



Esterification of free fatty acids in non-edible oils using partially sulfonated polystyrene for biodiesel feedstock



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ABSTRACT

Partially sulfonated polystyrene (PSS), synthesized from expanded polystyrene waste (EPS), was used as a catalyst for free fatty acid (FFA) conversion in non-edible oils. Acidic and water absorbing properties of the PSS facilitated the catalytic action for the FFA conversion by esterification reaction. The reaction was done on simulated acid oil (WCO) containing oleic acid and sunflower oil, and rubber seed oil (RSO). Effects of temperature, catalyst amount and alcohol to acid molar ratio were studied. FFA conversion increased with each of these factors. The advantage of this heterogeneous catalyst is that it is efficient as commercial ion exchange resin and easily removable from the reaction mixture. PSS is found to substantially reduce the acid value of WCO and RSO from 17 to 3.2 mg KOH/g and from 28.8 to 4.8 mg KOH/g respectively at 75°C. The WCO and RSO with reduced acid value may be used as a feedstock for biodiesel production.

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1. Introduction

Physical and chemical processes involved in industrial and scientific development are either pollution prone or energy intensive. Research and development are now redefined to be 'green' as the world is facing the twin perils of environmental pollution and energy crisis. The biggest contributions towards green environment initiatives include developing technologies for reducing waste and switching to renewable energy resources. Therefore, proper waste management and use of renewable energy resources are so indispensable for the survival of human society. Polymer waste management has emerged as a major concern these days. Modification of polymeric wastes into useful products is very attractive in this context. One of the high volume polymer waste is expanded polystyrene and the methods for utilization of this waste are reported by Sekharan et al. (2012) and Sulkowski et al. (2005). Our intention is to use this waste, after chemical modification, as a

catalyst for the production of low cost biodiesel feed stock. Biodiesel defines by the ASTM as the mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. It is an oxygenated, renewable, biodegradable and non toxic with similar flow and combustion properties as fossil diesel (Canakci, 2007; Sharma et al., 2008; Srivastava and Prasad, 2000).

Depletion of fossil fuel is imminent as we largely depend upon this fuel. Biodiesel, an alternative for fossil diesel is widely encouraged as a need for promoting environment-friendly fuel to attain sustainable development. It can be produced from vegetable oils, fats etc. by transesterification (Marchetti et al., 2007a; Endalew et al., 2011; Zabeti et al., 2009). However, its high cost and food scarcity restricts the use of refined oil for diesel manufacturing. A study conducted in 2009–2012 by the European Union found that green house gas emissions were on the rise because of the conversion of agricultural land for planting first-generation biofuel crops. This calls for phasing out first-generation biofuels and replacing them with second-generation counterparts. However, the development of second generation biofuels from crop residues such as organic waste, algae and waste cooking oil in a cost-effective manner has been a challenge before the research community. Though biodiesel can be cost-effectively produced from non-edible oils such as waste cooking oil (WCO), animal fat, rubber seed oil (RSO) and waste grease through transesterification, high fatty acid (FFA) level in these oils leads to unnecessary reactions like saponification

Abbreviations: PSS, Partially sulfonated polystyrene; EPS, Expanded polystyrene waste; T_g , Glass transition temperature; x , Degree of sulfonation; FFA, Free fatty acid; WCO, Simulated waste cooking oil; RSO, Rubber seed oil; DCE, 1,2-Dichloroethane; IEC, Ion exchange capacity; A, Acid value (mg KOH/g_{oil}); STM, Standard titration method; ITM, Indirect titration method.

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that badly effects the biodiesel production. So prior to transesterification the FFA levels in the non-edible oils should be reduced by esterification using low molecular weight alcohols (Hayyan et al., 2014; Berríos et al., 2007; Marchetti and Errazu, 2008a).

Homogeneous catalysts like sulfuric acid and heterogeneous catalysts like ion exchange resin, sulfonated zirconia and sulfonated carbon are used for the esterification of fatty acids in the biodiesel production (Cheng et al., 2012; Juan et al., 2007; Perez et al., 2012; Shu et al., 2010; Liliya et al., 2002; Tesser et al., 2005). Easy removal of catalyst from the reaction mixture, better efficiency and reusability are the advantages of heterogeneous catalysts over homogeneous catalysts. Various research papers have reported the use of high FFA oils for biodiesel production. Rubber seed oil and tobacco seed oil having FFA of 17% were esterified before transesterification and reduced the FFA level to 2%, which is equivalent to 4 mg KOH/g to avoid the difficulty of saponification (Ramadhas et al., 2005; Veljkovic et al., 2006). Though studies on the use of different ion exchange resins as heterogeneous catalyst for the FFA conversion has been undertaken earlier (Gan et al., 2012), ion exchange resin synthesized from the polymer waste and its application as catalyst in FFA conversion is reporting for the first time. Expanded polystyrene waste is utilized for the production of PSS, which is used as catalyst for the esterification of FFA in WCO and RSO. Effects of parameters like temperature, catalyst amount, alcohol to acid molar ratio and percentage composition of acid in the oil are proposed to be studied.

