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Optimisation of Reaction Time and Methanol Consumption for Esterification of Palm Fatty Acids and its Kinetic Study

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Abstract : Palm fatty acids are chosen for esterification . The esterified oil is obtained in the presence of fatty acids and methanol. Various parameters are considered for the esterification of fatty acids. Amount of methanol has added in different molar ratio and vigorous stirring was employed at constant temperature. The heating schedule of complete reaction system is differed. These parameters lead effects in the product formation and its purity.
The esterification reaction of FFAs in the esterified production from PFAD in batch reactor system employing methane sulphonic acid as the catalyst has been studied. The optimum condition was observed at 14 hours has been studied , the amount of methanol added was 180gm , catalyst concentration of 1-2%(w/w) , stirring rate 400 rpm , and at reaction temperature of 60 – 75 ^{0}C . At the optimum condition , the achieved conversion of FFAs was found to be 99.17%. A kinetic model for the esterification of FFAs was established using the second – order homogeneous kinetic model involving the rate of mass transfer.
Keywords: esterification, optimisation, conversion, mechanism, kinetics.

Broad Initiatives

Esterified oil from non-petroleum is a wide area of research. Vegetable oils and other minor oils are one of the renewable form of resources which can be utilised for various commercial commodities.

Palm fruit are handled during harvesting and transportation , normal bruising occurs causing the fat in the fruit to start degrading . The longer it takes for the fruit to be transported, processed and refined into palm oil , the larger part of the fats degrade. When palm oil is being refined into food grade oil, these degraded fats, free fatty acids areremoved by distilling to improve taste , odour and colour of the oil, as well as increase its shelf life.

Palm fatty Acid Distillate (PFAD) consists of these degraded fats that are undesired for food production and need to be removed during the palm oil refining process before the oil meets the food industry's quality standards.The annual production of PFAD totals approx. 2.5Mt as refining of palm oil generally yields approx..4-5% of PFAD as a processing residue (Informa Economics 2016).

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In addition to biofuels, PFAD is used, for example, to produce candles, soaps, other oleochemical products , as well as animal feed.

PFAD use does not increase pressure to expand oil palm refining:

Crude palm oil gives of higher price in market than selling of PFAD by most of the producers. PFAD is, however,generated despite producers' continuous efforts to improve their processes to minimise PFAD volumes and maximize the output of more valuable fractions from the refinery. Because PFAD is a non -desired output of the palm oil refining process, its use does not drive palm oil production or expansion of its cultivation, nor does it accelerate deforestation (Informa Economics,2016).

Some argued that PFAD should not be considered a residue because it has market value and many uses. In circular economy, however , all residues and wastes should have an avenue to be utilised , thus have value. PFAD fully meets the EU RED criteria for processing residues i.e.'A substance that is not the end product that a production process directly seeks to produce. It is not a primary aim of the production process and the process has not been deliberately modified to produce it'.

However, during the refining of palm oil, a lower – value by-product known as palm fatty acid distillate(PFAD) is generated in the fatty acid stripping and deodorisation stages. PFAD is potentially a valuable , low -cost feedstock for the production of biodiesel. 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.

PFAD is a by-product of physical refining of crude palm oil products and is composed of free fatty acids(81.7%) , glycerides(14.4%, squalene (0.8%) , vitamin E (0.5%) ,sterols (0.4%) and other substances (2.2%). PFAD is used in the animal feed and laundry soap industries as well as a raw material for the oleochemicals industry.Vitamin E, squalene and phytosterols are value added products which could be extracted from PFAD and are potential value for cosmetic industries.

Most biodiesel plants use the conventional sodium hydroxide / sodium methoxide based transesterification process , which requires highly priced refined oil feedstock. Although palm oil is one of the more competitive feedstocks for biodiesel production , it can be expensive because its price is linked to that of crude petroleum (Fry, 2010).

