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Research paper

Kinetic study of synthesis of bio-fuel additives from glycerol using a hetropolyacid ☆

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ABSTRACT

Concerns about the ever increasing quantities of glycerol produced as a by-product of the process of manufacture of bio-diesel serve as a fuel for research about the alternative uses of glycerol. The esterification of glycerol with acetic acid over Cesium supported heteropolyacid (CsPWA) serving as the catalyst was carried out. The products obtained were mono, di and tri acetins which have wide application as biofuels. A series of experiments were carried out with CsPWA as catalyst and parameters considered for studies were temperature, molar ratio of reactants (acetic acid:glycerol) and the catalyst loading weight percent. Each parameter was varied keeping the other two constant and the results were recorded. Temperature was varied from 80°C to 110°C; molar ratio of glycerol to acetic acid is between 3:1 and 9:1 and catalyst loading of 3%w/w to 7%w/w. The yield and conversion varied for different conditions, but in general, the yield of diacetin and triacetin increased with time. Optimum parameters were adjudged to be 110°C with a molar ratio of 9:1 of the reactants and catalyst loading being 5% weight of reaction mixture where maximum glycerol conversion of 98% was obtained. The results obtained indicate that the esterification of glycerol with acetic acid is a consecutive reaction and the kinetic model was developed based on homogeneous first order reaction series by optimization method using MATLAB, and rate constants (k_1, k_2 and k_3) were determined. From the rate constants at different temperatures, using Arrhenius equation the activation energies (E_1, E_2 and E_3) were also determined.

1. Introduction

The renewable fuel biodiesel has gained significant importance in the last decade with the exhaustion of fossil fuels and it is becoming an alternative to diesel fuel because of its high octane number [1]. Increase in the production of biodiesel results in surplus amount of glycerol. Therefore efforts are being taken for valorization of glycerol to value added products. The main products of the esterification of glycerol using acetic anhydride/acetic acid (with the latter being cheaper) are monoacetins, diacetins and triacetins. They have various applications in the field of polymers and cryogenics and many other areas. Triacetyl glycerides results in a final fuel having enhanced cold and viscosity properties, and it has also been used as an antiknock additive for gasoline and biodiesel and octane booster for gasoline as an alternative for commercial alkyl ethers [2]. Acetins also have wide applications as in cosmetic industry and pharmaceutical industry. It can also be used as emulsifier, antiseptic, etc. [3,4].

Both homogeneous and heterogeneous catalysts play a vital role in converting glycerol to acetins either using acetic acid or acetic anhydride. Traditionally esterification reaction was carried out using the homogeneous catalyst like sulphuric acid, phosphoric acid and hydrochloric acid. In view of difficulties encountered such has disposal of catalyst, corrosion of material etc. In order to add green credentials to the process the choice of heterogeneous catalyst is preferred. The usage of heterogeneous solid acid catalyst has been reported in recent literature such as amberlyst, niobicacid, zeolites [5–7] and heteropoly acids [8,9]. Even recently mixed oxides are promoted to be promising solid acid catalyst for esterification of glycerol to acetins because of their stability, regeneration capability and for being active for a wide temperature range [10]. The conversion of crude glycerol to propylene is achieved using metal oxides

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Nomenclature

G	glycerol
MA	monoacetin
DA	diacetin
TA	triacetin
t	time, sec
T	temperature, K
CGo	initial concentration of glycerol, mol/litre
C_G	concentration of glycerol at time t, mol/litre
CMA, CDA, CTA	concentration of monoacetin, diacetin and triacetin at time t, mol/m^3
k_1,k_2,k_3	rate constants for monoacetin, diacetin and triacetin, min^{-1}
E_1,E_2,E_3	activation energies of monoacetin, diacetin and triacetin, kJ/mol
$-r_G$, $-r_{MA}$, $-r_{DA}$	rate of reaction of glycerol, monoacetin and diacetin, moles/litre.sec
k_o	frequency factor, min^{-1}

