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Research Paper

ESTERIFICATION OF FREE FATTY ACIDS IN WASTE COOKING OIL BY CARBONACEOUS SULFATED ACID CATALYST: OPTIMIZATION AND KINETIC STUDY

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Catalyst plays an important role in the production of biodiesel from waste oils. Heterogeneous catalysts are gaining importance owing to the advantages in terms of separation and reusability over the traditionally used homogeneous catalyst. Catalyst from renewable sources such as biomass has been introduced to make the process fully 'green'. The carbon based materials are considered as ideal catalysts due to desirable features such as low material cost, high surface area and thermal stability. In the present work, a strong solid acid catalyst, prepared by sulfonating carbonized rice husk, was proved to be an efficient and environmental friendly catalyst for the esterification of waste cooking oil and methanol. A detailed kinetic study was carried out using first order kinetics. The kinetic parameters were obtained and activation energy was determined from the Arrhenius plot. The activation energy of 23.08 kJ mol⁻¹ was obtained under the optimum catalyst concentration of 6 wt %, stirring speed of 600 rpm and oil to methanol ratio 1:20 and at 338 K.

Keywords: Acid catalyst, Esterification, Kinetics, Sulfonated carbon, Waste oil

INTRODUCTION

Fatty acid methyl esters (FAME), also known as biodiesel, have been considered an interesting petrol-fuel replacement that can help meet the exceeding energy demands for the transport sector expected in future years (Al-Zuhair, 2007). Biodiesel is conventionally produced via transesterification of triglycerides (TG) with short chain alcohols (e.g., methanol) using homogeneous

base catalysts including Sodium Hydroxide (NaOH) or Potassium Hydroxide (KOH) and other heterogeneous protocols (Melero *et al.*, 2009). Various overviews of the latest technologies and heterogeneous catalysts employed for biodiesel production were recently compiled (Melero *et al.*, 2009; Serio *et al.*, 2008; Hara, 2008). Two of the most promising feedstocks to overcome the inherent economic, as well as food versus fuel,

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issues regarding the use of virgin oils for biodiesel production are microalgae and waste vegetable oils and/or animal fats (Luque *et al.*, 2008; Narashimharao *et al.*, 2007). Whereas microalgae have shown promising oil yields per unit of land, as well as potentially high oil content in species (ranging between 20-60%) (Luque *et al.*, 2008; Pienkos *et al.*, 2009; Luque, 2010; Williams *et al.*, 2010; Mata *et al.*, 2010), waste oils and fats have low market values in comparison to other feedstocks and can be obtained as recycled materials from other industrial sectors (Luque *et al.*, 2008; Narashimharao *et al.*, 2007; Echim *et al.*, 2009). Biodiesel production from waste oils and fats has been shown to be more efficient than any related biodiesel production, regardless of the utilized feedstock (Luque, 2010; Zhang *et al.*, 2003). Nevertheless, the use of such raw materials as biodiesel feedstock requires extra processing due to the high free fatty acid (FFA) content in the oils (generally 10-15% or even greater), which normally require neutralization and/or pretreatment steps prior to their utilization in transesterification reactions. Interestingly, there have been some examples in which heterogeneous solid acids were employed as catalysts for simultaneous esterification of FFA and transesterification of TG for biodiesel-like biofuel production from waste oils (Williams *et al.*, 2007; Kulkarni *et al.*, 2006).

These cases, however, tended to involve unusual reaction conditions and/or expensive and not particularly recyclable catalysts under a wide range of conditions. Some novel family of polysaccharide-derived acidic mesoporous carbonaceous materials that showed excellent activity, selectivity, stability, and reusability in a range of acid-catalyzed processes including alkylations, acylations, amidations, and esterifications. (Budarin *et al.*, 2007; White *et al.*, 2009).

In the present study, production of a solid carbon-based acid catalyst by a more environment-friendly, cost-effective and safe means was sought. Rice husk was employed as raw materials to prepare the carbon-based sulfonic acid catalyst through carbonization and sulfonation. The effects of the temperature, methanol/oil molar ratio, stirring speed and the catalyst dosage on the ester yield were systematically investigated and kinetic parameters were established.