However , during the refining of palm oil, a lower -value by-product known as PFAD is generated in fatty acid stripping and deodorisation stages .PFAD is potentially a valuable, low cost feedstock for production of biodiesel . The following table gives the details about the palm fatty acid distillate :

Appearance	**Tan to brown liquid**
Free Fatty acid	70% min as palmitic– 92.6 %
Moisture	1% min
Impurity	1% max
Saponifiable Value	95% min
Titer (^{0}C)	46.0 - 43.3
Specific Gravity @ 50^{0}c g/cc	00.8640- 0.8880
Water content	0.03 – 0.24
Iodine Value g/100 g	46.3 - 57.6

Experimental Procedure

Materials

Palm fatty acid along with methanol were the main reactants for the esterification process. This process was being acid catalysed named methane sulfonic acid.

Methods

Palm fatty acid is obtained on distillation which was subjected for heating to the desired temperature of reaction. Methanol and methane sulfonic acid were mixed and then added to the heated oil in the reactor. Methanol and oil are immiscible so the agitating speed was kept constant at 400 rpm to ensure maximum mixing. Samples were withdrawn from flask , washed with water and dried. Samples were analysed for acid value at different intervals. The autoclave is charged with reaction mixture. It is supported by mechanical stirrer and accessorized with temperature controller along with pressure gauge.

Analytical Analysis

Acid value was determined for the samples.The titration of FFA followed AOCS Cd 3d-63,which is a standard method for FFA titration in oil.

Experimentation

The process of esterification was carried out at constant temperature of 60^0C and constant agitation speed of 400 rpm. The product formation was carried with different parameters of change in amount of methanol and heating schedule.

i. Heating Schedule

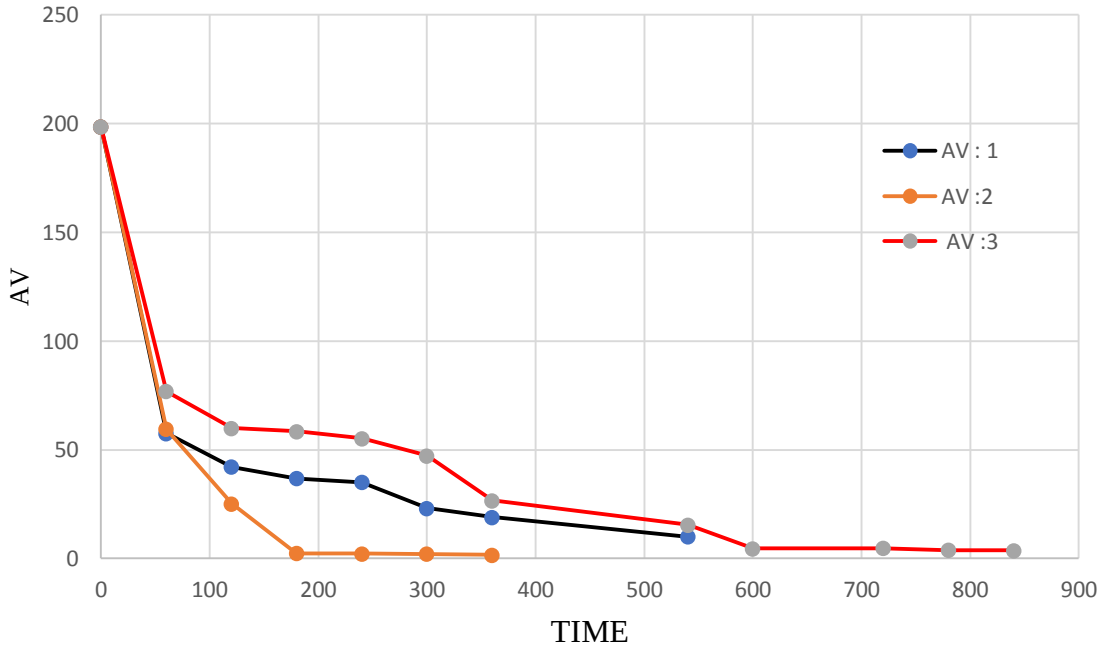
Three different batches were employed and heating schedule was differed . The B1 , B2 , B3 were the batches and were subjected for heating of 10 , 14 and 13 hours respectively. Samples were withdrawn and analysed at intervals for acid value.

ii. Methanol Added

Amount of methanol has been differently added to all the three batches. B1, B2, B3 were added with 80, 180 and 55 grams. The dependency of methanol has also been studied. Amount of methanol varied the conversion percentage of oil into esters.