and acid catalyst together [11]. In the recent literature much emphasis is given on numerical approach for the conversion of glycerol to syngas [12]. A biological approach is being made for conversion of crude glycerol to 1,3-propanediol using *Citrobacter freundii* [13]. For esterification reaction the enhancement of conversion is achieved by pervaporation process [14]. A considerable importance is given in research and development for the area of biofuels [15]. In literature the studies were done at high reactant mole ratio, high pressure and with more catalyst loading [16]. Since esterification is highly dependent on the reaction conditions used, it is difficult to go for comparison of activity among the catalysts that are reported. The cesium exchanged heteropoly acid is more active than its parent heteropoly acid due to its high acid strength [17]. The aim of the work was to study the effect of temperature, mole ratio of reactants and amount of catalyst on product distribution for esterification of glycerol with acetic acid using Cesium phosphotungstate as catalyst and to estimate the kinetic parameters of this reaction.

2. Experimental

2.1. Chemicals and catalyst preparation

Acetic acid and glycerol were supplied by SD Fine Chemicals Mumbai India. Phosphotungstic acid (PWA) and Cesium carbonate were purchased from Sigma Aldrich, India. All chemicals were used without any further purification. Deionized distilled water was used in the experiments. The catalyst Cesium phosphotungstic acid was prepared as given in the literature [17] and the obtained $Cs_{1.2}H_{0.5}PW_{12}O_{40}$ catalyst was characterized by XRD, FTIR, SEM and BET to confirm the physicochemical properties of CsPWA [18]. The synthesized CsPWA was used in performing the esterification of glycerol of acetic acid and further to estimate the rate constants and respective activation energies of the reaction.

2.2. Catalytic reaction procedure and product analysis

The esterification reaction between glycerol and acetic acid was carried out using a 100 ml three necked round bottom flask, placed in an oil bath that was being heated by a mantle equipped with a magnetic stirrer; the reaction temperature was controlled within an accuracy of ± 0.1°C by a PID controller. The setup also had a thermometer and Liebig condenser in order to prevent the loss of the reactants. The liquid phase esterification reaction was carried out at various molar ratios of glycerol to acetic acid of 1:3, 1:6, and 1:9 with excess of acetic acid at different temperatures at 80°C, 95°C and 110°C under atmospheric pressure, with different amounts of catalyst loading of 3%, 5% and 7% (by weight of reaction mixture). During all experiments the weight of the reaction mixture remained constant. Sufficient stirring speed is maintained to ensure proper mixing of the reactants with the catalyst and to eliminate external mass transfer resistance. Acetic acid and catalyst were charged into the reaction vessel. After the desired temperature was reached, glycerol was preheated to the same temperature and quickly added into the reactor. The reaction time was started after the addition of glycerol to the reactor. The samples were withdrawn initially with an interval of 10 minutes and later for every 30 minutes up to 2 hours. Samples were immediately cooled down to below 5°C to avoid further reaction and any evaporation losses. The samples were centrifuged to separate the catalyst from liquid phase. The obtained product was analysed in gas chromatography (Neon Pro) with flame ionization detector (FID) equipped with carbo stabil wax capillary column.

3. Results and discussion

The esterification reaction of glycerol with acetic acid is an acid catalysed consecutive reaction leading to the formation of ester isomers depending on the extent of reaction of the hydroxyl groups in glycerol with acetic acid [18]. The influence of temperature, mole ratio of reactants and catalyst loading were studied using CsPWA as catalyst for esterification of glycerol with acetic acid.

3.1. Effect of temperature on conversion of glycerol

The esterification of glycerol with acetic acid was studied for three different temperatures at 80°C, 95°C and 110°C with a mole ratio of acetic acid to glycerol of 9:1 and the amount of catalyst is 5%w/w for 2 h. From Figs. 1–3 it is observed that the conversion of glycerol increased with time for the three temperatures. The maximum conversion of 98.2% was obtained at 110°C in 2 h. It is found that the glycerol conversion in the reaction is enhanced at higher temperature due to the faster formation of acylium ions at these temperatures [18]. The suitable temperature for monoacetin formation was 80°C with acetic acid to glycerol molar ratio of 9:1 with 60% yield of monoacetin. The reaction rate is improved significantly with increase in the temperature and also facilitated the

