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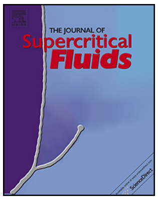

Analysis of optimal conditions for biodiesel production from *Jatropha* oil in supercritical methanol: Quantification of thermal decomposition degree and analysis of FAMEs

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ABSTRACT

Recent years have seen great efforts made to optimise the production of biodiesel as an alternative to fossil fuel. This study looks at the optimal conditions for producing second generation biodiesel in supercritical methanol from *Jatropha* oil. Triglyceride conversion and the yield of monoglycerides, diglycerides and fatty acid methyl esters (FAMEs) are analysed for different ranges of temperature and time. The maximum conversion of triglycerides (100 wt%) and maximum yield of FAMEs (99.5 mol%) were achieved at 325 °C with a reaction time of 90 min. The thermal decomposition of the biodiesel produced was greatest (24.16%) at 350 °C and 90 min. Quantification of individual methyl esters showed that the fatty acid chains affected by temperature were those of oleic and linoleic acids. Finally, a lineal regression model was applied to predict the effect of temperature on the biodiesel produced.

1. Introduction

The current energy crisis and global warming have encouraged interest in finding alternative fuels to replacing petroleum and its derivatives as sources of energy. Biodiesel is characterised by its low emission of particulate matter, carbon monoxide and unburned hydrocarbons and the absence of sulphur. Among many others, these reasons make biodiesel a promising substitute for fossil fuels. Many studies have identified vegetable oils such as soybean or sunflower oils as an option for producing first generation biodiesel [1–3], although the current trend consists of reusing non-edible oils such as *Karanja* or *Jatropha* oils [4,5].

Biodiesel is obtained by the transesterification of triglycerides (TG) in the presence of an excess of methanol, which allows high percentages of fatty acid methyl esters (FAMEs) to be obtained. This process can be catalysed by an alkali, an acid or by an enzyme [6–8], although the most widely used catalyst in industry is strong alkali since it allows the reaction time and the amount of catalyst to be reduced while increasing the conversion rate [9,10]. However, this technology has several important drawbacks including the saponification and the poor quality of biodiesel when the oils used contain more than 0.06 wt% and 0.5 wt% of water and free fatty acids (FFAs), respectively [11]. As a result, major efforts are currently being made to develop alternative processes which would help to overcome these disadvantages. One of the most promising options is to perform the reaction in supercritical methanol without a catalyst. In this case, transesterification process is not affected by the water or FFAs contained in the substrate, meaning that low quality substrates can be used. Moreover, since the process does not involve a catalyst, the final products do not need to be treated by means of a complex separation method and the subsequent wastes are neither acid nor alkali. This process also requires less time to reach equilibrium, which encourages the scaling-up of the continuous production of biodiesel [12–15]. When the transesterification of oil is performed in methanol under catalyst-free supercritical conditions, the direct contact between both reagents increases the rate of the reaction since it occurs in a homogeneous phase, the solubility of methanol being similar to that of vegetable oils in specific conditions of temperature and pressure [16–18].

The transesterification reaction consists of converting triglycerides into glycerol in three consecutive and reversible steps. During this process 1 mol of methyl ester is produced in each step (3 moles in total, see Fig. 1) [19,20]. As shown in Fig. 1, the final product is a

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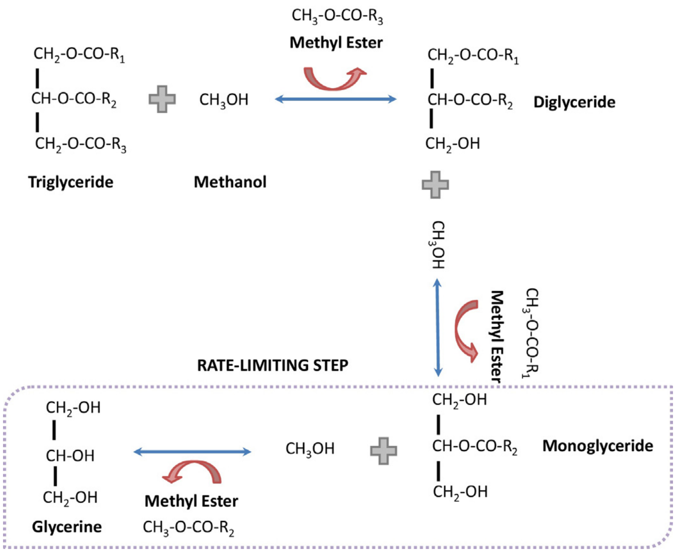

Fig. 1. Scheme of the typical transesterification process of TG and methanol.

mix of mono-, di- and triglycerides, glycerol, thermal degradation products and fatty acid methyl esters. However, the main products are fatty acid esters (biodiesel) while the presence of the other substances clouds the biodiesel and reduces its quality [3].

