

Efficient eco-friendly economic esterification for waste cooking oil

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Keywords: Aluminium chloride, Biodiesel production, Esterification, Waste cooking oil.

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1. Introduction

The increasing global population, growing industrial activity, and rising demand for comfort and energy have led to a significant rise in energy consumption and environmental issues, such as waste generation and pollution. With concerns about climate change, greenhouse gas emissions, and petroleum shortages, there is a growing need to find renewable alternatives to petroleum diesel. Biodiesel has emerged as a promising substitute, as it can be produced from renewable sources like vegetable oils, animal fats, waste cooking oils, and non-edible oils. It is biodegradable, non-toxic, and burns cleaner than petroleum diesel, reducing harmful emissions such as CO₂, CO, SO₂, and particulate matter. Biodiesel can be used in existing diesel engines either in pure form (B100) or blended with petroleum diesel, without requiring engine modifications (Elgharbawy *et al.* (2025); Ali *et al.* (2020)). Despite its benefits, biodiesel production faces challenges, mainly the high cost of feedstocks like edible vegetable oils, which also impact food prices and supply. A sustainable solution involves using low-cost, non-edible, or waste oils, though these typically have high free fatty acid (FFA) content, which reacts with alkali catalysts to form soap, hindering the transesterification process. This is addressed by a two-step method: acid-catalyzed esterification to lower FFAs, followed by alkali-catalyzed transesterification (Ali *et al.* (2025); Kamel *et al.* (2018)).

This work aims to utilize waste cooking oil (WCO) as a low-cost biodiesel feedstock to add value to it and avoid its incorrect disposal, which leads to sewage clogging and water streams pollution. The oil was esterified using AlCl₃ as a catalyst to convert FFA to biodiesel and avoid the saponification reaction. The efficiency of AlCl₃ has been investigated with varying parameters such as esterification reaction time, methanol to oil molar ratio, catalyst dose under ultrasonic irradiation effect and conventional heating and stirring to compare their effect on the AlCl₃ catalyst performance. The parameters related to the physical techniques used are also explored, such as the ultrasonic amplitude for the ultrasonic irradiation technique and the reaction temperature and stirring rate for the conventional technique.

2. Materials and methods

Waste cooking oil of clear dark yellow colour, which is liquid at room temperature, was collected from the house domestic after using 2–4 times at a frying temperature of 120–130 °C, AlCl₃ and methanol (CH₃OH, 99.8%) was supplied from Sigma Aldrich Chemicals.

For performing the esterification process, 50 ml WCO was weighed, methanol was added in different MTO molar ratios, and then the catalyst was added with different doses. This mixture is then located in an ultrasonic device with different amplitudes to investigate the effect of the different parameters which affect the esterification process. After reaction time, the mixture was centrifuged to separate the catalyst, and then the liquid phase was poured in a separating funnel to be washed with hot distilled water to stop the reaction and separate the alcohol from the oil phase. Finally, the acid value of the oil was determined before and after the esterification process and consequently, the % FFA conversion was calculated.

3. Results and discussion

Batch esterification experiments were performed using the Ultrasonic technique for WCO of high FFA in the presence of methanol and AlCl₃ as a catalyst. Different MTO molar ratios (3:1, 6:1, 12:1, 15:1, 18:1, and 24:1) were tested under constant sonicator amplitude 13%, time 5-25 min, and 0.5% of AlCl₃ catalyst dose. The results show that the % FFA conversion increases by increasing the MTO molar ratio. The methanol amount provides the necessary driving force to overcome the resistances to the mass transfer of methanol to the catalyst and the FFA. Increasing the MTO molar ratio also enhances the interaction between the reactants. Figure 1a shows that there is no significant increase in the FFA conversion by raising the MTO molar ratio beyond 18:1. Hence, 15:1 can be considered the optimum MTO molar ratio for this reaction. Figure 1b shows the effect of the AlCl₃ on the % FFA conversion at the reaction conditions of 15:1 methanol to oil molar ratio at sonicator amplitude 13%, time 5-25 min. The AlCl₃ dose varied from 0.25 to 3% wt./ oil wt. The results showed that the % FFA conversion increased by increasing the catalyst dose until 0.75%, then % FFA conversion decreased. There is a small difference in FFA