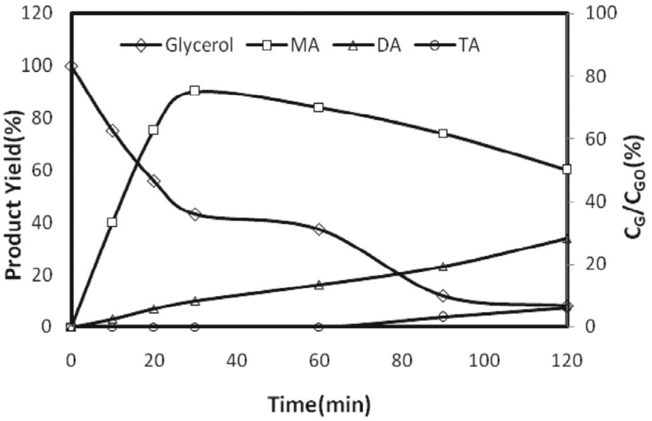

Fig. 1. Product distribution of glycerol esterification at 80°C, mole ratio of acetic acid to glycerol (9:1) and 5%w/w catalyst loading.

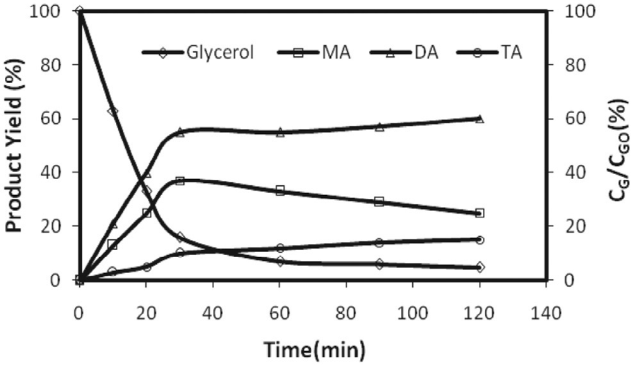

Fig. 2. Product distribution of glycerol esterification at 95°C, mole ratio of acetic acid to glycerol (9:1) and 5%w/w catalyst loading.

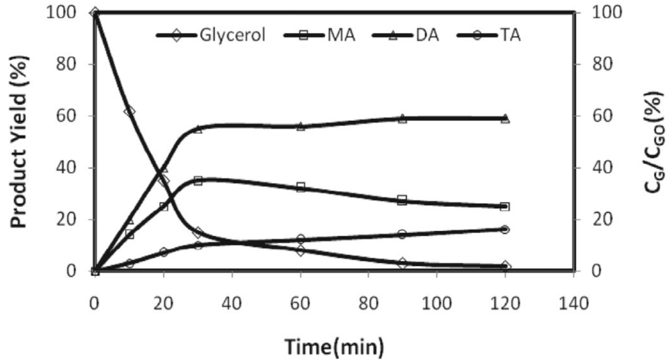

Fig. 3. Product distribution of glycerol esterification at 110°C, mole ratio of acetic acid to glycerol (9:1) and 5%w/w catalyst loading.

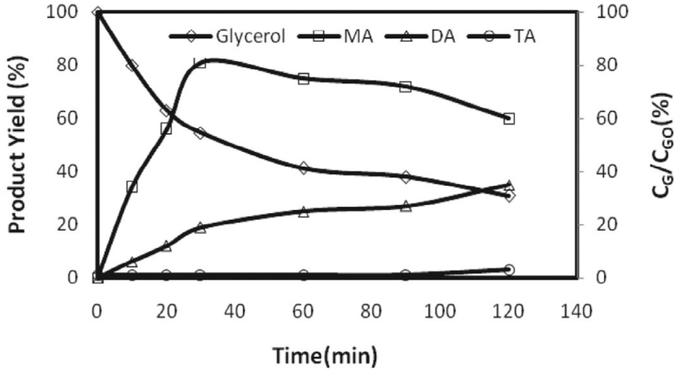

Fig. 4. Product distribution of glycerol esterification for mole ratio of acetic acid to glycerol (3:1) at 110°C, and 5%w/w catalyst loading.

