

Super phosphoric acid catalyzed esterification of Palm Fatty Acid Distillate for biodiesel production: physicochemical parameters and kinetics

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In the present study the esterification of palm fatty acid distillate (PFAD), a by-product from palm oil industry, in the presence of super phosphoric acid (SPA) catalyst was studied. The effects of various physico-chemical parameters such as temperature, PFAD to methanol molar ratio and amount of catalyst on the conversion of biodiesel were investigated. The percent conversion of FFA and properties of the biodiesel were determined following standard methodologies. Percent conversion of biodiesel was found to increase with the increase in PFAD to methanol molar ratio and at 1:12 molar ratio and 70°C temperature 95% conversion was achieved. Thermodynamic parameters were also evaluated in terms of Gibbs free energy, enthalpy and entropy at different molar ratio and temperatures. Both pseudo first and second order irreversible kinetics were applied to a wide range of experimental data. However, according to regression coefficient (R^2) the second order described better experimental behavior of kinetic data.

Keywords: Biodiesel, palm fatty acids distillate, Super Phosphoric Acid.

INTRODUCTION

Alkyl esters of fatty acids, commonly familiar as biodiesel, are produced from the vegetable oils and animal fats from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with alcohols¹. Lately it is much touted as a clean burning and non-toxic fuel of the future as a result of recent legislations that require a major reduction of vehicle emissions, as well as the increasing price of petroleum. Biodiesel has a higher cetane number than diesel fuel, no aromatics, almost no sulfur, and contains 10% to 11% oxygen by mass. These characteristics of biodiesel help reduce the noxious emissions in the exhaust gas compared to petroleum-based diesel fuel. It is almost neutral with regard to carbon dioxide emissions, and emits 80% fewer hydrocarbons and ~50% less particles. In addition, biodiesel production enjoys a positive social impact, by enhancing rural revitalization². In spite of its desirable properties as a diesel fuel substitute, biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel³. Albeit the pursuit of low cost alternative of non-food raw materials reports the use of numerous precursors, it has not brought techno-economically feasible solution hitherto for low-cost feedstock alternatives. Most bio-diesel plants still use conventional sodium hydroxide for process of transesterification requiring expensive refined oil feedstock.

Palm oil is one of the most widely used and versatile vegetable oils in the world. During the fatty acid stripping and deodorization stages of the palm oil refining process, a lower-value by-product, known as Palm Fatty Acid Distillate (PFAD) is generated. The price of PFAD is much cheaper than other refined oils which are major feed stocks for most of current biodiesel plants. Also, because PFAD consists of 85–95% fatty acids and 5–15% triglycerides, both of which are available for biodiesel production, recently there have been a few trials that directly utilize PFAD as a feedstock for biodiesel production. Chongkhong et al.⁴ investigated the production of fatty acid methyl ester (FAME) from PFAD having 93% FFA using sulphuric acid catalyst in batch and continuous reactor. The amount of FFA was reduced

from 93 wt% to less than 2 wt% at the end of the esterification process. Mongkolbovornkij et al.⁵ produced FAME by the esterification of PFAD in the presence of $\text{SO}_4\text{-ZrO}_2$ and $\text{WO}_3\text{-ZrO}_2$ catalyst. The authors observed that, among all synthesized catalysts, the reaction in the presence of $\text{SO}_4\text{-ZrO}_2$ and $\text{WO}_3\text{-ZrO}_2$ could enhance relatively high yield (84.9–93.7%) of FAME. Non-catalytic esterification of PFAD was accomplished in a single step by ensuring water-free reaction conditions whereby the acid value was reduced to below 0.5 (mg KOH/g). The reaction was completed (<0.5 mg KOH/g) within 180 min at relatively high temperature (>250°C) enough to be above boiling point of water and at moderate pressure (0.85–1.20 MPa) without any catalyst⁶. Yujaroen et al.⁷ (2009) investigated the effects of temperature, molar ratio of methanol to fatty acid (FA) components and water content in the feed on the esterification of palm fatty acid distillate (PFAD).

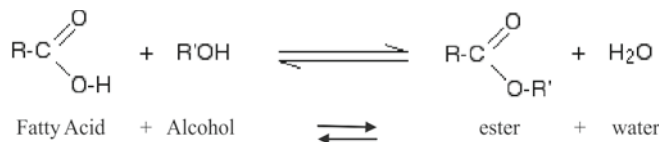
A major disadvantage of homogeneous catalyzed esterification reaction involving strong acid such as sulfuric acid is the difficulty in catalyst recovery and treatment, which generates a large amount of wastewater, increasing the overall operation cost of the process. Chances of acid corrosion of the reactors may pose additional problems. Generally the strength of acid is measured by the value of dissociation constant (K_a). The K_a value for Sulfuric acid is 1×10^3 where as for phosphoric acid the K_a value is 7.1×10^{-3} . $K_a > 1$ indicates strong acid and $K_a < 1$ indicates weak acid. From the K_a value it suggests that phosphoric acid is much weaker than sulfuric acid. Therefore comparatively super phosphoric acid (SPA) has got upper hand over sulfuric acid.

In the present work a new catalyst super phosphoric acid, which has not been reported earlier in literature, has been used. The aim of the work is to develop the process by using super phosphoric acid (SPA) catalyst and methanol to produce the biodiesel from PFAD feed stock containing < 90% FFA for biodiesel production. The effect of varying oil to alcohol molar ratios, catalyst (SPA) amount and temperature on the esterification reaction conversion were investigated. Also the kinetic study was carried out with a view to examine the influence

of operational variables on the kinetics of esterification of PFAD.

Reaction scheme

The reaction considered for the present study is the esterification of PFAD with methanol under acid catalyzed condition. The reaction is schematically depicted as follows:



The initial mechanistic step of acid catalyzed esterification of fatty acids is the protonation of the acid to give an oxonium ion (1), which can undergo an exchange reaction with an alcohol to give the intermediate (2), and this in turn can lose a proton to become an ester (3). Each step in the process is reversible, but in the presence of excess alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion as shown in Figure 1⁸.

