Ultrasonic-assisted biodiesel production from waste cooking oil over novel sulfonic functionalized carbon spheres derived from cyclodextrin via one-step: a way to produce biodiesel at short reaction time†

Panya Maneechakr,* Jittima Samerjit* and Surachai Karnjanakom

In this study, a novel sulfonated carbon catalyst was synthesized via the one-step hydrothermal carbonization of cyclodextrin, hydroxyethylsulfonic acid and citric acid. Ultrasonic-assisted biodiesel production from waste cooking oil in the presence of the catalyst was investigated. The novel catalyst was characterized by BET, XRD, PSD, SEM-EDS, TGA, FT-IR, XPS and TPD. The catalyst exhibited a high acidity of up to 1.87 mmol g⁻¹. 2² factorial and Box–Behnken designs were applied to find the optimum conditions to obtain a maximum fatty acid methyl ester (FAME) yield. The results of the optimization imply that a catalyst loading of 11.5 wt%, a reaction time of 8.8 min and a reaction temperature of 117 ºC provide a maximum FAME yield of up to 90.8% in ultrasonic-assisted biodiesel production. The reusability of the catalyst was studied for 4 cycles under the optimum conditions and the results showed that the regenerated catalyst can be reused without any serious reduction of the FAME yield. Kinetic studies showed that the reaction followed first order reaction kinetics with an activation energy of 11.64 kJ mol⁻¹.

1 Introduction

The current declining reserves of fossil fuels are a concern due to growing environmental and technological needs. Recently, biofuels are considered to be one of the next generation of alternative fuels because they can generally be found around the world, and also utilized easily.¹,² Biodiesel is a kind of renewable energy for diesel engines, which are required for transportation. The advantages of biodiesel are that it is a biodegradable, non-toxic, and eco-friendly fuel.³ The potential feedstocks include edible oils and non-edible oils.⁴ The conventional edible oils have been identified as palm oil, soybean oil and sunflower oil. However, waste cooking oil and non-edible oils such as Jatropha oil and rubber seed oil are more attractive as their use does not affect food consumption.⁵ For example, about 7% of edible oil supplies were applied for biodiesel production in 2007, leading to a food versus fuel issue. As a result, waste cooking oil was used in this work as the raw material for biodiesel production as its use does not rely on the food supply, unlike the reported literature.⁶-⁸ Unfortunately, because waste cooking oil has a high amount of free fatty acids (FFAs), it is not compatible with a wide range of base catalysts. It is well known that saponification can occur between FFAs and alkali catalysts to form soap and water.⁹ To solve this problem, acid catalysts should be used. The conventional homogeneous acid catalysts that are mostly used for biodiesel production are HCl and H₂SO₄. However, the use of these catalysts causes many problems: (1) reactor corrosion, (2) a large amount of waste water and (3) difficulty reusing the catalysts, resulting in an increase of the overall cost of biodiesel production.¹⁰-¹² Recently, Lee and Yoo¹³ reported that heterogeneous catalysis was the most important technology in chemical industry as well as other environmental, energy applications, etc. Heterogeneous acid catalysts are offered as an optimum solution because they can eliminate issues such as corrosion, toxicity and separation. They can also be reused. Recently, heterogeneous acid catalysts have been reported such as sulfonated zirconia, aminophosphonic acid resin D418, Amberlyst-15, SO₃H-SBA-15 and heteropolyacid catalysts.¹³-¹⁷ Some catalysts are not suitable due to their low catalytic activity, low stability and high cost. Acid activated carbons derived from sugar and synthesized by sulfonation are regarded to have good catalytic performance for esterification. They contain soft aggregates of polycyclic aromatic hydrocarbons compared to carbon materials which are directly obtained from lignocellulose.¹⁸ Usually, the sulfonic groups can be easily leached from the structure when the reaction is carried out at high temperature (>100 ºC). For these reasons, glucose was used as the

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