MATERIALS AND METHODS

Chemicals and Catalyst Preparation

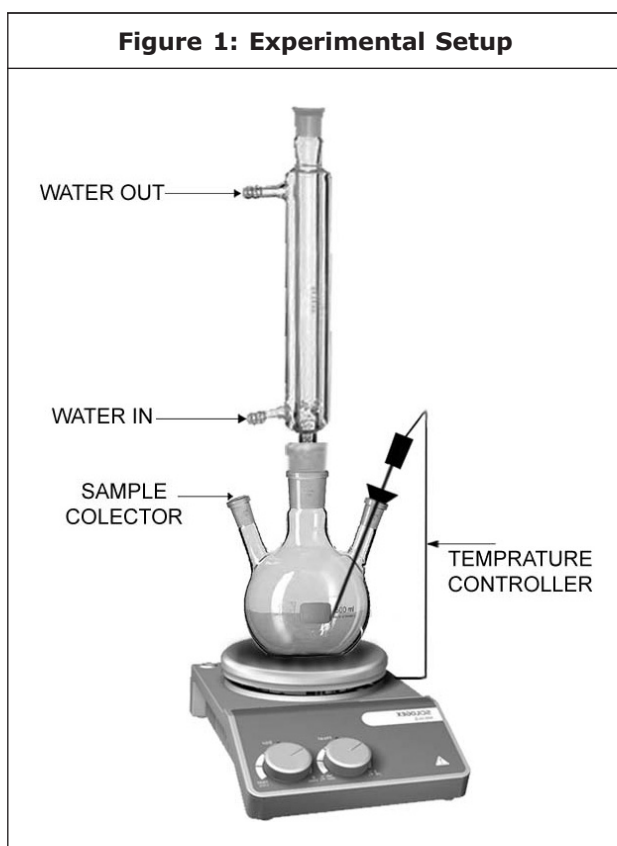
The chemicals used were methanol (99% purity), sulphuric acid (99% purity), Sodium Hydroxide (NaOH, 99.9% purity) and phenolphthalein indicator, which were purchased from SD Fine Chemicals (India). All the chemicals and reagents were of analytical grade. The waste oil was purchased from local market and the acid value of the waste oil was found to be 28 mg KOH/gm of oil. Rice husk (2 g) was heated under N₂ flow for 2 h at 773 K in a tube reactor. An amount of 0.8 g of the carbonized materials and 10ml sulfuric acid were combined in a 100ml flask and heated in an oil bath at 363 K for 4 h. After cooling to room temperature, the mixture was diluted with distilled water and the black precipitate was collected by filtration using a water-circulating vacuum pump and rinsed thoroughly with hot distilled water (>353 K, 1000 ml) to remove impurities such as sulfate ions. The resulting black solid catalysts were dried at 333 K for 4 h in vacuo.

Catalyst Characterization

X-ray Diffraction (XRD) pattern of the catalyst was recorded using CuK α radiation. The intensity data were collected over a 2 θ range of 2-80°.

Apparatus and Procedure

The esterification was carried out in a three-necked glass reactor of 500 ml capacity operating in a batch mode (Figure 1). A reflux condenser was used to avoid the loss of volatile compounds. A temperature controlled magnetic stirrer (REMI make, model 5MLH plus) was used to carry out reaction at particular temperature and stirring speed. In all the experiments, a known amount of oil, methanol and the catalyst were charged into the reactor and heated to the desired temperature. Temperature inside the reactor was controlled within the accuracy of ± 0.5 K. The reactants charged in the reactor were volumetrically measured. The progress of the reaction was measured by withdrawing samples at regular intervals, small enough to consider them negligible compared to the volume of the reaction mixture.



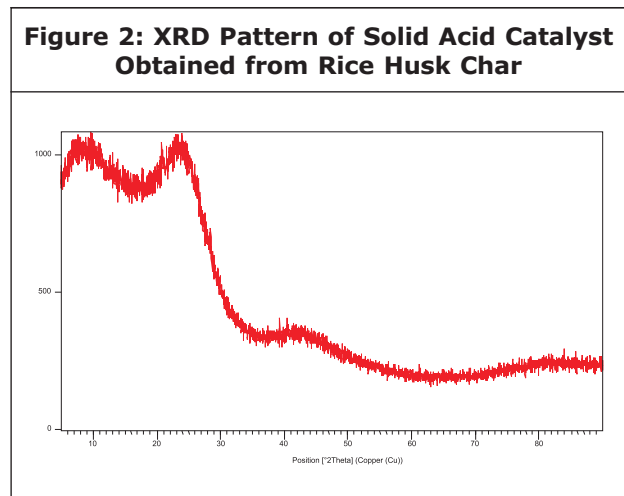
Analysis of Free Fatty Acid Value Content