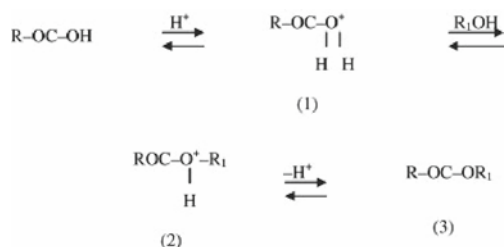


Figure 1. Mechanism of acid-catalyzed esterification of fatty acids⁸

MATERIAL AND METHODS

Chemicals used

PFAD was purchased from Gujarat Ambuja Exports Limited, Kadi, Gujarat. It was a light yellow solid at room temperature consisting of < 90 wt% FFA. Super phosphoric acid was purchased from National Chemicals Ltd, and methanol was purchased from S. D. Fine Chemicals Limited, Baroda, Gujarat, India. The super phosphoric acid used was a concentrated grade of phosphoric acid (85% P₂O₅) with density 2.05 g/cm³ and boiling point 530°C. All the chemicals were used without any further treatment.

Fatty acid profile of the PFAD

The fatty acid profile of the PFAD was determined by gas chromatography GC-2010 Shimadzu with flame ionization detector (FID) and capillary column (ZB-5HT Inferno, 15 m × 0.32 mm × 0.10 μm). The initial temperature of 50°C for 1 min was used; the heating rates were 15°C/min up to 180°C, 7°C/min up to 230°C and 10°C/min up to 380°C. The oil contains 38.79% Palmitic Acid, 2.47% Stearic Acid, 27.83% Oleic Acid, 7.07% Linoleic Acid and 20.15% Ureasic Acid by mass.

Esterification of Palm Fatty Acid Distillate

The initial acid value, a measure of the FFA content of the oil, was found to be 177.49 mg KOH/g that means the PFAD contains 89.19% FFA and remaining 10.8% is triglycerides. Esterification of FFA was carried out

with methanol and super phosphoric acid as the catalyst in a 1000 ml capacity three-necked round bottom flask equipped with mechanical stirrer, digital temperature controller, dean and stark water condenser and heating mantle. Different oil to alcohol ratios ranging from 1:6 to 1:12 were employed, catalyst amount was varied between 5 to 9% by mass. The reactions at 50 and 60°C temperature, the dean and stark condenser was kept open at the top as chances of escaping of vapors were nil, whereas at 70°C the condenser was closed from the top to avoid vapor escaping from the condenser; slightly elevated pressure. The mixture was stirred at the same rate for all runs. The effects of molar ratio, reaction temperature, and catalyst amount on the acid-catalyzed conversion of free fatty acids to methyl esters were investigated for different reaction conditions.

After completion of reaction the content was allowed to settle for overnight. The Lower layer of methyl ester was separated out for further purification from upper layer containing the excess methanol, catalyst and small amount of water produced during esterification. The separated lower layer was purified using hot demineralised water. After washing, the methyl ester was heated up above 100°C to remove excess methanol and water. Then, the transesterification of the ester phase was carried out using KOH as catalyst under optimum conditions of catalyst 1% by weight at 60°C with oil to methanol ratio of 1:6. The amount of KOH (10 g per liter of pretreated PFAD oil) was calculated based on the amount needed to neutralize the unreacted acids (i.e., 5 mg KOH/g) after esterification plus 0.5% for catalyst³. The acid value during the esterification reaction was determined by the standard titrimetry procedure. The fuel properties were determined by standard American Society for Testing and Materials (ASTM) methods. The progress of the reaction was monitored by measuring the elimination of the FFAs using American Oil Chemists' Society Official Method Cd 3a-63 for Acid Value, AOCS, 1988. To study the effects of temperature experiments were carried out at three different temperatures viz 50, 60 and 70°C.

Analytical methods

Determination of acid value

Acid value (AV) is expressed in mg KOH required to neutralize the free fatty acids present in 1 g sample and has been calculated by using eq. (1).

$$AV = \frac{V \times c \times 56.1}{m} \quad (1)$$

Where AV is acid value of the sample, V is the volume of the KOH solution of the titration (ml), c is the concentration of the KOH solution (mol/L), m is the mass of the sample (g), and 56.1 is the molecular weight of KOH. The FFA conversion was calculated by using the Eq. (2)

$$FFA\text{conversion} (\%) = \left(1 - \frac{AV_2}{AV_1}\right) \times 100 \quad (2)$$

Where, AV₁ is the initial acid value of the mixture and AV₂ is the final acid value of the mixture after the reaction. This procedure was developed according to ISO 660, 1996.

Density and viscosity of biodiesel

The density of biodiesel was measured by using the standard pycnometer bottle with reference to water at ambient temperature and then tested for biodiesel. The viscosity of the biodiesel was measured (after knowing the density) with Ostwald U-tube viscometer.

Flash point, cloud point and carbon residue

The flash point of the biodiesel was determined by the method of ASTM D93, using Pensky-Martens closed cup apparatus. The pour point was measured following ASTM D97 method by recording the onset temperature of biodiesel transition from translucent to opaque. The carbon residue of the biodiesel sample was determined by using the conradson carbon apparatus following ASTM D89 method.

Estimation of thermodynamics parameters

The activation energy of the reaction mixture at different molar ratio and different temperature was calculated by using the Arrhenius equation as shown in Eq. (3).

$$K = A \cdot \exp\left[\frac{-\Delta E}{RT}\right] \quad (3)$$

Where A is frequency factor and $-\Delta E$ is the activation energy of the reaction mixture.