Observations and Calculations

The reaction mixture was observed at intervals of time and the samples were analysed by the parameter of Acid Value.All the three batches were compared with time duration of heating for respective batches. As initially the fatty acid shows higher acid value and then value decreases resulting in formation of ester. Accuracy of experimentation and the lowest acid value of all the three batches has been plotted and compared in the graph.



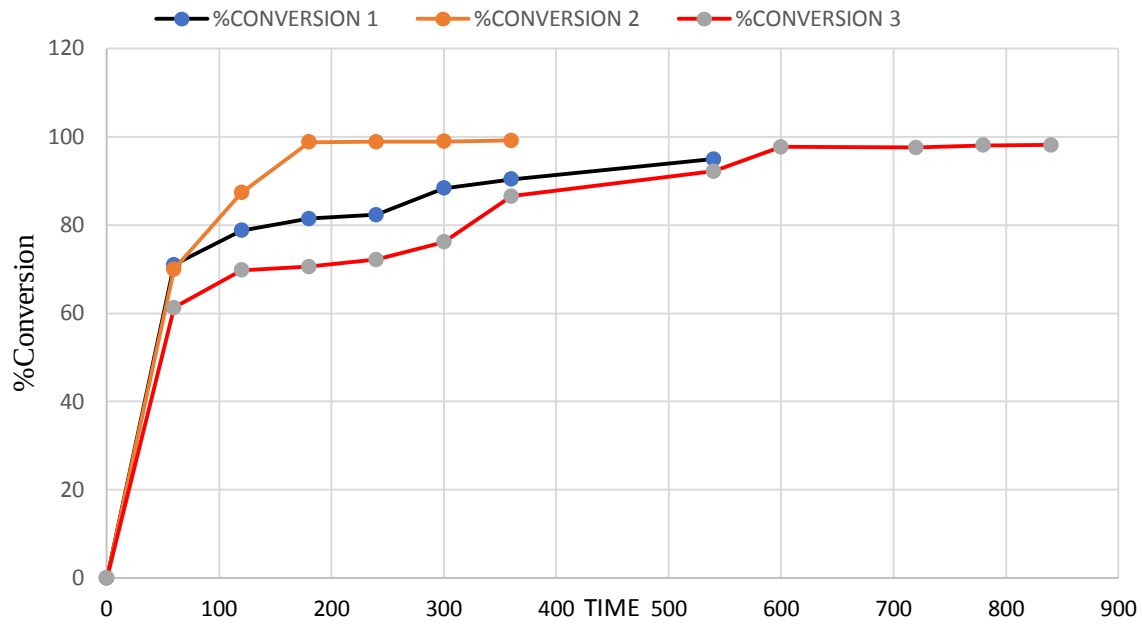
Graph 1 : Acid value of esterified product

Amount of methanol added varied along with the heating schedule of different batches also varied. Total time of … hours in batch 2 was required and a amount of … ml of methanol required to achieve the least AV of 1.7which indicated that conversion of fatty acid of palm distillate which mainly contained palmitic acid(70%) was almost converted into esters . For batch 1 the Acid value achieved at the end product was 10.12 and that for the batch 3 was 3.67. Hence it can be said that for batch 2the process being carried was appropriate and the conditions maintained were optimum.

Methane sulphonic acid catalyst provided medium for the better ester formation by getting a transition of state of alcohol – acid ion which is reactive and unstable during the mechanism. Hence gets easily converted into esters.