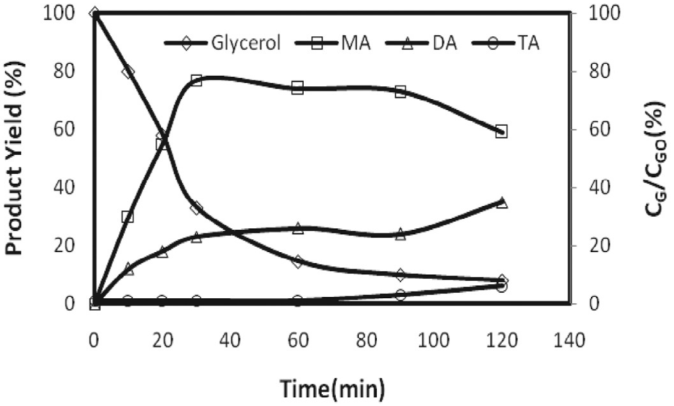

Fig. 5. Product distribution of glycerol esterification for mole ratio of acetic acid to glycerol (6:1) at 110°C and 5%w/w catalyst loading.

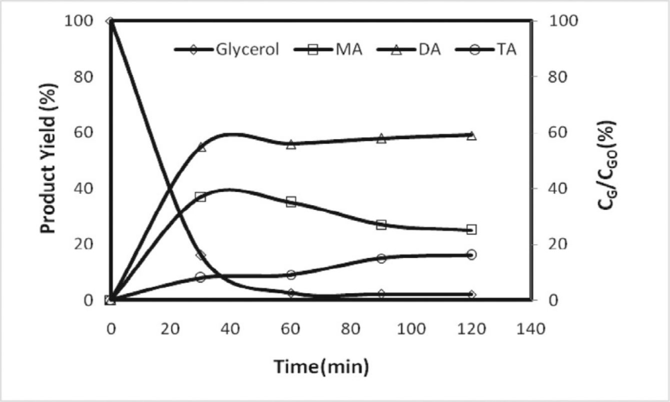

Fig. 6. Product distribution of glycerol esterification at 110°C, mole ratio of acetic acid to glycerol (9:1) and 5%w/w catalyst loading.

distribution of monoacetin, diacetin and triacetin. The most desirable temperature for glycerol esterification was 110°C due to faster rate of reaction and high conversion of glycerol to its substituent esters. Under these conditions for esterification reaction the glycerol conversion of 97% was reported in literature for Amberlyst-15 ion exchange resin [19].

3.2. *Effect of reactants molar ratio on conversion of glycerol*

The esterification of glycerol with acetic acid was studied for three different reactants mole ratios of acetic acid to glycerol 3:1, 6:1 and 9:1 at reaction temperature 110°C and catalyst loading of 5%w/w for 2 h. From Figs. 4–6 it can be seen that the conversion of glycerol increased with increased acetic acid loading (mole ratio) from 3:1 to 9:1 due to increase in availability of excess acetic acid for glycerol. With time the glycerol conversion and the yield of acetins increased. At low mole ratio 3:1 however, even the higher temperature of 110°C did not significantly improve glycerol conversion. For 6:1 the maximum glycerol conversion obtained is 92% with increase in yield towards monoacetin, diacetin and triacetin. The maximum conversion of 98.2% was obtained for 9:1 mole ratio of reactants at 110°C in 2 h and the yield for esters is also increased. For reaction conditions of 9:1 mole ratio of reactants, Catalyst A15 = 82.86 mmol H + /L in equivalent and temperature 110°C for 5 hrs, the conversion of glycerol is 97.1% and the selectivity of monoacetin is 7.59%, diacetin is 46.29% and triacetin is 43.23% [19].

3.3. *Effect of catalyst loading on glycerol conversion*

The effect of catalyst loading on esterification of glycerol with acetic acid was studied with 3%w/w, 5%w/w and 7%w/w for mole ratio of acetic acid to glycerol of 9:1 at reaction temperature of 110°C for 2 h. From Figs. 7–9 it was observed that the glycerol conversion increased with increase in catalyst concentration with the increase in active sites for esterification reaction. However at higher temperature of 110°C with increase in catalyst loading there is no significant variation in glycerol conversion and yield of acetins. Maximum conversion of glycerol and high yield of esters were obtained at 5 wt%.