To measure the concentration of unreacted acid in the reaction mixture, each sample was analyzed volumetrically by 0.2 N NaOH as titrant and phenolphthalein as an indicator. The titration gave the conversion of FFA under all conditions. All experiments were carried out at atmospheric pressure. The standard error obtained in analysis was $\pm 1-2\%$ for the duplicate set of reactions.

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD pattern of the solid sulfated catalyst from rice husk char is shown in Figure 2. The broad and weak diffraction peak ($2\theta = 8-30^\circ$) attributable to amorphous carbon composed of aromatic sheets oriented in a considerable random fashion.



Parametric Study

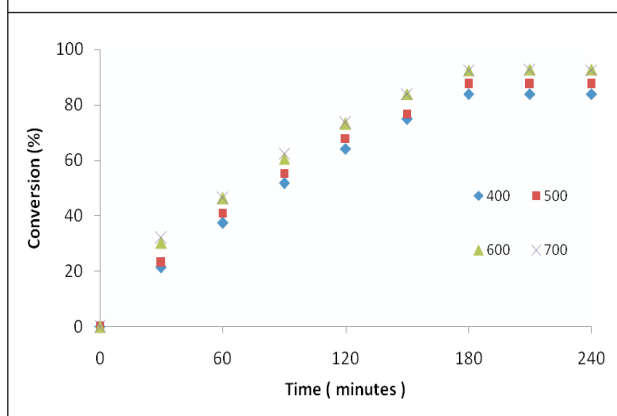
A parametric study was carried out to establish the optimum parameters for the esterification reaction between FFA of waste oil and methanol using carbonaceous catalyst. The parameters included: catalyst loading (as wt% of oil), molar ratio of oil to methanol, reaction temperature and time of reaction. The presence or absence of

mass transfer effect was also established by carrying out experiments at different agitator speeds.

Effect of Stirring Speed

To determine the optimum stirring speed, four runs were carried out at stirrer speed of 400, 500, 600, and 700 rpm using acid to alcohol molar ratio of 1:20, temperature of 338 K, catalyst loading of 6%, for each run. As shown in Figure 3 there was a slight increase in maximum percentage conversion for each run when the stirrer speed was increased from 400 to 600 rpm but above 600 rpm the difference in maximum percentage conversion for each run can be considered to be negligible. This indicates the absence of external mass transfer limitations above 600 rpm. Therefore, all experiments were conducted at 600rpm so as to neglect the effect of external mass transfer and to avoid the breakage of catalyst at higher rpm.

Figure 3: Conversion at Different rpm With Oil to Methanol Ratio 1:20, Catalyst Concentration 6.0 wt% and at Temperature 338K

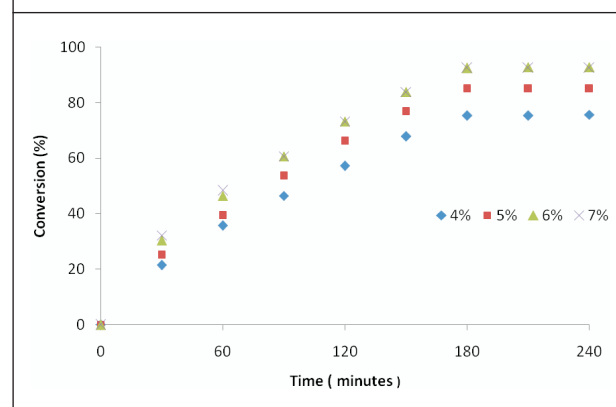


Effect of Catalyst Loading

Experiments were carried out at 4% to 7 wt. % (weight of the catalyst/weight of waste oil) at a temperature 338K, molar ratio 1:20 (oil/alcohol) and stirrer speed of 600 rpm. The conversion of