The other thermodynamic properties such as Gibbs free energy were determined using the Eq. (4)

$$\Delta G = -RT \ln K^* \quad (4)$$

and enthalpy and entropy were determined by using Eq. (5)

$$\ln K^* = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (5)$$

Kinetic Model

The kinetic studies presented in the work assume both pseudo first and second order irreversible kinetics. It is assumed that the esterification occurs via the initial heterogeneous regime, followed by the pseudo-homogenous regime where the mass transfer and the chemical reaction control the overall process kinetics, respectively. These regimes are well-recognized by the other researchers^{9, 10}. The esterification of FFA is the irreversible pseudo second-order reaction in the early period of the second phase, as shown by¹¹. Due to the excess of methanol and the low product concentration, one can expect the reverse reactions to be negligible.

The pseudo-first order rate equation can be written as shown in Eq. (6)¹².

$$\ln \frac{1}{(1 - X_A)} = k t + C_1 \quad (6)$$

Where k is reaction rate constant for the irreversible pseudo-first-order reaction and C_1 is the integration constant.

For pseudo-second order

$$-r_A = -\frac{dC_A}{dt} = k C_A^2 \quad (7)$$

Where k is reaction rate constant for the irreversible pseudo-second-order reaction. Integration of Eq. (7) yields:

$$-r_A = -\frac{dC_A}{dt} = k C_{A0} t + C_1 \quad (8)$$

The reaction rate and integration constants can be estimated from the slope and intercept of the linear dependence of $1/(1 - X_A)$ versus time, respectively.

The reaction rate close to equilibrium is represented by Eq. (9)

$$-r_A = -\frac{dC_A}{dt} = k_2^{\rightarrow} C_A C_B - k_2^{\leftarrow} C_R C_S \quad (9)$$

Where k_2^{\rightarrow} and k_2^{\leftarrow} are the reaction rate constants for the forward and reverse reactions, respectively and C_B , C_R and C_S are the actual concentrations of methanol, ester and water, respectively.

The equilibrium constant K^* can be calculated from the equilibrium degree of FFA conversion, X_{Ae} , which can be experimentally determined by Eq. (10)

$$K^* = \frac{3M X_{Ae}^2 - (1 + 3M)X_{Ae} + 1}{3M X_{Ae}^2} \quad (10)$$

Where $M = C_{A0}/C_{B0}$ is the initial molar ratio of PFAD to methanol.

RESULTS AND DISCUSSION

Effect of Molar ratio

The effect of molar ratio on % conversion of PFAD was investigated at four different molar ratios of oil (PFAD) to methanol viz. 1:6, 1:8, 1:10 and 1:12 with three combinations of constant temperatures (50°, 60°, and 70°C) and super-phosphoric acid catalyst concentrations (5%, 7% and 9% by). The results are presented in Figure 2. As observed from Figure 2, the % conversion of PFAD increased with the increase in molar ratio of methanol to PFAD. At 5% catalyst concentration, the maximum conversion of 90.63% was achieved at 60°C and 1:10 molar ratio, whereas at 7% catalyst the maximum conversion was 92% at 70°C temperature and 1:10 molar ratio. At 9% catalyst the conversion was 95% highest of all the catalyst concentration at 1:12 molar ratio. A perusal of the Figure 2 also indicates that the percent conversion of PFAD decreased marginally at the molar ratio of 1:10 with 9% catalyst concentration and at 60°C temperature, but once again at 1:12 molar ratio the conversion increased. This decrease in conversion was

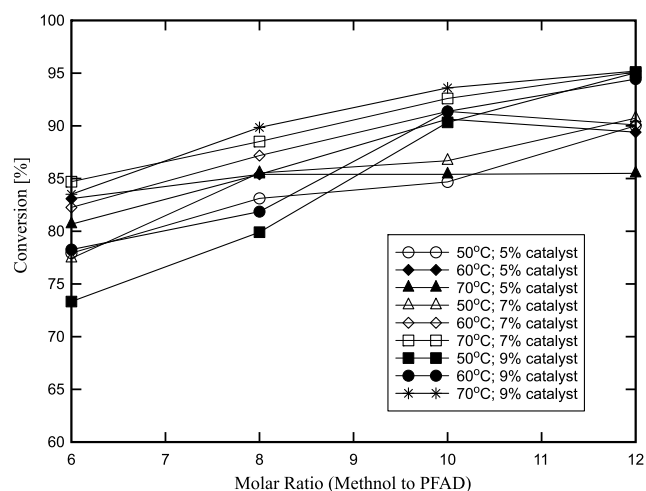


Figure 2. Effect of molar ratio of PFAD to methanol on the percent conversion of PFAD at various combination of constant temperature and catalyst concentration

plausibly due to dilution of catalyst concentration and also high methanol content.

The esterification reaction between PFAD and methanol follows a reversible path. Higher equilibrium conversion can only be accomplished if the backward reaction is minimized. Conventionally, the means for retardation of the rate of backward reaction involve either the efficient removal of water continuously or the use one of the reactants in excess (methanol in the present study). However, under the present experimental setup it was not easy to remove water, as the system was a closed one. Thus, the option of using excess methanol was employed in the present study. Further, it merits mentioning that the dependency of the conversion of PFAD on the mole ratio assumes more significance in the present case as compared to the case of reaction between other fatty acids and isopropanol. This can be attributed to the formation of two different layers during the progress of the reaction which ensures easy removal of water of reactions into the aqueous layer while the reaction usually occurs at the emulsion interface of the droplets formed in the reaction mixture. But in case of isopropyl alcohol the higher solubility of PFAD in isopropyl alcohol ensures homogeneous nature of the resultant system¹³. The similar trend of increase in PFAD conversion with PFAD to methanol mass ratio was observed by Chin et al.¹⁴, however with sugar cane bagasse as solid catalyst. Although, excess amount of methanol was sensibly applied in order to shift the equilibrium of the esterification to the forward direction, the use of too high amount of methanol could increase the water content from commercial methanol and cost of production. Hence, an optimum methanol ratio should be chosen on the foundation of general economics and the equilibrium conversion¹⁴.

