Production of Bio-diesel (Butyl Oleate) by Reactive Distillation Technique

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Abstract : *Fossil fuels demand to meet energy requirements, is increasing every day and oil reserves are reducing dramatically. For this reason, the production of renewable fuels has acquired great importance in the last few years in order to satisfy this energy necessity. The Biodiesel makes part of these kinds of fuels. However, currently there are problems in its separation and purification. Therefore, new alternatives are needed to be explored like non-conventional separation processes among which Reactive Distillation can be considered. The Esterification of oleic acid with n-butanol by reactive distillation has been performed; this work is totally based on practical experiments done. In this project the possibility of producing the corresponding ester with help of reactants like oleic acid and n-butanol is investigated. Hence, kinetics of esterification reaction is been studied in Reactive Distillation.*

Key Words: Reactive Distillation, Biodiesel, Esterification, n-Butanol, oleic acid.

1.INTRODUCTION

Reactive distillation is emerging technology which as considerable potential as an alternative process for carrying out equilibrium limited liquid phase chemical reaction. it is key opportunity for improving the structure of process. Reactive distillation is a unit operation that combines simultaneous chemical reaction and multicomponent distillation in single vessel which in tern reduces reactor cost [17].It is receiving increasing attention because of its high potential for process intensification. It is applicable to certain reaction in which the maximum conversion is limited by chemical equilibrium by that in conventional reactor [24].

It offers various advantages over conventional approach of reactor followed by separation. Reactive distillation consists of three parts that are rectifying section, catalytic section, stripping section. Rectify and stripping section is having a function of separation and catalytic sections have function of chemical reaction. The combination of distillation is possible if the condition of both operations can be combined. This means that reactions have to show data for reasonable conversion at pressure and temperature level that are capable with distillation condition. The type of the catalyst is also important in reactive distillation. There are two types of the catalyst namely heterogeneous and homogenous catalyst which can be used in reactive distillation column. homogenous catalyst is possible in most cases of RDC but needs separation steps to recycle the catalyst. This can be avoided in heterogeneous catalyst but here special constructions are necessary to fix catalyst in reactive zone. In this column the catalytic zone consist of sulzer packing and the rectifying and stripping section consist of hyflux packing [1].

In this work studied the viability of obtaining Biodiesel from oleic acid with n-butanol by reactive distillation is carried out. The reactants are taken in various mole ratio, different catalyst, different catalyst loading, different heat load, speed of stirring with simple batch reactor and checked the feasibility of reaction, rate constant, conversion in reactive distillation.

2. LITERATURE SURVEY:

Reactive distillation is an emerging technology that has considerable potential as an alternative process for carrying out equilibrium limited liquid phase chemical reactions.

It is receiving increasing attention because of its high potential for process intensification.

Definition:

"Reactive distillation is a unit operation that combines simulations chemical reaction and multicomponent distillation in same vessel."

Reactive Distillation (RD) is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. It improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that are offered by RD. The introduction of an separation process in the reaction zone or vice versa leads to complex interactions between vapor–liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems. RD being a relatively new field, research on various aspects such as modeling and simulation, process synthesis, column hardware design, non-linear dynamics and control is in

progress[24]. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature.[17]

The esterification of Oleic acid with alcohol n-butanol falls in a typical class of reacting systems. Butyl-Oleate is manufactured by the esterification of Oleic acid with n-butanol in the presence of catalyst Amberlyst-15. The alcohol is sparingly soluble in water and the ester is almost insoluble. Another interesting feature of this system is that it is associated with the formation a minimum boiling ternary azeotrops of alcohol and water which is heterogeneous in nature. Hence. In a typical reactive distillation column that consists of both reactive and non reactive zones, the the heterogeneous azeotropes or a composition close to the azeotropes can be obtained as distillate product. Moreover, the aqueous phase that forms after the condensation of the vapor is almost pure water. Depending on the requirement either of the phases can be withdrawn as a product and the other phase can be recycled back as reflux. The pure ester that is butyl Oleate is the least volatile component in the system is released as a bottom product.[17] The present work is aimed at performing a detailed experimental investigation on a reactive distillation setup/column operated in batch mode.[17]
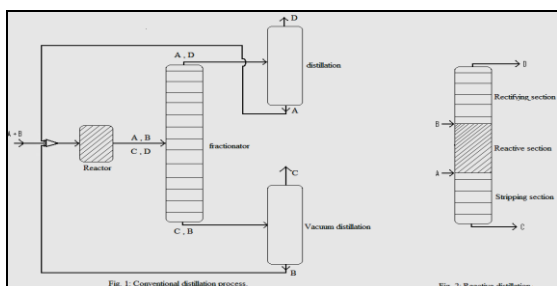