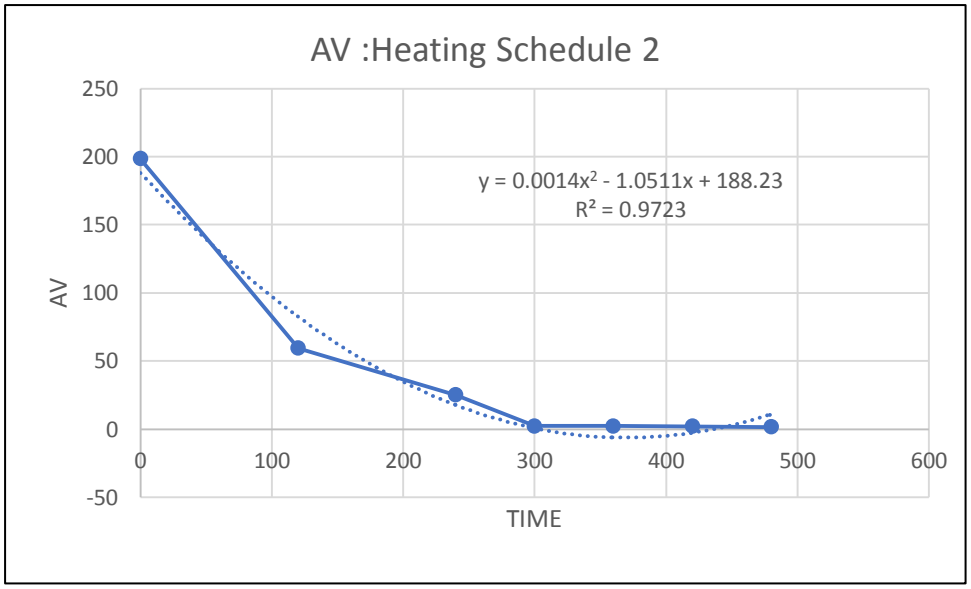
From graph 1 it can be observed that the lowest value of Acid Value has been achieved in B2 i.e. 1.7 . Also the conversion for the complete process was calculated and plotted in graph 2.

From graph 2 it is observed that the maximum conversion is achieved in B2 i.e. 99.14% .



Graph 2: Conversion of reactants

The individual graphs for the batch 2 process has been plotted for Acid value and conversion with respect to time.



If samples are taken at intervals from mixture at room temperature and titrated, a slow decrease in acidity can be observed, but it takes longer time to achieve the minimum acid value. Hence, in this experimentation the minimum value of 1.7 was achieved showing maximum conversion into esters.

Like most other reactions, the speed of esterification approximately doubles with 10^0C rise in temperature .Heat is used up to speed the reaction. However in most instances, heating alone does not speed up esterification to a practical rate. Except in the case of a high boiling alcohol, such as glycerol, with a high

boiling acid such as stearic, esterification cannot be effected at atmospheric pressure in reasonable time without the use of a catalyst.

Methanol and PFAD both are the main reactants. Methanol is always taken in excess for maximum conversion .the theoretical ratio given is 1:3 which does not give desired amount of ester conversion hence analysis of samples at intervals also gives the amount of methanol to be added to the process. Initially the mole ratio of reactants was maintained low and the theoretical value was maintained. Hence on gradual heating and the time interval the amount of methanol to be added is given by the acid value obtained of the product and further the reaction is carried out.

As the reaction proceeds glycerol formation takes in basic reaction of acetic acid and alcohol whether it may be primary , secondary and tertiary ester and water is formed. With time , if water isn't removed the reaction is reversible in nature . Hence removal of water, i.e. glycerol in this case is important.

Reaction of esterification

PFAD + Methanol $\rightleftharpoons$ Esters + Glycerol

Single and multiple reactions

We have a single reaction

FEED 1 + FEED 2 $\longrightarrow$ PRODUCT + BYPRODUCT

From the above reaction it can be seen that a single stoichiometric equation gives the product formation.