Effect of Catalyst concentration

Effect of catalyst concentration was investigated at three different concentrations viz. 5%, 7%, and 9% (percent by mass of PFAD) of catalyst loading with constant reaction temperature (60°C), and molar ratio 1:12 (PFAD:Methanol). The effect of catalyst concentration on the percent conversion of PFAD has been shown in Figure 3. It can be observed from the Figure that increase in rate of reaction is significant for increase in the

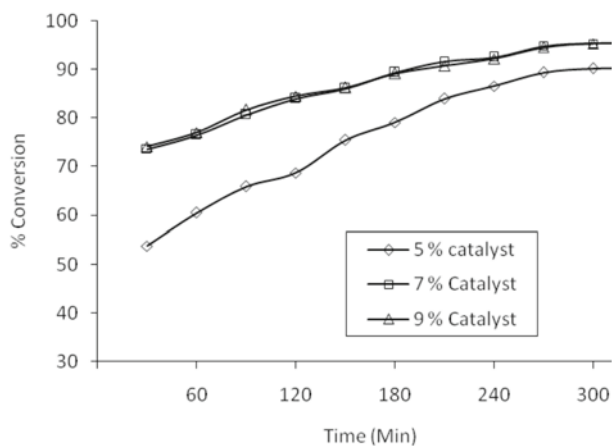


Figure 3. Effect of catalyst concentration on the percent conversion of PFAD at constant temperature of 60°C and PFAD to methanol molar concentration of 1:12

catalyst concentration from 5% to 7% as compared to further increase in the catalyst concentration from 7% to 9%. Also, an increase in the catalyst concentration beyond 9%, did not result in any further increase in rate of reaction and equilibrium conversion (data not shown). Kelkar et al.¹⁵ and Wen et al.¹⁶ have reported similar effects of catalyst concentration on the ultrasound assisted esterification reactions.

Reaction rates in acid-catalyzed processes may also be increased by the use of larger amounts of catalyst. Typically, catalyst concentrations in the reaction mixture have ranged between 1 and 5 wt % in most academic studies using sulfuric acid¹⁷. Canakci and Van Gerpen³ used different amounts of sulfuric acid (1, 3, and 5 wt %) in the transesterification of grease with methanol. In these studies, a rate enhancement was observed with the increased amounts of catalyst, and ester yield went from 72.7 to 95.0% as the catalyst concentration was increased from 1 to 5 wt %. Crabbe et al.¹⁸ has also verified the same kind of trend. However, that large quantity of acid catalyst can promote ether formation by alcohol dehydration¹⁹. Sridharan and Mathai²⁰ noticed that the transesterification of small esters was retarded by the presence of spectator polar compounds. According to their findings, the presence of polar compounds during acid-catalyzed alcoholysis reactions significantly reduced reaction rates. These authors attributed this retardant effect to the interference that polar compounds pose to the reaction by competing for hydrogen ions, hindering the availability of these ions for catalysis. Considering the strong affinity that sulfuric acid has for water, it is likely that the acid will interact more strongly with water molecules than with alcohol molecules. Thus, if water is present in the feedstock or produced during the reaction, the acid catalyst will preferentially bind to water, leading to a reversible type catalyst deactivation.

Effect of reaction temperature

The equilibrium conversion of PFAD into methyl esters via esterification has noticeable dependency on the reaction temperatures. Percent conversion of PFAD as a function of temperature is presented in Figure 4 for different combinations of constant PFAD to methanol

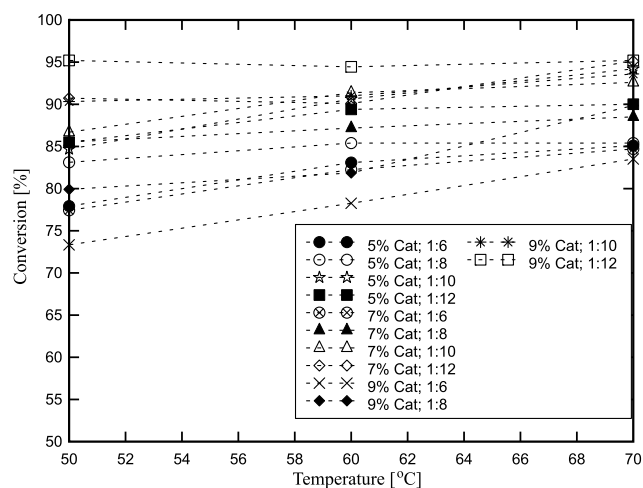


Figure 4. Effect of reaction temperature on the percent conversion of PFAD at various combinations of constant PFAD to methanol molar ratio and catalyst concentration

molar ratio and catalyst concentrations. The general trend of Figure 4 indicates that the conversion of PFAD increased with the increase in reaction temperature irrespective of catalyst concentration and molar ratio. Maximum conversion was observed at 70°C, 9% catalyst concentration and 1:12 molar ratio amongst all the combinations. The increased PFAD conversion might be not only due to the effect of increase of the reaction rate by increasing temperatures but also some improvement of the mass transfer between reactant and catalyst²¹. The results showed that the reaction was typically endothermic; when the temperature increased, the final conversion increased as well. This result corroborates those obtained by previously reported^{4,22}. However, for an increase in temperature from 60 to 70°C the equilibrium conversion seemed to be marginally affected. Further higher temperatures (>70°C) could not be evaluated in the present work due to limitations of the experimental system but based on the trends it is not expected to yield a significant increase in the equilibrium conversions. Besides, in case of 5% catalyst and 1:12 molar ratio, the conversion decreased from 90% to 83%. This inhibition effect can be attributed to the equilibrium constraint, whereby esterification reaction might have shifted to the left, favoring the hydrolysis of the ester due to water formation during forward reaction²³. Freedman et al.²⁴ observed the complete conversion in the butanolysis of soybean oil catalyzed by 1 wt% H₂SO₄ at 117°C in 3 h as compared to 77°C which required 20 hrs. At higher temperatures, the extent of phase separation decreases and rate constants increase, due to the higher temperature as well as improved miscibility, leading to substantially shortened reaction times. Under such conditions, high-FFA feed-stocks (e.g., 44 wt% FFAs) could easily be transformed with continuous water removal. However,

side reactions such as alcohol etherification could also be observed under such severe conditions, which ultimately may lead to decrease in conversion²⁵. In addition, a higher temperature will provide a higher possibility of methanol losing and produced darker product⁴.