Fig -1: comparison of RD with conventional method

2.1 Advantages of reactive distillation [17]:

- Simplification or elimination of the separation system can lead to significant capital savings.

- Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.

- Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products[10].

- Significantly reduced catalyst requirement for the same degree of conversion.

- Avoidance of azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several

azeotropes with each other. RD conditions can allow the azeotropes to be reacted away in a single vessel.

- Reduces by-product formation.

- Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty.[12]

- Avoidance of hot spots and runaways using liquid vaporization as thermal fly wheel [24].

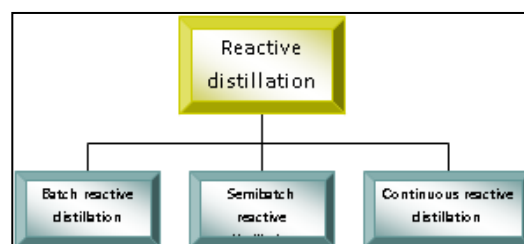The RD is classified in to three types that are [24]:

Fig -2: Classification of reactive distillation

RD can be also classified as homogeneous & heterogeneous

2.2 Esterification and Transesterification:

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry. Esterification is a reversible reaction. Hydrolysis- literally "water splitting" involves adding water and a catalyst (commonly H_2SO_4) to an ester to get the sodium salt of the carboxylic acid and alcohol. As a result of this reversibility, many esterification reactions are equilibrium reactions and therefore need to be driven to completion according to Le Chatelier's principle. Esterifications are among the simplest and most often performed organic transformations.

Transesterification is the process of exchanging the alcohol group of an ester compound with another alcohol. These reactions are often catalyzed by the addition of an acid or base. [8]
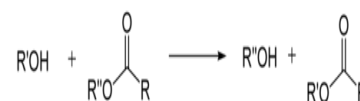
(Reaction 1)

Transesterification:

Alcohol + ester → different Alcohol + different ester

Acids can catalyse the reaction by donating a proton to the carbonyl group, thus making it more reactive, while bases can catalyse the reaction by removing a proton from the alcohol, thus making it more reactive.

2.3 The Mechanism of estirification reaction:

This looks in detail at the mechanism for the formation of esters from carboxylic acids and alcohols in the presence of Amerlyst-15 acting as the catalyst. It uses the formation of Butyl Oleate from oleic acid and butanol as a typical example.

2.4 The Mechanism for the formation of Butyl Oleate:

A reminder of the facts:

Oleic acid reacts with butanol in the presence of Amerlyst-15 as a catalyst to produce the ester, Butyl Oleate. The reaction is slow and reversible. To reduce the chances of the reverse reaction happening, the ester is distilled off as soon as it is formed.[13]

$$C_{17}H_{33}COOH + C_4H_9OH \rightleftharpoons C_{17}H_{33}COOC_4H_9 + H_2O$$
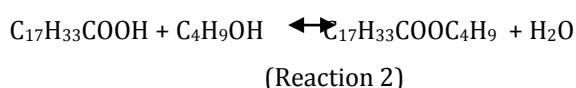
(Reaction 2)

Table 1: Boiling point of components in experiment

Components	Boiling points ^{0}C
Oleic acid	324
n-Butanol	117.7
Butyl acetate	222
Water	100

3. EXPERIMENTAL WORK:

3.1 Batch reactive distillation:

Definition: "Batch reactive distillation is defined as a batch distillation system wherein reaction takes place in either reboiler or condenser or in the column or at more than one of these locations." It has a potential to lower the capital and energy cost of the process.[24]