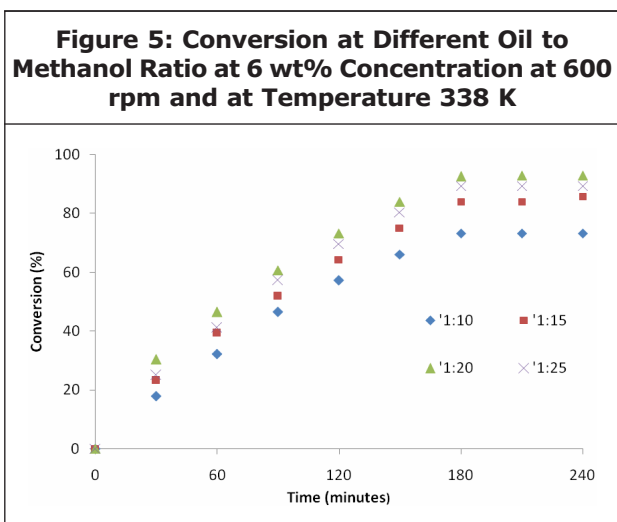
FFA as a function of time with different catalyst loadings is shown in Figure 4. It can be seen from this figure, with increasing catalyst loading the conversion increases due to the increase in the total number of available active catalytic sites for the reaction. The percent conversion of FFA to methyl ester becomes almost constant as the catalyst loading is increased after 6%. Therefore, the optimum catalyst loading was taken as 6%.

Figure 4: Conversion at Different Catalyst Concentration at 600 rpm With Oil to Methanol Ratio 1:20 and at Temperature 338K



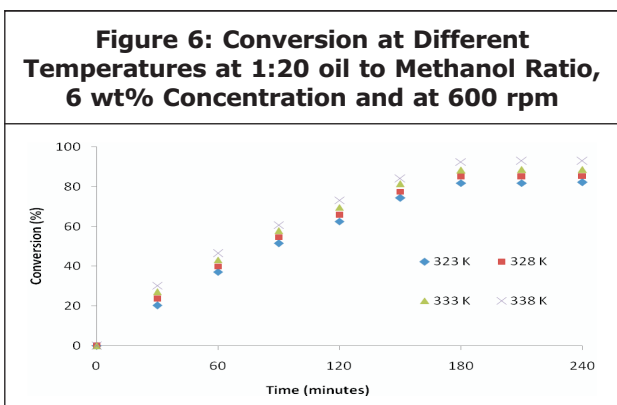
Effect of Oil to Methanol Molar Ratio

Esterification of FFA with methanol is equilibrium limited chemical reaction and the position of equilibrium controls the amount of ester formed. The esterification reaction is generally slowed down by the reversible reaction so use of an excess of methanol drives the equilibrium toward the formation of an ester and enhances the forward reaction. The molar ratio of oil to methanol was varied from 1:10 to 1:25 at a reaction temperature 338 K, 6 wt% catalyst loading, and stirrer speed of 600 rpm (Figure 5). FFA conversion increases with the increase in the amount of methanol till the acid to methanol ratio 1:20. Beyond molar ratio 1:20, there is decrease in the conversion of acid and 1:20 molar ratio was taken as optimum ratio.



Effect of Temperature

To investigate the effect of temperature on the esterification rate, the reactions were carried out in the temperature range of 323 to 338 K while keeping the molar ratio of acid to alcohol at 1:20 and catalyst loading of 6 wt. % (Figure 6). The ester conversion was found to increase with an increase in reaction temperature. Increasing the temperature is apparently favourable for the acceleration of the forward reaction, but required using a pressure above atmospheric level. The reaction temperature above boiling point of methanol (338 K) cannot be used since at higher temperature, it tends to loss methanol. The maximum conversion achieved at 6% catalyst loading, 1:20 oil to methanol molar ratio, 600 rpm and at 338 K is 92.86%.



Effect of Time of Reaction

Figures 3, 4, 5 and 6 also depict the influence of reaction time on FFA conversion.. The conversion efficiency increased with reaction time but the acid values were almost the same after 3 hours. For economical reasons, the best process is the one that reaches the highest conversion in the shortest period of time. Results obtained from the present experiments reveal that 3 hours is sufficient for the completion of the reaction.