Since the effect of operating temperature was more significant than the other operating parameters such as the mole ratio and catalyst concentration, it was thought prudent to obtain more kinetic details in terms of the activation energy for the reaction. The feasibility of a reaction can be adjudged from the thermodynamic parameters. Arrhenius equation was used to study the influence of temperature on specific reaction rate. Rate constants obtained from the kinetics study at various temperatures were fitted with the Arrhenius equation. The plot of ln k as a function of the reciprocal temperature (1/T), the values of Activation energy and frequency factor were obtained for three different molar ratios. Figure 5 shows the variation of the rate constant for the forward desired reaction with temperature.

The value of the activation energy for the esterification reaction using 1: 10 molar ratio of oil (PFAD) to methanol was found out to be 5.35×10^3 kcal/mol. Deshmane et al.¹³ reported that the activation energy of the acid catalyzed synthesis of isopropyl ester from palm fatty acid distillate was 1.07×10^4 kcal/mol although in presence of ultrasonic irradiation. There was a decreasing trend of the activation energy, as the molar ratio of PFAD to methanol increased. For the molar ratio 1:30 the activation energy of esterification was found out to be 2.27×10^3 kcal/mol, which was the lowest amongst the three molar ratios studied. Table 2 represents the Gibbs free energy, enthalpy and entropy at different molar ratio and different temperatures range of 313 K to 333 K using Eqs. (4) and (5). The Gibbs free energy increased

Table 1. Thermodynamic properties of reaction mixture at different molar ratio and temperature

1:10 oil to methanol molar ratio, 10% catalyst			
Temperature [K]	Gibbs free energy ΔG [Cal/mol]	Enthalpy ΔH [cal/mol]	Entropy ΔS [cal/mol]
313	-146.482	5865.624	18.27
323	43.66422		
333	218.8034		
1:20 oil to methanol molar ratio, 10% catalyst			
313	-316.689	3419.458	22.87
323	95.07024		
333	235.227		
1:30 oil to methanol molar ratio, 10% catalyst			
313	334.3514	1903.546	7.07
323	345.0335		
333	478.7442		

Table 2. Reaction rate constant *k* for pseudo-second order reaction and equilibrium constant *K*^{*} values at different temperatures

1:10 PFAD to methanol molar ratio, 10 % catalyst					
C _{A0} [mol ml ⁻¹]	C _{B0} [mol ml ⁻¹]	Molar Ratio [mol oil/mol methanol]	Temperature [K]	<i>k</i> [ml mol ⁻¹ min ⁻¹]	<i>K</i> [*] [ml mol ⁻¹ min ⁻¹]
0.0014	0.0139	0.1	313	2.85	1.72
			323	7.85	0.855
			333	9.28	0.467
1:20 PFAD to methanol molar ratio, 10 % catalyst					
0.000898	0.0179	0.05	313	5.61	3.23
			323	30.33	0.711
			333	32.58	0.6290
1:30 PFAD to methanol molar ratio, 10 % catalyst					
0.000652	0.0194	0.033	313	141.1	0.189
			323	215.88	0.290
			333	233.12	0.290

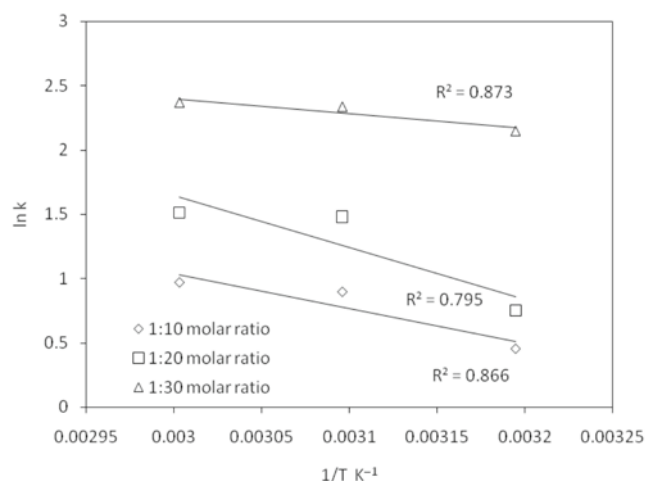


Figure 5. Influence of temperature on the specific reaction rate (Arrhenius equation) at three different molar ratios of PFAD to methanol

with the increase in molar ratio and found out to be the highest value of 478.74 cal/mol at molar ratio of 1:30, whereas enthalpy and entropy of the mixture decreased with the increase in molar ratio and were found out to be 1903.54 cal/mol and 7.07 cal/mol respectively. Plot of $\ln K^*$ against $1/T$ gave a straight line (not shown) having slope is $\Delta H/R$ and intercept $-\Delta S/R$.

Reaction Kinetics

Biodiesel consists of methyl or ethyl esters of long chain fatty acids derived from triglycerides (TG) by alcoholysis with low molecular weight alcohols. The formation of surface active compounds like mono and diglycerides facilitate formation of a stable emulsion of very small drops. As a result the reaction mixture are presumed to be in a pseudo-homogeneous system, where chemical reaction controls the kinetics¹². In line with that, the present kinetic study assumed an irreversible reaction mechanism of pseudo second order away from equilibrium stage. Figure 6 and Figure 7 presents the best fitting results for the first stage of esterification under pseudo first order and pseudo second order respectively. According to regression coefficient (R^2) the second order describes better experimental behavior of data.