3.4. *Kinetics of reaction*

The studies of the effects of the foregoing parameters on conversion and rates of reactions suggested that the reaction was

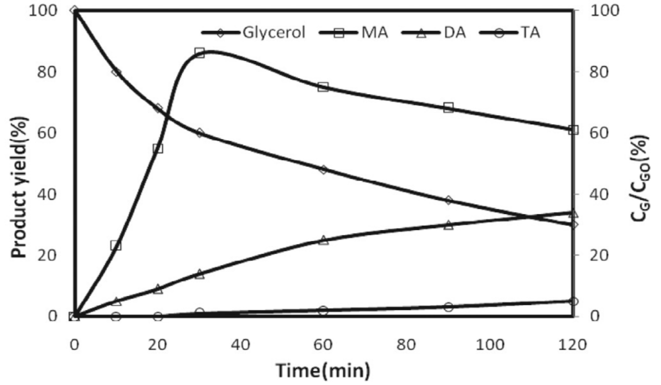

Fig. 7. Product distribution of glycerol esterification for catalyst loading of 3%w/w, mole ratio of acetic acid to glycerol (9:1) at 110°C.

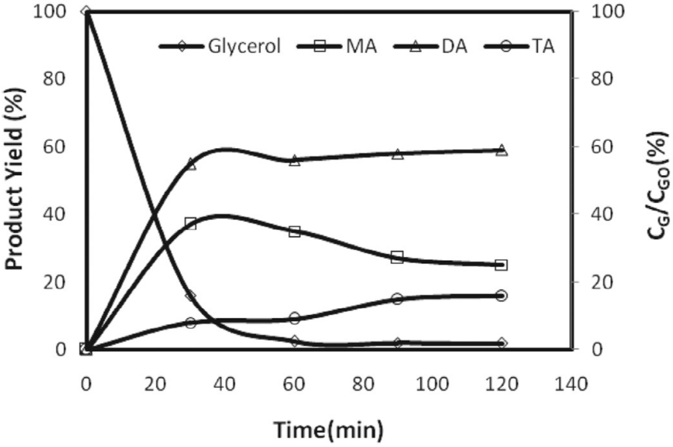

Fig. 8. Product distribution of glycerol esterification for catalyst loading of 5%w/w, mole ratio of acetic acid to glycerol (9:1) at 110°C.

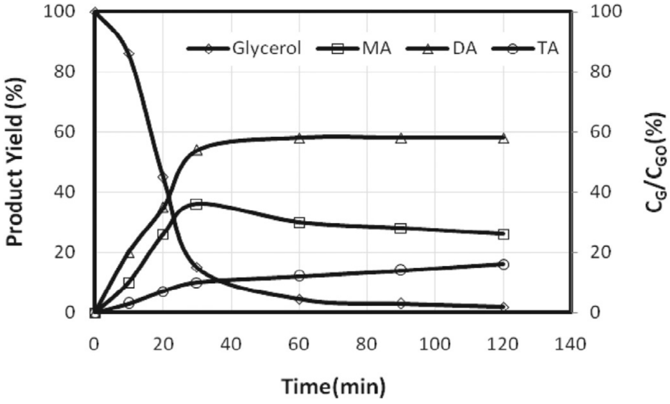

Fig. 9. Product distribution of glycerol esterification for catalyst loading of 7%w/w, mole ratio of acetic acid to glycerol (9:1) at 110°C.

