One-step production of biodiesel from high acid value waste cooking oil using supercritical methanol

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Most of the energy used by the developed world is derived from fossil fuels, despite their environmental and economical challenges. Burning fossil fuels has been considered as the main source of global warming and the greenhouse gases. Moreover, the instability in prices and the limited reserves of the petroleum resources made fossil fuels unreliable source of energy. Consequently, the search for an alternative renewable and sustainable fuel has been considered an essential need [4].

Biodiesel has been recently a sustainable competitive fuel to the petroleum diesel fuel. It is non-toxic and biodegradable fuel which provides free sulphur and aromatics combustion. Although first generation biodiesel has shown significant impact and reliability, there are some concerns about extending the usage of first generation feedstock which might lead to food crisis. Thus, resulted food insecurity has made this first-generation biodiesel less attractive and an unsustainable source. Alternatively, second-generation biodiesel is socially and environmentally sustainable since it does not compromise food industry [1].

Waste cooking oil (WCO) has been recognised as a significant feedstock for second generation biodiesel production. However, free fatty acid (FFA) content in the WCOs is frequently high; hence they require pre-treatment before processing [2]. Biodiesel reaction under supercritical methanol conditions has proven a successful direct conversion for WCO of relatively high FFA content. Moreover, it reduces the cost of catalyst preparation and separation since it is a non-catalytic reaction [3].

In this study, biodiesel production from typical Egyptian waste cooking oil with high acid value (18 mg KOH/g) has been studied. Supercritical conditions of methanol have been used to run the reaction in the absence of catalyst. Chromatographic analysis of the WCO showed that it mainly consists of palmitic, oleic and linoleic fatty acids. Overall conversion of these fatty acids and their triglycerides has been investigated. Moreover, free fatty acids (FFA) conversion of the oil was analysed using ASTM D974. Response surface methodology (RSM) *via* Central Composite Design (CCD) was employed to study the significance and interactive effect of methanol to oil (M:O) molar ratio, reaction temperature, pressure and reaction time on reaction responses. Four

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quadratic model equations for each fatty acid's overall conversion and the oil FFA conversion have been obtained describing the interrelationships between dependent and independent variables. In addition, the validity of the predicted models has been confirmed using the Analysis of Variance (ANOVA) method. Using numerical optimisation technique, optimum conditions for maximum overall conversion of palmitic, oleic, linoleic fatty acids and the oil FFA conversion has been concluded to 99.2%, 99.39%, 99.16% and 97% respectively at a methanol to oil molar ratio of 27.25:1, reaction temperature of 257 °C, pressure of 110 bar and reaction time of, 17 minutes.

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