2. Materials and methods

2.1. Materials

Expanded polystyrene, a waste collected from packing cartons, was used for the synthesis of partially sulfonated polystyrene (PSS). PSS was synthesized from EPS using Sulfuric acid 98% (Merck) and Silver sulfate (Nice) in 1, 2-dichloroethane (DCE) (Merck). PSS was dissolved in toluene/methanol (Merck) mixture to cast film. Pure Oleic acid (Loba Chemie) and acid free commercial refined sunflower oil from local market were used to simulate the waste cooking oil. Crude rubber seed oil used in this study was obtained from Vignesh Traders, Virudhanagar, Tamilnadu. The esterification of fatty acid was done using 1-butanol (Merck). Diethyl ether-99.5%, ethanol-99.9%, triethanolamine and isopropanol (Merck) were used for FFA conversion analysis. Standard titration for the acid value of the oil was carried out using burette to an accuracy of 0.02 ml.

2.2. Sulfonation of expanded polystyrene waste

Partial sulfonation of EPS to PSS was carried out earlier by our group and the PSS was characterized by NMR and FTIR (Antony et al., 2014). Ion exchange capacity (IEC) of the PSS was determined by measuring the amount of H⁺ ions that was exchanged with Na⁺ ions when PSS film was soaked with NaCl solution. It is the number of milli equivalence of H⁺ ions released by 1 g of dry polymer. A known weight of dry polymer (0.2 g) was soaked in 100 ml 0.1 M NaCl solution and shaken occasionally for 24 h. The amount of H⁺ released by the polymer was determined by titrating a definite volume of the NaCl solution against 0.01 M NaOH solution (Inagaki et al., 1999).

$$IEC = (C_{NaOH} * V_{NaOH} * 100) / V_{NaCl} * 0.2 \quad (1)$$

where C_{NaOH} is the concentration (mol/L) of standard NaOH, V_{NaCl} the volume of NaCl (ml) used in the titration and V_{NaOH} the volume of NaOH (ml) required for the neutralization of released H⁺ ions.

Degree of Sulfonation (x), is defined as the mole fraction of sulfonated monomers in PSS ($0 \leq x \leq 1$). It was determined by titrating

PSS solution with standard NaOH solution. About 0.1 g PSS dissolved in 10 ml methanol/toluene (6:4) mixture and titrate against standard methanolic NaOH solution (Bajdur et al., 2002).

$$x = 0.104 * C_{NaOH} * V_{NaOH} [W - (0.08 * C_{NaOH} * V_{NaOH})] \quad (2)$$

where C_{NaOH} and V_{NaOH} are the concentration (mol/L) and volume of standard methanolic NaOH solution (ml). W is the weight of PSS (g). ' x ' was also calculated from the ¹H NMR spectrum of PSS and compared with that obtained by titration.

IEC can also be calculated using ' x ' (Smitha et al., 2003; Guan et al., 2005).

$$IEC = 1000x/104 + 80x \quad (3)$$

2.3. Thermal analysis

Differential Scanning Calorimetric (DSC) analysis of EPS and PSS were done in universal TA instruments, Q 100, under nitrogen atmosphere. Samples of about 6 mg taken in the pan were heated to 250 °C at 20 °C/min and cooled to 40 °C at 20 °C/min in nitrogen atmosphere. After keeping under isothermal condition for 5 min, the second run heating and cooling were done as in the first run. Thermal stability of EPS and PSS were compared using TGA/DTA of universal TA instruments Q50. The samples were heated from 25 °C to 700 °C at 10 °C/min in nitrogen atmosphere.

2.4. Swelling capacity

Water absorption capacity of the PSS film was determined using 'Tea bag' method (Kaiser et al., 2003). A known weight of dry PSS film was placed in a tea bag made of filter paper and soaked in distilled water at room temperature. A blank tea bag was also soaked in distilled water under same conditions. These bags were taken out at different time intervals and suspended for 5 min to allow the surface water to drop off. Weighed the bags to find the water retained by the film. Two more sets of bags were soaked and weighed to take the average. The amount of water (W) held by the film sample in the tea bag was determined. (Supplementary data)

2.5. Free fatty acid (FFA) esterification using PSS as catalyst

Oleic acid in simulated waste cooking oil (WCO) and fatty acids in RSO were esterified in lab scale three-neck, round-bottom flask by heating in oil bath under magnetic stirring. Stirring speed was adjusted to 300 rpm. To check the evaporation loss, Liebig's condenser was fitted to the centre neck; a thermometer was connected to the side neck and the reagents were fed through the third neck. WCO or RSO was stirred with 1-butanol. On attaining the desired temperature a definite percentage (w/w relative to oil) of the PSS catalyst was added. A known weight (1 g) of the sample drawn out from the reaction mixture at regular intervals and determined the FFA conversion by titration analysis (Ozbay et al., 2008).

2.5.1. Titration analysis

A weighed amount of the withdrawn sample was dissolved in diethyl ether and ethanol mixture. It was titrated against aqueous solution of 0.02 M NaOH. Acid value of the sample (A), expressed in mg KOH/g oil was determined using the following equation (Aricetti and Tubino, 2012; Marchetti and Errazu, 2008b).

$$A = 56.1 * C * V / M \quad (4)$$

where C and V are the concentration (mol/L) and volume of NaOH (ml) respectively at the equivalence point. Acid value of the sample was also determined using indirect titration method (ITM), in which the withdrawn sample was dissolved in isopropanol – water

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