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Research Paper

Methyl ester synthesis of *Pistacia khinjuk* seed oil by ultrasonic-assisted cavitation system

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ABSTRACT

Synthesis of biodiesel from a non-edible source as *Pistacia khinjuk* seed oil via ultrasonic cavitation (UC) system is reported in this study. A heterogeneous catalyst sulphated tin oxide impregnated with silicon dioxide (SO_4^{2-}/SnO_2–SiO_2) was employed during the transesterification reaction in an UC reactor. Parametric optimisation results revealed the maximum *Pistacia khinjuk* methyl ester (PiKME) yield was 88 wt.% at reaction time of 50 min, amplitude of 50%, catalyst amount of 3.5 wt.% and molar ratio of 13:1 (alcohol:oil). Performance of UC at optimised values was compared with mechanical stirring (MS). UC proved advantageous over MS with 3 times more time efficient. Hence, the superiority of UC over MS was established. About 3.2 fold higher reaction rate constant using UC (0.029 min^{-1}) compared to MS (0.009 min^{-1}). PiKME production via UC can potentially subsidise the overall cost of production by having 3.2 fold higher reaction rate constant than MS. PiKME met most of the fuel properties enlisted in EN14214 and ASTM D6751 standards.

1. Introduction

Anthropogenic emissions of greenhouse gas are reckoned as chief contributors towards drastic climatic changes. These changes coupled with growing levels of carbon dioxide are likely to affect the developed and developing countries in a different manner. However, regions located at low latitude are more vulnerable to such change (Chuah et al., 2015a). Researchers are fretful about the potential peril to treasured ecosystems and expect that climate change would increase the probability of large-scale ecological instabilities (Chuah et al., 2016a). Mitigation and stabilisation of the carbon footprint in response to fossil-fuel utilisation, technology developments, and industrial revolution (Bokhari et al., 2017) demand for cleaner and sustainable fuel options. Serious environmental penalties pinned with fossil fuels usage have spurred the quest for renewable and environmentally benign bio-fuels (Chuah et al., 2016b). Meanwhile, biodiesel is acknowledged worldwide as a cleaner and a better replacement fuel in a diesel engine (Chuah et al., 2016c). Biodiesels from indigenous renewable bio waste oils (Rozina et al., 2017) via intensified technologies are a recent and innovative addition in feasible alternatives fuels.

Abbreviation: PiKSO, *Pistacia khinjuk* seed oil; PiKME, *Pistacia khinjuk* methyl ester; TG, triglyceride; UC, ultrasonic cavitation; MS, mechanical stirring; FFA, free fatty acid; FAME, fatty acid methyl ester; AOCS, American oil chemist's society; FTIR, Fourier transform infrared spectroscopy; X, methyl ester conversion; RSM, response surface methodology; CCD, central composite design; KOH, potassium hydroxide; CaO, calcium oxide; H_2SO_4, sulphuric acid; SO_4^{2-}/SnO_2–SiO_2, sulfated tin oxide impregnated with silicon dioxide; SnO_2–SiO_2, sulfated tin oxide; MR, methanol to oil molar ratio; GC, gas chromatography; ANOVA, analysis of variance; p-value, probability of obtaining result; F-value, variance of group means; C.V., coefficient of variation; Adeq. Precision, adequate precision; Std. dev., standard deviation

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Current work explores the viability of relatively under utilised oil seed feedstock, *Pistacia khinjuk* seed oil (PiKSO), a nonconventional indigenous feedstock towards biodiesel production. *Pistacia khinjuk* belongs to genus *Pistacia* (Anacardia ceae/cashew family). It is an important genus because of the economic value of its member namely; *Pistachia vera* (Kafkas et al., 2002). PiKSO is native to Irano-Turanian regions and its plantation is widely spread across Pakistan, Afghanistan, Syria, Iran and Turkey. The *Pistacia khinjuk* trees are 2–5 m long. These trees are highly adapted to irradiated and low nutrient soils, hot and arid conditions even with an annual rainfall of 100–600 mm. Trees of PiKSO potentially can withstand the severest climatic conditions also (Behboodi, 2003). Locations having the temperature range within $T = 10–25$ °C are suitable for seeds growth. Researchers are of the view that PiKSO plant is not much sensitive towards extensive heat, the amount of rain, dryness, height and other climatic conditions of the region. *Pistacia khinjuk* is the best species which can be cultivated in many regions with diverse climates (Behboodi, 2003). It is a rich gene pool species due to its scatteredness across harsh climatic zones and among local populations. Anemophily is another significant characteristic which adds to its diversity. (Taran et al., 2009). It has been reported that *Pistacia khinjuk* trees occupy approximately $2.5–3 \times 10^6$ ha areas in several parts of Iran and its seeds are the waste (Alaei et al., 2012). It contains about 60 wt.% oil. Under these conditions, the use of PiKSO hold a better potential for a renewable energy source for future.