Reagents and materials: The materials used are oleic acid, butanol and ion exchange resin (catalyst). The oleic acid is 65-88 % pure and butanol is 99 % pure. Both the reactant used is AR (Analytical reagent) grade. The ion exchange resin is amberlyst 15.
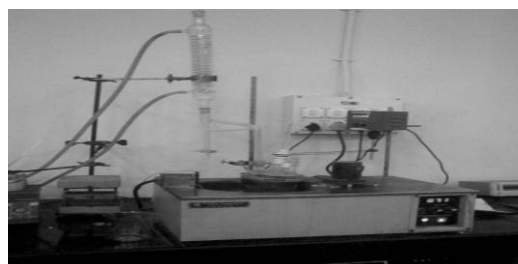
Batch Reactive Distillation Setup

3.2 Experimental setup:

The setup consists of one reactor of about 1 Lit. Capacity. The reactor is externally heated with the help of heating oil bath, the oil bath consist of silicon and paraffin oil. The reactor is also equipped with temperature indicating thermometer, turbine type impellers (agitator), baffles and valve for sample removal. The agitator is driven with help of driven belt which is connected to motor. The speed of motor is 400 rpm. The reactor is connected to dean stark apparatus. The dean stark arrangement is used to provide reflux to reactor. The cock is provided at bottom of dean stark arrangement to withdraw the water formed in the reactor. The condenser which is attached at top of dean stark arrangement serves as reflux condenser to reactor. The setup is insulated with help of cotton wool, which reduces the heat loss from system.

3.3 Preparation procedure:

- Initially the reactor is charged with given mole ratio of oleic acid: n-butanol and catalyst 0 to10 % Weight of reaction mixture.
- Start water supply to condenser and switch on power supply to heating bath for reactor and put the stirrer on.
- Allow temperature to raise it to required point.
- After attaining required temperature remove the sample (5ml) from reactor.
- At the same time remove the water from dean stark and allow the reflux of the butanol.
- Perform the analysis of all samples by titrating with 0.5N NaOH. And by HPLC.
- The analysis will give the indication of oleic acid content in mixture.
- Repeat the same procedure after each half an hour till 7-8 hr.

3.4 Procedure for sample removal:

The sample from reactor is collected by opening the head valve about 5 ml samples is collected and valve is closed. This sample is collected in sample bottle and used for carrying out the analysis.

3.5 Analysis:

Analysis by titration:

Remove the sample (2.5ml) in conical flask by a ppt.

The sample should be free from resin particles. Titrated with the standard 0.5N NaOH solution and phenolphthalein as indicator.

Analysis by HPLC:

The HPLC system, an Agilent Technologies make, consists of a degasser, quaternary pump, wavelength detector and manual injector. Data was collected and analyzed using Chem Station software. The mobile phase was acetonitrile at a flow rate of 1.0ml/min. The sample injector volume was 25 µl and the wavelength was kept constant at 205nm. The HPLC analysis was carried out two times for each sample and butyl oleate ester/oleic acid conversion was calculated. The conversion was defined as the amount of oleic acid converted into butyl oleate is determined by HPLC. The resulting chromatogram was compared with the chromatograms of pure esters. Based on the retention time of specific esters and acids, the compounds present in biodiesel were identified.

4. EXPERIMENTAL METHOD:

Table-2: Titration reading for 1:4 mole ratios of O.A. & BuOH

Sr. No.	Time (min)	Water Collected (ml)	Normality	Final Conc. (gm/lit)	Initial Conc. (gm/lit)	% conversion
1	0	0	1.92	542.3424	542.3424	0
2	30	0.8	1.6	451.952	542.3424	16.6666
3	60	2.4	1.26	355.9122	542.3424	34.3750
4	90	2.2	1.06	299.4182	542.3424	44.7916
5	120	2.2	0.86	242.9242	542.3424	55.2083
6	150	1.8	0.7	197.729	542.3424	63.5416
7	180	1.8	0.56	158.1832	542.3424	70.8333
8	210	1.2	0.42	118.6374	542.3424	78.1250
9	240	0.8	0.35	98.8645	542.3424	81.7708
10	270	0.4	0.28	79.0916	542.3424	85.4166
11	300	0.4	0.2	56.494	542.3424	89.5833
12	330	0.3	0.16	45.1952	542.3424	91.6666
13	360	0.2	0.14	39.5458	542.3424	92.7083
		Total = 14.5				

Calculations:

By titration

Normality of acid

  Acid   Base

  N_1V_1 = N_2V_2

   N_1 = N_2V_2 / V_1 = ...N

N_1 = Normality of acid.