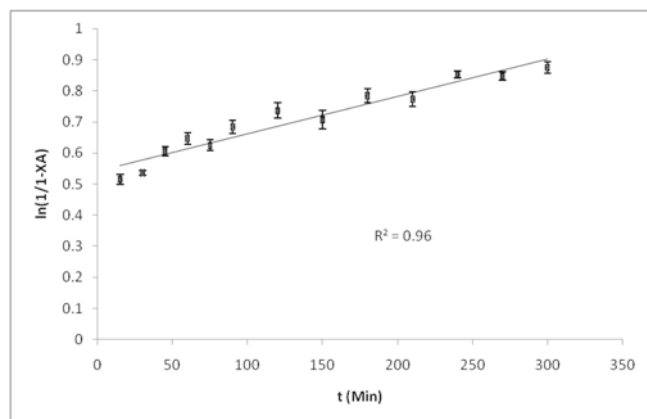


Figure 6. The best fitting results of the irreversible reaction stage of Pseudo-first order, reaction initial conditions 1:10 oil to methanol molar ratio, 60°C temperature and 10% catalyst by weight. The values presented for each data point in the Table are the average of a minimum of duplicate experiments and percentage error is less than $\pm 1.2\%$

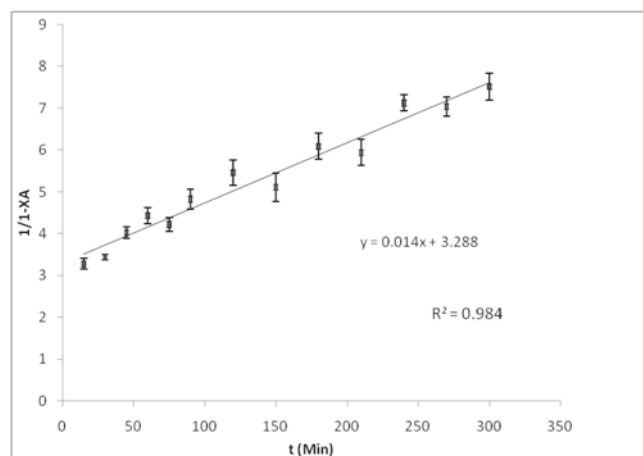


Figure 7. The best fitting results of the irreversible reaction stage of Pseudo second order, reaction initial conditions 1:10 oil to methanol molar ratio, 60°C temperature and 10% catalyst by weight. The values presented for each data point in the Table are the average of a minimum of duplicate experiments and percentage error is less than $\pm 1.2\%$

Using Eq. (8) the constant C_1 value was found out to be 3.31; the reaction rate constant value k was 0.013/ C_{A0} . Considering that 50 gm of oil and varying mass of methanol based on the oil to alcohol molar ratio selected, methanol were weighed and mixed in round bottom flask and mixed in flask every time, and that the mixture average density based on the total volume at the beginning of each reaction was 0.8212 g/ml. The average molecular weight of the oil (273.03) was estimated based on the composition given in Table 2. The initial concentrations of oil (C_{A0}), methanol (C_{B0}), molar ratio M and the corresponding reaction rate constant k for pseudo-second order reaction and equilibrium constant K^* values at different temperatures are tabulated in Table 3 at three different temperatures. As expected, all the rate constants increased by increasing the reaction temperature.

Table 3. Property comparison of PFAD biodiesel with petro-diesel and ASTM D6751 standard

Fuel properties	PFAD Biodiesel [present study]	ASTM D6751
Specific gravity [kg/m ³ at 15°C]	862	860–900
Kinematic viscosity at 40°C [mm ² /s]	5.4	4–6
Flash point, °C	190	100–170
Cloud point, °C	18	–3 to 12
Pour point, °C	16	–15 to 10
Acid value [mg KOH/g]	0.91	0.8 max.
Carbon residue [wt%]	1	–

Characterization of PFAD biodiesel

The quality control of biodiesel is of paramount importance in view of its commercialization and market acceptance. The PFAD biodiesel obtained in this work is tested for its important properties and were compared with the ASTM D6751 standard, 2012. These are presented in Table 4. The calculated properties of the biodiesel, obtained are close to values, reported by other authors^{4,30}. Some general parameters, like specific gravity, kinematic viscosity and content of sulfur, mainly depend on the choice of vegetable oil and cannot be influenced by different production methods or purification steps.

The flash point, however, strictly corresponds to the content of methanol and the viscosity correlates with the content of unreacted triglycerides.

A perusal of the properties indicates that the process could yield biodiesel having comparable properties with the standards. But the pour point of the PFAD biodiesel was a bit higher than that of the standard as the principal components of the PFAD were saturated FFA. However, the pour point could be depressed by blending PFAD biodiesel with diesel in suitable ratios. Therefore, the PFAD biodiesel obtained in the present study has the potential to be an alternative to the petrodiesel for using in unmodified diesel engines. Conradson carbon residue is one of the most important indicators for the quality of biodiesel despite the fact that the experimental procedure for determination seems to be an old-fashioned method compared to modern analytical techniques, it can be shown in different investigations that this parameter is an excellent indicator for the quality of biodiesel²⁶; it corresponds strictly to the content of glycerides²⁷, as well as free fatty acids, soaps, remaining catalyst and other impurities.

Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters is important to control within an acceptable level to avoid negative impacts on fuel injector system performance. Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose. Pour point of a fuel reflects its cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petro-diesel. Normally either pour point or CFPP are specified. Pour point is the lowest temperature at which the oil specimen can still be moved. French and Italian biodiesel specifications specify pour point where as others specify CFPP. Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Conradson Carbon Residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. Biodiesel based on fatty acid ethyl esters has the advantage of being entirely based on renewable raw materials and moreover it displays a higher specific energy, higher cetane index, better lubricity, and enhanced cold flow behavior because of the lower melting points of ethyl esters²⁸.