Processing of cleaner biodiesel is hinged on the development of process intensification technology (Chuah et al., 2016d). Process intensification technique offers many primacies like; less reaction time, a low molar ratio (MR) of oil and alcohol, high conversion rate, low catalyst concentration and lower energy consumption hence less operating cost. Among intensification technologies, ultrasonic cavitation (UC) is usually considered as one of the most suitable ones for transesterification reaction (Chuah et al., 2016e). UC surges the emulsification rate of immiscible reactants (oil and alcohol) and solves the poor mass transfer problem between reactant species (Chuah et al., 2017b). Reaction kinetics of intensification process was obeyed the pseudo first order reaction kinetics as a conversion of triglycerides (TG) to respective methyl ester for transesterification process. The detailed reaction kinetics mechanisms for intensification transesterification process has been discussed in our previous publish research (Chuah et al., 2017a). Homogenous (Samani et al., 2016) and heterogeneous (Salamatinia et al., 2010) catalysts for transesterification via UC have been studied by several researchers. Samani et al. (2016) synthesised the Pistacia atlantica Desf. methyl ester (96.6 wt.% yield) via UC system under homogenous catalysed transesterification reaction. UC increased the methyl ester conversion by 7.5 wt.% as compared to mechanical stirring (MS). The UC work on biodiesel synthesis by calcium oxide (CaO) heterogeneous catalyst on *Salvadora alii* and *Thespesia populneoides* oil has been conducted. More than 90 wt.% biodiesel yield was reported for both non-edible feedstocks. The UC was found to be 3 fold more efficient in reaction rate and reduced 3 fold reaction time compared to MS (Asif et al., 2017). Free fatty acid (FFA) content of kapok seed oil was reduced by acid esterification process using UC reactor and it is found to be 4.5 times efficient as compared to MS approach (Chuah et al., 2017c).

Transesterification of PiKSO was steered to optimise several process variables. The response surface methodology (RSM) was statistically confirmed the significance of mathematical model for heterogeneously catalysed transesterification process variables. The central composite design (CCD) was designed the experimental runs for transesterification process. It is capable to give a parametric effect of a solo independent variable or with the combination of other variables with respect to output response. It gives affirmative responsive results for parametric interactions and considered for being cost, time and material effective (Ahmad et al., 2014). Later, the effect of these parameters on fatty acid methyl ester (FAME) yield was monitored also. Experimentally obtained results were processed by RSM to estimate optimum reaction conditions. Reaction kinetics at optimum results was conducted along comparison with MS approach. Hence prepared biodiesel from indigenous non-edible oil was tested to meet the standard fuel properties. Obtained results were compared with EN 14214 and ASTM D6751 biodiesel standards.

Fig. 1. *Pistacia khinjuk* mature seeds.

2. Experimental section

2.1. Materials

Mature seeds for PiKSO extraction (Fig. 1) were collected from different parts of Baluchistan, located in the southwestern region of Pakistan. Seeds were dried under shade for several days. Dried seeds were later kept in a controlled ambience of a laboratory to avoid any humid effects. Prior to oil content estimation seeds were dried at 60 °C in an oven for overnight. Oil estimation was carried out with the help of soxhlet apparatus by using organic solvent (*n*-hexane) extraction method (Ahmad et al., 2011).

2.1.1. Chemicals

Sigma Aldrich, Malaysia provided the standard mixture containing 37 FAME. Utilised analytical grade chemicals were; sulphuric acid (H_2SO_4), wijs solution, cyclohexane, acetic acid (glacial), potassium iodide, starch, acetone, ethanol, hydrochloric acid, anhydrous methanol, anhydrous sodium sulphate, toluene, potassium hydroxide (KOH) pellets, chloroform, sodium thiosulphatepentahydrate, phenolphthalein and 2-propanol. All the aforementioned chemicals were procured from Merck Malaysia.

2.2. Oil estimation

Dried seeds (50 g) were ground by mortar and pestle till fine powder was obtained. Obtained powder was fed to a soxhlet type apparatus comprised of three neck round flasks (250 mL) and a reflux condenser. Oil was extracted with *n*-hexane at $T = 45–55$ °C for 6–8 h. The difference in sample weight before and after extraction was accounted as the weight of the oil possessed (oil content) by seed. All the experiments were performed in triplicate and the average values are reported for further consideration. Once extraction was accomplished, the remaining solvent was removed at 55 °C under moderate vacuum conditions by using a rotary evaporator. American Oil Chemists Society (AOCS-Cd 3d-63) official method was conformed to estimate the acid values and water contents of both oils.

2.3. Catalyst selection and preparation

In this study super acid solid heterogeneous catalyst–sulphated tin oxide impregnated with silicon dioxide ($SO_4^{2-}/SnO_2–SiO_2$) was used for transesterification reaction. Literature review supported the selection of this catalyst for one step transesterification of feedstock with high FFA value. Lam et al. (2009) synthesised, characterised and applied the said