Also no other competitive product is formed during the process. Hence the multiple reactions do not occur. Hence here the reaction is termed to be a single stoichiometric reaction.

Elementary and non – elementary reactions

A single reaction with stoichiometric equation

$A+B \longrightarrow P$

Reactions in which the rate equation corresponds to a stoichiometric equation are called elementary reactions.

As observed during the process of esterificationprocess the methanol added is in excess than the theoretical ratio of 1:3. Hence the reaction is non-elementary in nature.

Reversible and irreversible reactions

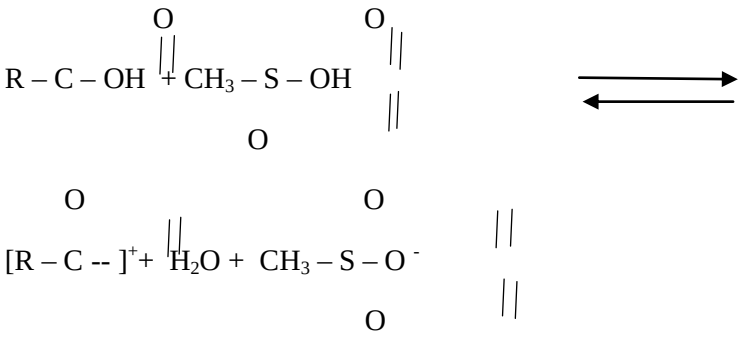
The reaction product formation from raw materials is a forward reaction but along with it formation of glycerol leads the reaction in backward direction.Hence it is a reversible reaction in nature.

Mechanism of reaction

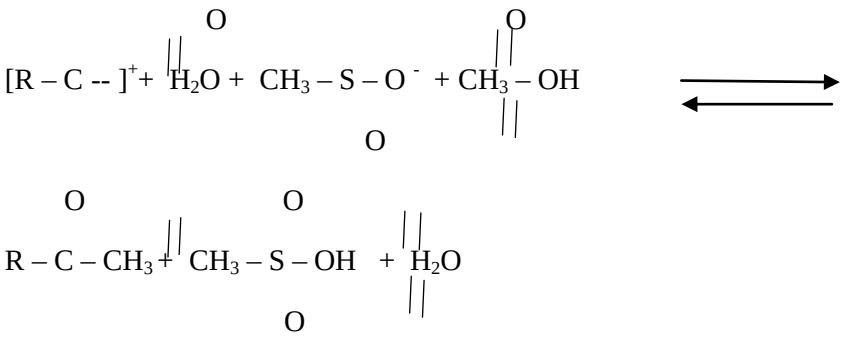
1. An ester is usually defined as a compound formed by substituting an organic radical for an ionizable hydrogen of an acid.
2. The selectivity of bond breaking process is found in the electronic structure of the reactants and products. Since oxygen is more electronegative than carbon , the carbonyl carbon is more positive than the carbonyl oxygen.
3. The transition state can lose the negative charge by the loss either of hydroxyl ion or of the species which originally attached the positive centre.
4. Methyl shows the greatest initial rate of esterification and the highest limit. The primary alcohols, ehyl , propyl and butyl have approximately the same initial rate and limits but are inferior to methyl alcohol in both of these respects.
5. Esterification catalyst are compounds which are acidic in nature.
6. When an acid is added to an esterification mixture the oxygen present will act as bases and coordinate with the acid.

7. Also it is a fact that the alcohol oxygen also can act as base toward the acid. However , this reaction hinders esterification and in addition , may lead to dehydration of alcohol.
8. When the acid is sufficiently strong , the esterification is self- catalysed.
9. Methane sulfonic acid has the rates of hydrolysis of esterification reaction is 97.9%.
10. Sulfuric acid is dibasic in nature , whereas ethane sulfonic acid are among the strongest catalyst but sulfuric acid can lead dehydration of an alcohol being used for the esterification process.
11. One way of completing an esterification is to remove the water as it is formed. The removal of the water is aided by bubbling an inert gas through the mixture or by the application of a vacuum.

