



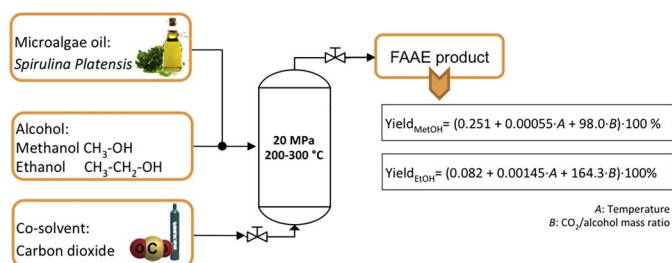
Supercritical transesterification of microalgae triglycerides for biodiesel production: Effect of alcohol type and co-solvent

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GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, biodiesel produced by supercritical transesterification (non-catalytic) from *Spirulina* oil with alcohol (methanol and ethanol) was investigated. A factorial experimental design 2² with two central points for each alcohol was used. The effect of temperature (200 and 300 °C) and the amount of co-solvent (0.0005–0.003 g CO₂/g methanol and 0.0003–0.001 g CO₂/g ethanol) on the reaction yield was studied. Results showed that yield increased from 42% to 65% (at 200 °C) and from 46% to 72% (at 300 °C) when the amount of CO₂ increased from 0.0005 to 0.003 g CO₂/g methanol. By using CO₂ as a co-solvent, it is possible to reduce the critical point of the reaction mixture (oil + alcohol) and thereby increase the reaction yield. For ethanolysis, the effect of selected variables was not statistically significant in the range of studied reaction conditions.

1. Introduction

Biodiesel consists of a long-chain of Fatty Acid Ethyl (FAEE) or Methyl (FAME) Esters formed from the transesterification of triglycerides (TG) with alcohol, generally methanol or ethanol, in a chemical reaction also known as alcoholysis. It also produces glycerol as a by-product, which has some commercial value. Biodiesel has combustion-related properties similar to those of petroleum diesel; it also operates in compression ignition (diesel) engines and requires very little or no engine modifications [1]. Biodiesel can be blended in any proportion with petroleum diesel to create a biodiesel blend or can be used in its pure form. The use of biodiesel instead of diesel in conventional engines

can result in substantial reduction in emission of unburned hydrocarbons, carbon monoxide and particulate matters [1,2]. Therefore, biodiesel could alleviate the high demand for energy and fossil fuels, such as diesel and coal, and could give abilities to achieve sustainable development pathways.

Main sources of TG are edible oils/fats, such as animal fats and vegetable oils (soybean, canola and palm oil) so they compete with their destination as food for human consumption (first generation of biofuels). Recently, sources of non-edible oils (so-called second generation) such as *Jatropha curcas* have been investigated as an alternative to the edible vegetable oils [3–5]. These sources of raw materials do not satisfy the existing demand for transport fuels [6–9], so there has been

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Nomenclature

Variables and parameters

A	Temperature ($^{\circ}\text{C}$)
B	CO_2 -to-alcohol ratio (w/w)
DI	Inner diameter (mm)
L	Length (mm)
M_{FAEE}	Mass of FAEE product (g)
M_{oil}	Mass of oil (g)
P_c	Critical pressure (bar)
MW	Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)
R^2	Coefficient of determination (–)
T_c	Critical temperature ($^{\circ}\text{C}$)
V	Reactor volume (cm^3)
Y_i	Yield reaction (% w/w) ($i = \text{MetOH}, \text{EtOH}$)
\hat{Y}_i	Yield reaction (% w/w) predicted for the model ($i = \text{MetOH}, \text{EtOH}$)

Greek letters

δ	Hildebrand solubility parameter ($\text{MPa}^{0.5}$)
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Acronyms

ANOVA	Analysis of variance
DW	Durbin-Watson statistic
FAME	Fatty Acid Methyl Esters
FAEE	Fatty Acid Ethyl Esters
FAAE	Fatty Acid Alkyl Esters
MAE	Mean Absolute Error
SC	SuperCritical
SEE	Standard Error of the Estimate
TG	Triglycerides
MetOH	Methanol
EtOH	Ethanol

an increasing interest to produce biofuels from other sources such as lignocellulosic materials from industrial wastes (included in the second generation of biofuels) and microalgae (third generation). Potentially, they offer great opportunities in the longer term and do not need to compete for arable land and precious freshwater [10,11].