The key factors in biodiesel production under supercritical conditions are temperature, the molar ratio of methanol/oil and the reaction time, although pressure, the total volume of the mixture used and the stirring rate of the reactor also affect the yield of biodiesel. Fig. 2 summarises the optimal conditions applied by most of researchers [3,14,15].

A thorough investigation into the optimal conditions for producing biodiesel from *Jatropha curcas* L. oil in supercritical methanol was carried out in a catalyst-free process in shaken-batch mode, using a methanol/oil molar ratio of 42:1. The conversion of triglycerides, the evolution of mono- and diglycerides and the production of biodiesel (FAMEs) were analysed over a temperature range of 250–350 °C and for times ranging from 15 to 90 min. Finally, the degradation of biodiesel due to thermal cracking in the condition selected was also evaluated, and the individual methyl esters affected by this process were determined. Finally, the relation between the area of some chromatographic peaks observed during the analysis of glycerides and the degree of decomposition was studied.

2. Materials and methods

2.1. Materials

Natural *J. curcas* L. oil extracted from *Jatropha* seeds by cold-pressing and supplied by Delhi Technological University (India) was used for biodiesel production. The fatty acid composition of this non-edible oil is shown in Table 1. Panreac Química, S.A.U. (Spain) provided anhydrous methanol and Sigma–Aldrich (Spain) supplied 1,2,3-tricaproylglycerol (tricaprin), methyl heptadecanoate, 1,2,4-butanetriol, mono-, di- and triolein, and glycerol.

Table 1
Fatty acid composition of *Jatropha curcas* oil selected.

Fatty acids	Percentage (%)
Palmitic (C16:0)	16.77
Stearic (C18:0)	4.63
Oleic (C18:1)	41.49
Linoleic (C18:2)	37.04
Other acids	0.07
Total	100

2.2. Procedure

The influence of the reaction time and temperature was analysed in a stainless steel cylindrical autoclave tank reactor of 83 mL capacity operated in shaken batch mode. As mentioned above, the temperature and time ranges selected were 250–350 °C and 15–90 min, respectively. Fifty grams of a methanol–*Jatropha* oil mixture (42:1) were loaded into the reactor in each essay. No external pressure was applied to the system, the pressure reached was produced by the temperature. Using a mechanical arm, the reactor was inserted pneumatically into a smelted salts bath, which allowed the reaction mix to reach the selected temperature in about 10 min. The beginning of the reaction was taken as the time when the reactor was introduced into the salt bath, where it was shaken at 70 rpm. When the selected reaction time finished, the reactor was immersed in a cold water bath to stop the reaction. Finally, a rotavapor was used to evaporate the residual methanol in the final product and then it was stored in a refrigerator until analysis.

2.3. Analysis

A Varian gas chromatograph with a CP8400 Varian autosampler and a FID detector (GC/FID) was used to analyse the amount of mono-, di- and triglycerides and methyl esters in the biodiesel produced.

2.3.1. Monoglycerides, diglycerides and triglycerides

Mono-, di- and triglycerides were analysed according to UNE-EN standard 14105:2003. This procedure consists of obtaining the silylated derivatives from the respective glycerides, whose vapour pressure is lower, using N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) and pyridine. Two internal standard solutions are required to perform this procedure, the following being used in our case: (1) 50 mg of 1,2,4-butanetriol dissolved in 50 mL of pyridine; (2) 80 mg of 1,2,3-tricaproylglycerol (tricaprin) dissolved in 10 mL of pyridine. The above standard solutions (80 μL and 100 μL respectively), and 100 μL of MTSFA were added to a 10 mL vial containing 100 mg of the sample. The vial was then closed, shaken and left for 15 min at room temperature. Finally, heptane (8 mL) was added and 2 μL of the final solution was injected into the GC/FID.

A Factor Four VF-5ht capillary column (10 m × 0.32 mm, 0.1 μm film) was coupled to the chromatograph. The carrier gas selected

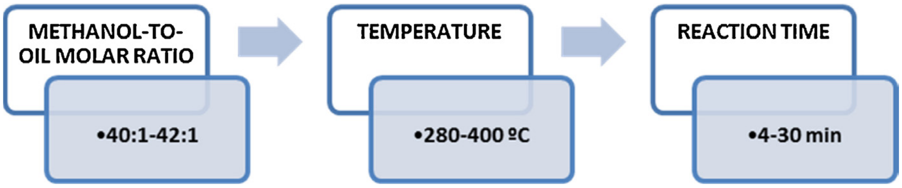

Fig. 2. Scheme of the optimal conditions for biodiesel production under supercritical conditions.