N_2 = Normality of base.

V_1 = volume of acid (ml).

V_2 = volume of base (ml).

Strength = Normality * Equivalent Weight of acid

    = N_1*Eq.Wt. = ...gm/lit.

Concentration= Strength = ...gm/lit.

Conversion (X) = 1- (Final Conc. / Initial Conc.)

% Conversion = X*100 =................%.

4.2 Analytical method:

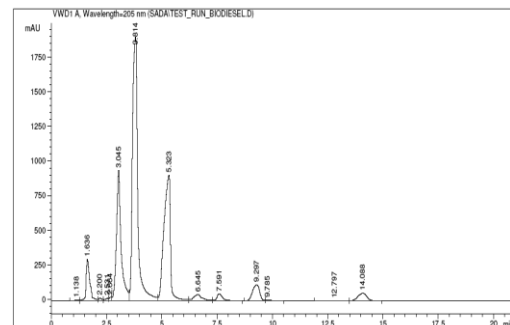At initial condition the HPLC graph is shown below for 1:4 mole ratio O.A. & BuOH.

Fig -3: Initial condition by HPLC for 1:4. O.A. & BuOH

Final reading by HPLC graph for 1:4 mole ratio.
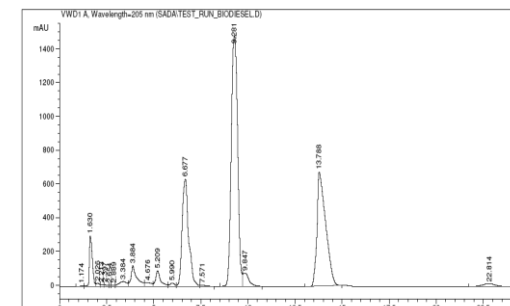
Fig-4: Final condition by HPLC for 1:4 mole ratio O.A. & BuOH

For pure Biodiesel (butyl oleate) the HPLC is given by

Mole ratio = 1:4 (By HPLC)
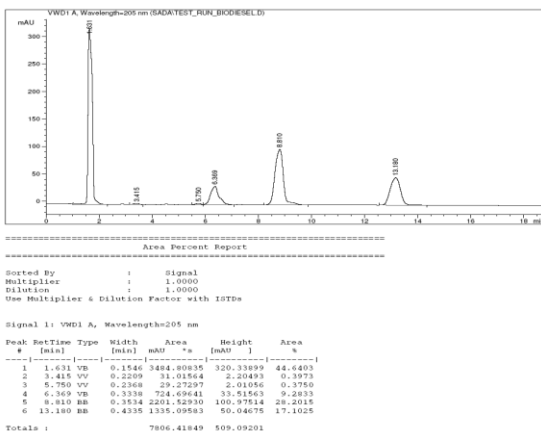
Fig-5 HPLC graph for pure Biodiesel

Table 3: HPLC reading for1:4, O.A. & BuOH

Response factor = from calibration chart.

Wt. of sample = wt. ratio *wt. of solvent.

Conversion (X) = (initial wt. of oleic acid-final wt of oleic acid)/initial wt of oleic acid.

%Conversion =X*100 = ...%.

Comparison of conversion by titration & by HPLC method

Fig. 6: Conversion of oleic acid (mole ratio 1:4)

