The use of heterogeneous catalysts can decrease downstream processing but will require longer reaction times. Use of heterogeneous acid-catalysts potentially may mitigate equipment corrosion associated with their homogeneous counterparts [22].

Due to their resilience to feedstock contaminants as well as potential benefits in interesterification reactions, acidic, heterogeneous catalysts are of particular research interest to provide a low cost and robust reaction. However, reagent loadings, overall yield, and reaction kinetics must be improved to allow these catalysts to be competitive with their basic counterparts. Studies using solid acid catalysts are sparse and an appropriate catalyst alternative has yet to be determined. Battistel et al. have surveyed a number of catalysts for the interesterification of tributyrin, a short chain triglyceride, to methyl butyrate [23]. They found

that Nafion SAC-13 could be an effective candidate with 83% yield of the methyl ester at 130 °C and 20 h of reaction time. However tributyrin is not a representative biodiesel component as typically biodiesel components have chain lengths of at least 14 carbons [24], which changes the properties and reactivities of the parent triglycerides. Usai et al. [25] synthesized a sulfonic acid-functionalized mesoporous silica-based catalyst (SBA-15-phenyl-SO<sub>3</sub>H) for the interesterification of olive oil with ethyl acetate. They were able to achieve a 48% yield in 6 h at 130 °C using a 20:1 mol ratio of ethyl acetate to oil and a mass fraction of 30% catalyst loading. Tin octoate was recently explored as a Lewis acid catalyst for the interesterification of rapeseed oil with methyl and ethyl acetate [18]. The authors found that high alkyl acetate to oil mole ratios (40:1) were necessary for sufficient reaction yields (61%) within 20 h at a temperature of 210 °C.

Ferric sulfate has been used as an acidic catalyst in several transesterification reactions. Notably, it has great potential to be used in systems that have high amounts of FFA and water [26,27]. These reactions are often provided in two step processes with the additional use of KOH for a secondary base catalyzed step [27,28]. While evaluated for transesterification of triglycerides and also esterification of FFA, studies regarding the ability of ferric sulfate to catalyze the interesterification reaction have not been published.

An additional consideration when using heterogeneous catalysts is the potential for mass transfer resistance to hinder overall reaction rates. Co-solvents may be used to decrease mass transfer resistance in these multi-phase systems, facilitating increased reaction rates at mild temperatures [29]. While the role of co-solvents (including diethyl ether, dichlorobenzene, acetone, and tetrahydrofuran) has been explored in the transesterification of triglycerides to FAME [29–32], their role has not been assessed in interesterification reactions. Generally the use of non-polar solvents can lead to higher conversions to FAME [31]

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