Kinetics of Esterification Reaction

In absence of internal diffusion & external mass transfer resistances, the kinetic equation could be written as (Yadav *et al.*, 2005).

$$-r_A = \frac{k_2 w K_A K_B [A] [B]}{(1+K_A [A]+K_B [B]+K_C [C]+K_D [D])^2} \quad \dots(i)$$

Where

r_A = rate of reaction, mol/cm³.sec

k_1 = rate constant ,cm³.sec/mol

w =catalyst loading, gm/cm³

[A] = concentration of FFA in waste oil, mol/cm³

[B]= concentration of methanol, mol/cm³

K_A, K_B, K_C, K_D = Adsorption equilibrium constant for waste oil, methanol, methyl ester and water respectively.

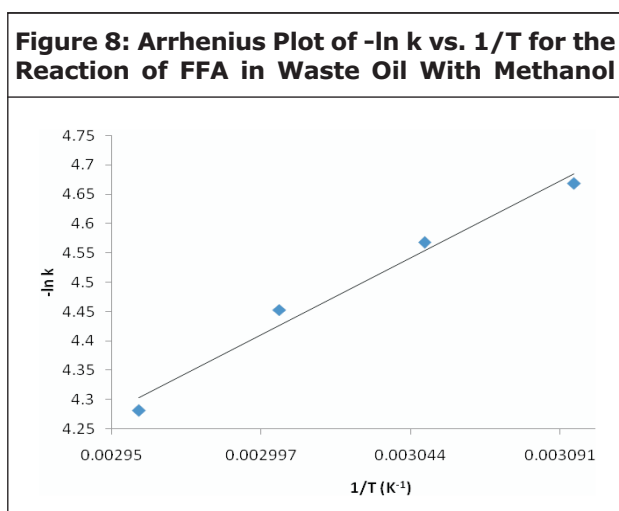
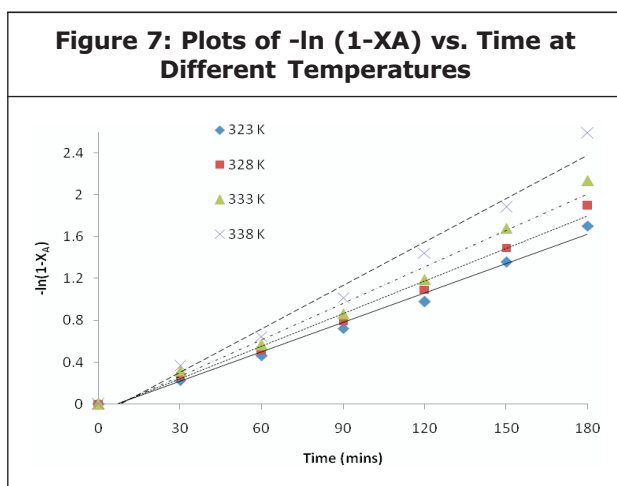
It is assumed that there is a weak adsorption of both reactants and products, hence the denominator term $(1+K_A+K_B+K_C+K_D)$ is taken as 1. And equation (i) can be written as

$$-r_A = K_2 w [A] [B] \quad \dots(ii)$$

$$\text{Where } k_2 = k_1 K_A K_B \quad \dots(iii)$$

Since methanol was taken in excess, equation (ii) becomes a pseudo-first order equation and a plot of $-\ln(1-X_A)$ as a function of time is linear (Figure 7) where X_A is the fraction conversion of

FFA. The slopes of these lines are $k_2w[B]$ from which Arrhenius plot was used to determine the apparent energy of activation (Figure 8). The calculated activation energy was 23.08 kJ/mol, which was less than the reported values for other catalysts (Yadav *et al.*, 2005; Srilatha *et al.*, 2009; Srilatha *et al.*, 2012).



CONCLUSION

A catalyst prepared from sulfonating carbonized rice husk showed good dispersion in polar solvent, because of the incorporation of conjugate aromatic carbon ring with sulfuric acid groups, which exhibited better catalytic activity in esterification of FFA in waste oils. Therefore, a

novel method for fatty acid methyl ester (biodiesel) production via the esterification of higher fatty acid waste oil with methanol was proposed, with the advantages in the recycling of waste biomass and the reduction of waste residue. The optimum parameters which gave maximum conversion of 92.86% using 6 wt% catalyst, 1:20 oil to alcohol molar ratio, at 338 K in 3 hours. A pseudo-first order kinetic model was used to analyze the data and the apparent activation energy was 23.08 kJ/mol.

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