Economic outlook

Biodiesel is probably the only alternative fuel currently available that has an overall positive life cycle energy balance – it yields as much as 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle, compared to only 0.83 units for petroleum diesel²⁹. The feasibility of a biodiesel production process includes both technological and economic aspects. Thus, apart from assessing the technological feasibility of the different process designs for biodiesel, an economic

evaluation of these processes is highly needed. In the present study using PFAD as raw material the approximate cost of production of biodiesel was estimated to be 192.63 INR (3.1 US\$) per liter. The estimation was based on 1: 4 PFAD to oil molar ratio and considering 4.9 units of electricity consumed for one batch of reaction. The actual market price including local taxes of PFAD, methanol and super phosphoric acid were considered to have a more realistic estimate.

The major advantage of super phosphoric acid being the weaker acid as compared to sulfuric acid so the cost of storage, handling and the MOC for materials will be reduced. On the other hand the critical issue is that the high concentration of catalyst as high as 9% is really a costly affair, but that can be addressed by recovering the acid from the waste stream; if the reaction can be performed under pressure, the catalyst quantity can be reduced. Also other alcohols such as propanol, butanol can reduce the quantity of catalyst as they are having higher boiling point compared to methanol. The high temperature favors the high reaction rate for acid catalyst³. This way use of high quantity of catalyst can be minimized.

The topic that arouses controversy today is whether biodiesel is an economically sustainable initiative, given the costs of production, fossil and non-fossil energy spent for producing energy from biodiesel, opportunity costs for the respective plant oils, and the contending fuels (mainly fossil fuels) already available. Most biodiesel plants use the conventional sodium hydroxide/sodium methoxide-based transesterification process, which requires highly priced refined oil feedstock. It also makes the much-debated “food vs. fuel” argument a non-issue as PFAD is generally sold as a source of industrial fatty acids for non-food applications. It has also been used as a fuel in power plants and industrial boilers. But the fact remains that biodiesel produced from PFAD appears pretty expensive than other fuel options. Thus, if technology improvements succeed in bringing down costs, it is likely to play a major role in the economy in the future. Additionally, rigorous techno-economic analyses are necessary to draw a cost-effective comparison between biodiesel from PFAD and the various other conventional feedstocks. An economic survey, based on feed stock estimation, turns out to somewhat complicated when applied in practical terms. This is mostly because of the intervening large number of other techno-economic parameters. The socially relevant costs of bringing any fuel to market must also include such factors as pollution and other short-term and long-term environmental costs, as well as direct and indirect health costs. When these factors are taken into consideration, together with the initial cost competitiveness, biodiesel from low cost feed stocks such as PFAD is surely the most logical choice as a worldwide energy medium.

CONCLUSIONS

The potential of palm fatty acid distillate (PFAD), a byproduct from production of consumable palm oil, was used as feedstock for biodiesel production using a novel catalyst, super phosphoric acid. The effect of various physico-chemical parameters such as, oil to alcohol

molar ratios, catalyst (SPA) amount and temperature on the esterification reaction conversion was investigated. The percent conversion of PFAD to biodiesel increased with the increase in molar ratio and at 1:12 molar ratio 95% conversion was achieved. Also, the conversion of PFAD increased with the increase in reaction temperature irrespective of catalyst concentration and molar ratio. Maximum conversion was obtained at 70°C, 9% catalyst concentration and 1:12 molar ratio amongst all the combinations. The increase in percent conversion with molar ratio, temperature and catalysts concentration underscores the need to optimize the process variables to economize the cost of production. The kinetic study was carried out following the pseudo first order and second order irreversible kinetics amongst which the second order kinetics better described the experimental behavior of data according to regression coefficient (R^2). The fuel properties of the biodiesel produced in the process met the bio diesel standards and were comparable with the literature values. The data obtained in the present study could be used as a guideline to scale the process for a continuous pilot-plant construction with small production demand on an industrial scale.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. V S Patel, Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat.