Microalgae are considered the most promising non-edible source of TG for producing biofuels. Some microalgae are excellent sources of lipids with cell contents of up to ca. 30% w/w in actively growing cells, and over 50% w/w in stationary phase cells [12] (e.g., *Scenedesmus obliquus* has between 30 and 43% w/w of lipids [13]; *Nannochloropsis sp* 21.6–35.8% [14]; *Chlorella emersonii* 63% [15]; *Chlorella pyrenoidosa* 16–64% [16]), and these lipids can be converted to biodiesel by transesterification. Moreover, they have rapid growth, and the productivity of intensive outdoor microalgae cultivation is approximately 5–27 times that of the oilseeds such as canola, soybean, and palm oil [11]. *Spirulina platensis* (blue-green algae) is a species that can be a good source to produce biodiesel [17], since its multicellular structure and self-aggregation capacity it can be sedimented by gravity in the harvesting process, which is a relatively inexpensive separation method [18].

Industrial production of biodiesel has faced two major problems. First, when using a homogeneous catalyst, usually sodium hydroxide or potassium hydroxide, it is necessary to separate the biodiesel from the catalyst after the reaction, which is complex and expensive. Also, a high purity of the raw material with low contents of free fatty acids and water is required [19], because the presence of such compounds results in soap formation, catalyst consume reducing its effectiveness, and finally negatively affecting the reaction yield [20]. Second, conventional biodiesel is synthesized at low temperatures ($\sim 60^{\circ}\text{C}$) and atmospheric pressure [21], which implies 1–4 h of reaction [22].

An attractive alternative is the supercritical transesterification process because reaction time is shorter and it is avoided the use of a catalyst. The reaction conditions in supercritical transesterification are much higher ($> 240^{\circ}\text{C}$ and $> 8.1\text{ MPa}$) than conventional transesterification, which could result in the degradation of the fatty acid esters formed and promote side reactions affecting the reaction conversion [3]. However, in a more recent development in the area it has been proposed process intensification by using a co-solvent with a critical point lower than that of the alcohol in the non-catalytic supercritical transesterification [23–29]. This would allow decreasing the critical point of the mixture such that the reaction is carried out at moderate conditions, enhancing the mutual solubility of the oil-alcohol mixture, reducing the transport limitations, and increasing the reaction rates [25,26,30]. In the literature there are several studies regarding the use of co-solvents in the non-catalyzed supercritical transesterification of

vegetable oils, using carbon dioxide [26,27,31,32] or hexane [28,29,33]. To the best of our knowledge, there is only one work that used microalgae as a source of TG [29]. Najafabadi, et al. [29] investigated the effect of different types of co-solvents, such as diethyl ether, chloroform and hexane, for *in situ* transesterification of *Chlorella Vulgaris C* oil. In that work, it was shown that the addition of hexane as co-solvent almost did not increase the reaction yield from 6% w/w (weight of FAME/dry weight of biomass) without co-solvent to 7% w/w at 290°C and 60 min without pressure control along the reaction.

Among the potential co-solvents for supercritical transesterification, SuperCritical (SC) carbon dioxide (CO_2) is one of the most promising because is non-flammable, non-toxic, not corrosive in the presence of water, and can be obtained from renewable resources in large quantities with high purity and low cost [34,35]. It is easily removable solute leaving no residue in the final product (high volatility) because it is a gas at atmospheric conditions, therefore is readily recoverable by recycling processes. Also, it has favorable critical parameters, compared to typical alcohols used in biodiesel synthesis (Table 1) and it is a suitable co-solvent for short and intermediate chain length organic molecules [26,36].

Han et al. [26] obtained that as the CO_2 /methanol ratio increased (at constant temperature), the FAME yield for the supercritical reaction of methanol with soybean oil increased. They found that the optimum temperature was 280°C when the molar ratio of CO_2 to methanol was 0.1, and at higher molar ratios this curve remains almost unchanged. Similar results were obtained by Jiang and Tan [23] on supercritical transesterification reaction of coconut oil with methanol. They indicate that by adding CO_2 in the 30:1:3 molar ratio (methanol/oil/co-solvent) the FAME yield was increased from 42% w/w (without co-solvent) to 63.6% w/w.

In general, the experimental conditions set for obtaining high yields (70–> 95% ester content) by supercritical transesterification are between $270\text{--}350^{\circ}\text{C}$, $10\text{--}45\text{ MPa}$, 1:20–1:43 oil to alcohol molar ratio, and 4–110 min [3]. There is some restrictions, for example, pressures

Table 1
Critical properties of typical alcohols, CO_2 co-solvent [56], and alcohols + CO_2 mixtures estimated by the Chueh–Prausnitz approximation [57].

Compound	MW (g mol^{-1})	T_c ($^{\circ}\text{C}$)	P_c (MPa)
Ethanol	46.07	241	6.3
Methanol	32.04	240	8.1
CO_2	44.01	31	7.4
CO_2 + Methanol (0.1 mol fraction)	–	64	10
CO_2 + Ethanol (0.1 mol fraction)	–	72	13

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