STEP 1: INITIATION AND PROPOGATION

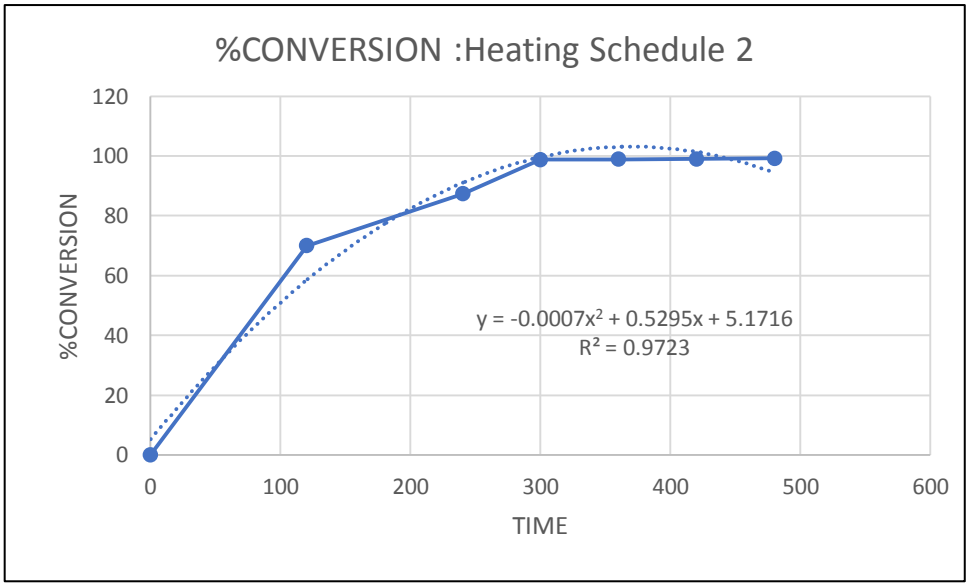


STEP 2: PRODUCT FORMATION



Kinetic Model

Order of reaction



From the above graphs it can be stated that the error in the process is very minimum and the value of square of R obtained is very close to 1. Hence the process opted was very apt.

Batch 2 :

%conversion = $\frac{amount\ of\ limiting\ reactant\ reacted}{total\ amount\ of\ limiting\ reactant\ fed.}$

= 178.452 / 180

= 99.14%

Thegraph depicts the relation between formation of product i.e. the %conversion of fatty acids and the time of reaction. Astime increases that is the heating schedule increases and esters are obtained by time.

Also, the trade line in the graph gives the relation as:

$y=-0.0007x^2 + 0.5295x + 5.1716$

The above equation can be inferred as it is equation in power of 2. Hence the overall order of equation is second. Therefore the esterification of palm fatty acid distillate is a second order reaction. Also:

$R^2 = 0.9723$

This value states that it is nearer to value of 1, inferred that the reaction order calculated has least error into its value and calculation.

The studied reaction is the chain reaction .the intermediate is formed in a first reaction called the chain initiation step.it then combines with reactant to form product and more intermediate in the chain propagation step. The essential feature of the chain reaction is the propagation step. In this step the intermediate is not consumed but acts simply as a catalyst for the conversion of material.

Conclusions

- Esterification reaction of palm fatty acid has been carried out successfully with maximum conversion of 99.17%.
- The least acid value of product achieved till date is 1.7.
- The reaction was optimised to its best operating condition of temperature 60^0C – 75^0C and the amount of methanol added to volume of 180 grams.
- The heating schedule of 14 hours gave the best product of esters.
- Homogeneous reaction in a non-elementary way followed the path of second order reaction
- The mechanism for the reaction with catalyst of methane sulfonic acid has been studied.

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