conversion between using 0.5 and 0.75% AlCl_3 dose; hence, 0.5% can be considered the optimum one from the economical point of view. Figure 1c shows the effect of % ultrasonic amplitude on the % FFA conversion at the reaction conditions of 15:1 MTO molar ratio and 0.5% AlCl_3 dose. By increasing the % ultrasonic amplitude, the % FFA conversion increased until 13%, then the % FFA conversion slightly increased by increasing the amplitude till 15% then decreased by increasing the % sonicator amplitude more than 15%. The slight increase in the % FFA conversion by raising the % ultrasonic amplitude from 13 to 15% led to considering 13% the optimum ultrasonic amplitude, which is more economical. Figure 1d shows the effect of esterification reaction time on the % FFA conversion at the reaction conditions of 15:1 MTO molar ratio at 0.5% of AlCl_3 dose, ultrasonic amplitude 13% with varying the reaction time from 5 min to 25 min. The results showed that the % FFA conversion increased by increasing the reaction time till 20 min, then decreased at the reaction time more than 20 min. Finally, AlCl_3 can be used as a catalyst for the esterification process of WCO to convert FFA to biodiesel under the abovementioned optimum operating conditions (Elgharbawy and Ali (2022); Elgharbawy *et al.* (2025)).

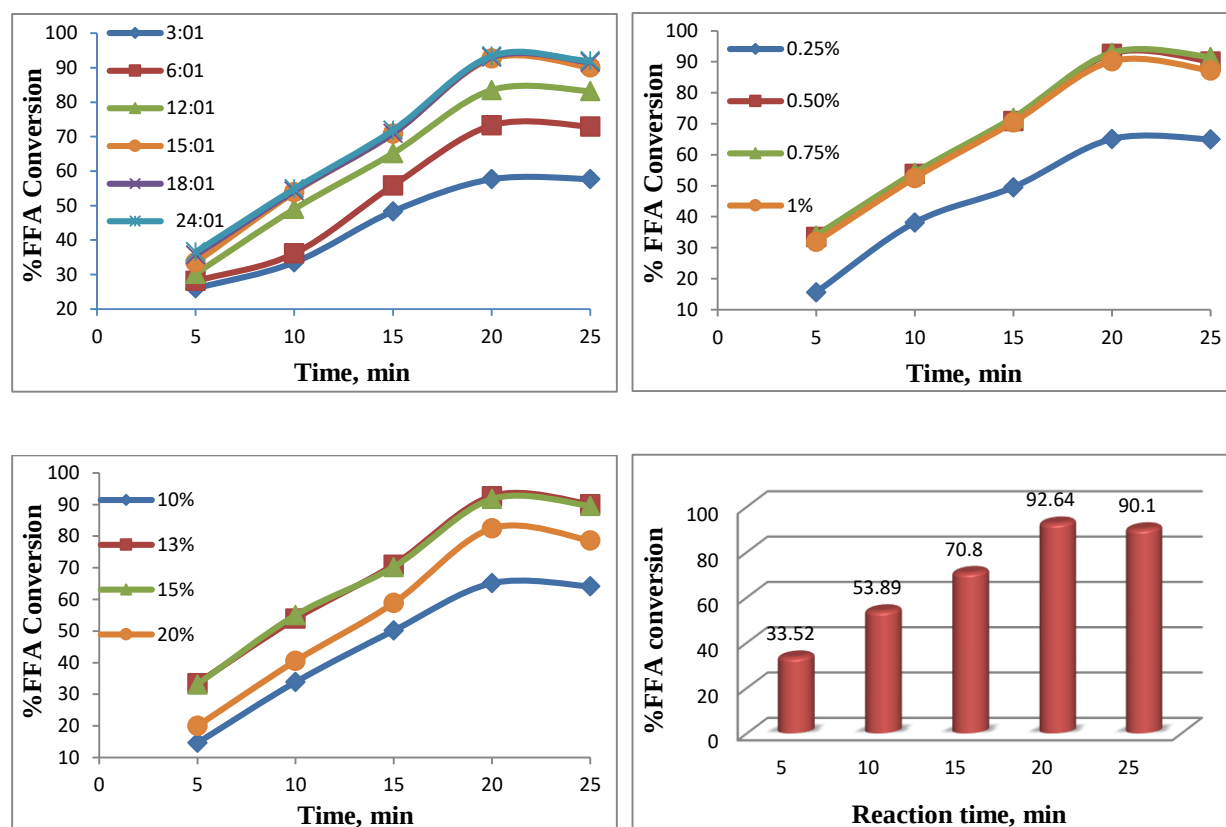


Figure 1. Effect of **a)** MTO molar ratio, **b)** % AlCl_3 loading, **c)** % ultrasonic amplitude, and **d)** time on % FFA conversion.

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