LITERATURE CITED

1. Van, Gerpen, J., Shanks, B., Pruszko, R., Clements, D. & Knothe, G. (2004). Biodiesel production technology NREL/SR-510-36244. Springfield VA: Iowa State University and Renewable Products Laboratory USDA/NCAUR.
2. Kiss, A.A., Dimian, A.C. & Rothenberg, G. (2006). Solid Acid Catalysts for Biodiesel Production Towards Sustainable Energy. *Adv. Synth. Catal.* 348 (1–2), 75–81. DOI: 10.1002/adsc.200505160.
3. Canakci, M. & Van, Gerpen, J. (1999). Biodiesel production via acid catalysis. *Transactions of ASAE* 42(5), 1203–1210. DOI: 0001-2351/99/4205-1203.
4. Chongkhong, S., Tongurai, C., Chetpattananondh, P. & Bunyakan, C. (2007). Biodiesel production by esterification of palm fatty acid distillate. *Biomass and Bioenergy* 31(8), 563–568. DOI: 10.1016/j.biombioe.2007.03.001.
5. Mongkolbovornkij, P., Champreda, V., Sutthisripok, W. & Laosiripojana, N. (2010). Esterification of industrial-grade palm fatty acid distillate over modified ZrO₂ (with WO₃-, SO₄ -and TiO₂-): Effects of co-solvent adding and water removal. *Fuel Processing Technology* 91(11), 1510–1516. DOI: 10.1016/j.fuproc.2010.05.030.
6. Cho, H.J., Kim, S.H., Hong, S.W. & Yeo, Y.K. (2012). A single step non-catalytic esterification of palm fatty acid distillate (PFAD) for biodiesel production. *Fuel* 93(1), 373–380. DOI: org/10.1016/j.fuel.2011.08.063.
7. Yujaroen, D., Goto, M., Sasaki, M. & Shotipruk, A. (2009). Esterification of palm fatty acid distillate (PFAD) in supercritical methanol: effect of hydrolysis on reaction activity. *Fuel* 88(10), 2011–2016. DOI: 10.1016/j.fuel.2009.02.040.
8. Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management* 50(1), 14–34. DOI: 10.1016/j.enconman.2008.09.001.
9. Nouredini, H. & Zhu, D. (1997). Kinetics of transesterification of soybean oil. *J. Ame. Oil Chem. Soc.*, 74(11), 1457–1463. DOI: 10.1007/s11746-997-0254-2.
10. Vicente, G., Martinez, M., Aracil, J. & Esteban, A. (2005). Kinetics of sunflower oil methanolysis. *Industrial & Engineering Chemistry Research* 44(15), 5447–5454. DOI: 10.1021/ie040208j.
11. Darnoko, D. & Cheryan, M. (2000). Kinetics of palm oil transesterification in a batch reactor. *J. Ame. Oil Chem. Soc.* 77(12), 1263–1267. DOI: 10.1007/s11746-000-0198-y.
12. Stamenkovic, O.S., Todorovic, Z.B., Lazic, M.L., Veljkovic, V.B. & Skala, D.U. (2008). Kinetics of sunflower oil methanolysis at low temperatures. *Biores. Technol.* 99(5), 1131–1140. DOI: 10.1016/j.biortech.2007.02.028.
13. Deshmane, V.G., Gogate, P.R., & Pandit, A.B. (2009). Ultrasound assisted synthesis of isopropyl esters from palm fatty acid distillate. *Ultrasonics Sonochemistry* 16(3), 345–350. DOI: 10.1016/j.ultsonch.2008.09.004.
14. Chin, L.H., Abdullah, A.Z. & Hameed, B.H. (2012). Sugar cane bagasse as solid catalyst for synthesis of methyl esters from palm fatty acid distillate. *Chem. Engine. J.* 183(1), 104–107. DOI: 10.1016/j.cej.2011.12.028.
15. Kelkar, M.A., Gogate, P.R. & Pandit, A.B. (2008). Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation. *Ultrasonics Sonochemistry* 15(3), 188–194. DOI: 10.1016/j.ultsonch.2007.04.003.
16. Wen, B., Eli, W., Xue, Q., Dong, X. & Liu, W. (2007). Ultrasound accelerated esterification of palmitic acid with vitamin C. *Ultrasonic Sonochemistry* 14(2), 213–218. DOI: 10.1016/j.ultsonch.2006.02.003.
17. Freedman, B., Pryde, E.H. & Mounts, T.L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Ame. Oil Chem. Soci.* 61(10), 1638–1643. DOI: 10.1007/BF02541649.
18. Crabbe, E., Nolasco-Hipolito, C., Kobayashi, G., Sonomoto, K. & Ishizaki, A. (2001). Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. *Process Biochem.* 37(1), 65–71. DOI:10.1016/S0032-9592(01)00178-9.
19. Keyes, D.B. (1932). Esterification processes and equipment. *Ind. Engine. Chem. Res.* 24(10), 1096–1103. DOI: 10.1021/ie50274a003.
20. Sridharan, R. & Mathai, I.M. (1974). Transesterification reactions. *J. Sci. Ind. Res.* 33, 178–187.
21. Caetano, C.S., Fonseca, I.M., Ramos, A.M., Vital, J. & Castanheiro, J.E. (2008). Esterification of free fatty acids with methanol using heteropolyacids immobilized on silica. *Catalysis Communications* 9(10), 1996–1999. DOI: 10.1016/j.catcom.2008.03.036
22. Berrios, M., Siles, J., Martin, M.A. & Martin, A. (2007). A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. *Fuel* 86(15), 2383–2388. DOI: 10.1016/j.fuel.2007.02.002.
23. Kusdiana, D. & Saka, S. (2004). Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresource Technology* 91(3), 289–295. DOI: 10.1016/S0960-8524(03)00201-3.
24. Freedman, B., Butterfield, R.O. & Pryde, E.H. (1986). Transesterification kinetics of soybean oil. *J. Ame. Oil Chem. Soc.* 63(10), 1375–1380. DOI: 10.1007/BF02679606.
25. Khan, A.K. (2002). Research into biodiesel kinetics & catalyst development. Uni of Queensland Brisbane Queensland.
26. Hodl, P. & Schindlbauer, H. (1994). Gas chromatographic determination of free glycerol involving extraction. In *Handbook of Analytical Methods for Fatty Acid Methyl Esters used as Diesel Fuel*. FICHTE Institute, Vienna.
27. Mittelbach, M., Pokits, B. & Silberholz, A. (1992). Diesel fuel derived from vegetable oils, IV: production and fuel properties of fatty acid methyl esters from used frying oil. In *Liquid Fuels from Renewable Resources*, Proc. Alternative Energy Conj, (14–15 December 1992) Ame. Soc. Agric. Eng. Michigan, USA, p. 74.
28. Boros, L., Batista, M.L.S., Vaz, R.V., Figueiredo, B.R., Fernandes, V.F.S., Costa, M.C., Krhenbuhl, M.A., Meirelles,

A.J.A. & Coutinho, J.A.P. (2009). Crystallization behavior of mixtures of fatty acid ethyl esters with ethyl stearate. *Energy Fuels* 23(9), 4625–4629. DOI: 10.1021/ef900366z.

29. Sheehan, J., Camobreco, V., Duffield, J., Graboski, M. & Shapouri, H. (1998). National Renewable Energy Laboratory. Golden, Colorado, 314.

30. Malvade, A.V. & Satpute, S.T. (2013). Production of Palm fatty acid distillate biodiesel and effects of its blends on performance of single cylinder diesel engine. *Procedia Engineering* 64(1), 1485–1494. DOI: 10.1016/j.proeng.2013.09.230.