free from internal diffusion and external mass transfer resistances. The rate of reaction for the glycerol esterification with acetic acid can be expressed with Langmuir–Hinshelwood–Hougen–Watson (LHHW) model, which assumes that there is a weak adsorption of both reactants and products on the surface of catalyst with surface reaction as the determining step. In LHHW model resistance term could be ignored. Since acetic acid was taken in excess over glycerol, the glycerol esterification reaction proceeds in forward direction for products before equilibrium, and the backward reactions in each step can be ignored for developing the kinetics. Then homogeneous pseudo first-order series reaction was used to describe the glycerol esterification [20]. The reaction under consideration is as follows

$$\text{Glycerol} + \text{Acetic Acid (excess)}$$

$$\text{Glycerol} + \text{Acetic Acid (excess)}$$
$$k_1 \rightarrow \text{Monoacetin}\, k_2 \rightarrow \text{Diacetin}\, k_3 \rightarrow \text{Triacetin}$$

$$-r_G = -dC_G/dt = k_1 C_G \tag{1}$$

$$r_{MA} = -dC_{MA}/dt = k_1 C_G - k_2 C_{MA} \tag{2}$$

$$r_{DA} = -dC_{DA}/dt = k_2 C_{MA} - k_3 C_{DA} \tag{3}$$

where G = glycerol, MA = monoacetin, DA = diacetin, $-r_G$, r_{MA}, r_{DA} are the rates of reaction of glycerol, monoacetin and diacetin. C_G, C_{MA} and C_{DA} are the concentrations of glycerol, monoacetin and diacetin at time t in the reactor.

If glycerol is the only source of MA, DA and TA, C_{GO} be the initial concentration of glycerol (t = 0), the balance at any time t is:

$$C_{GO} = C_G + C_{MA} + C_{DA} + C_{TA} \tag{4}$$

Let yield $Y = C_i / C_{G0}$ where i = G, MA, DA, TA, expressing the equations in terms of yield is given as:

$$-dY_G/dt = k_1 Y_G \tag{5}$$

$$-dY_{MA}/dt = k_1 Y_G - k_2 Y_{MA} \tag{6}$$

$$-dY_{DA}/dt = k_2 Y_{MA} - k_3 Y_{DA} \tag{7}$$

The best estimates of rate constants k_1, k_2 and k_3 were obtained by optimization method using the MATLAB. Hence k_1, k_2 and k_3 for different temperatures were determined. The temperature dependency of rate constant is well expressed by Arrhenius equation.

$$k_i = k_{i0} \exp(-\Delta E/RT)$$

$$\ln k_i = \ln k_{i0} - \Delta E/RT$$

where i = 1, 2, 3 and ki0 is the frequency factor.

Plotting a graph of log k_i vs 1/T, slope obtained is $-\Delta E / R$ from which value of activation energy is obtained. The apparent rate constants (k_1, k_2 and k_3) and their activation energies determined for acetic acid to glycerol mole ratio of 9:1 are at 5%w/w catalyst. The temperature dependency of rate constants is expressed as:

$$k_1(\text{min} - 1) = \exp(127 - 3006/T),\ E_1 = 24.99\,\text{kJ/mol}$$

$$k_2(\text{min} - 1) = \exp(258 - 3380/T),\ E_2 = 28.10\,\text{kJ/mol}$$

$$k_3(\text{min} - 1) = \exp(75984 - 6223/T),\ E_3 = 51.73\,\text{kJ/mol}$$

From the literature the rate constants were determined using polymath and the activation energies for conversion of glycerol to acetins using Amberlyst-15 were reported to be 13.90–57.26 kJ/mol [19].

4. Conclusions

The effect of temperature, molar ratio of reactants and catalyst loading on product distribution of esterification of glycerol with acetic acid is studied. It can be concluded that CsPWA as a catalyst was the obvious choice as it gave superior conversions clubbed with high yield for the desired products. The optimum parameters for the reaction were found to be temperature of 110°C, molar composition of 1:9 (glycerol:acetic acid) and 5% catalyst loading by weight of reaction mixture. The method suggested in this work produces high value products that find application in a plethora of industries ranging from food and pharmaceuticals to automobiles. The backbone of any chemical reaction is its underlying kinetics. So this work is approached to the estimation of the reaction rate constant. Experimental results of glycerol esterification confirmed the mechanism of consecutive reactions and the rate constants of k_1, k_2 and k_3 are found using MATLAB and their activation energies E_1, E_2 and E_3 were determined.

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