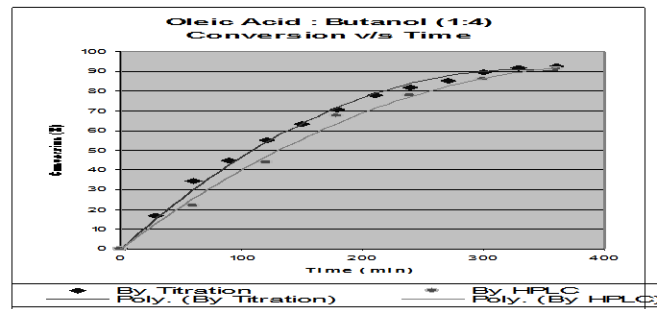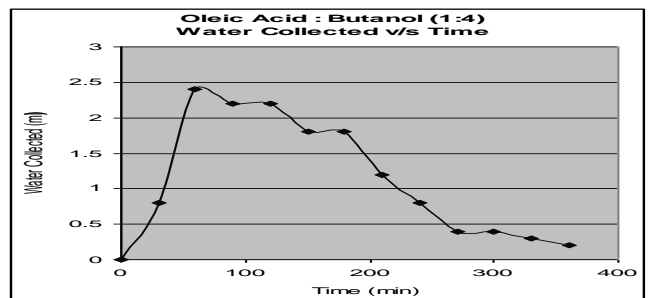**Fig. 7**: Water collection for 1:4 mole ratio O.A. & BuOH.

Sr. no	Time (min)	Area of oleic acid	Area of IPA	Area ratio	R.F	Wt. ratio	Wt. of IPA	Wt. of sample	Int. wt. of sample	% conversion
1	0	64350.20	3503.11	18.36	0.973	17.88	4.9	87.66	87.660	0
2	60	46058.96	3221.28	14.29	0.973	13.92	4.9	68.23	87.660	22.162
3	120	32486.74	3146.65	10.32	0.973	10.05	4.9	49.26	87.660	43.796
4	180	22625.16	3810.69	5.93	0.973	5.78	4.9	28.33	87.660	67.678
5	240	13817.07	3414.28	4.04	0.973	3.94	4.9	19.31	87.660	77.969
6	300	8010.235	3197.70	2.50	0.973	2.43	4.9	11.95	87.660	86.363
7	360	5243.671	3278.22	1.59	0.973	1.55	4.9	7.63	87.660	91.292

Calculation:

By HPLC

Area of Oleic Acid = ...mAU.

Area of Solvent (IPA) =............mAU..

Area Ratio = area of oleic acid/ area of solvent.

Wt. ratio = area ratio*response factor.

5. RESULTS AND DISCUSSION:

Batch reactive distillation

5.1 Effect of mole ratio:

Fig.8 Shows the relationship between the oleic acid conversion v/s time at various mole ratios at 5 wt % of amberlyst -15 catalyst at bath temperature of 125^0C. As seen in fig. the oleic acid conversion and the degree of oleic acid conversion depend largely up on molar ratio of butanol and

oleic acid. The mole ratios taken are 1:3, 1:4, and 1:5 for the esterification reaction.

From these results we can conclude, for the esteification of oleic acid and butanol as the mole ratio increases the conversion increases that is 1:5 gives the maximum conversion, but from above graph we can say that 1:4 is the optimum mole ratio. Hence, for rest of the runs where taken with 1:4 mole ratio.
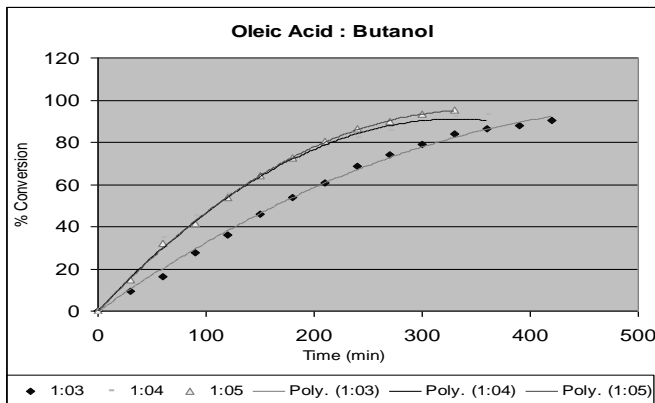

Fig. 8- Comparison graph of mole ratios.

5.2 Effect of catalyst loading:

In catalyst loading the different weight ratios such as 0%, 3%, 5% of catalyst where taken without changing the other parameters, and it is observed that as catalyst loading increases conversion increases. So the above graph shows maximum conversion at 5% catalyst loading. Hence, for rest of the runs where taken with 1:4 mole ratio and 5% wt of catalyst.
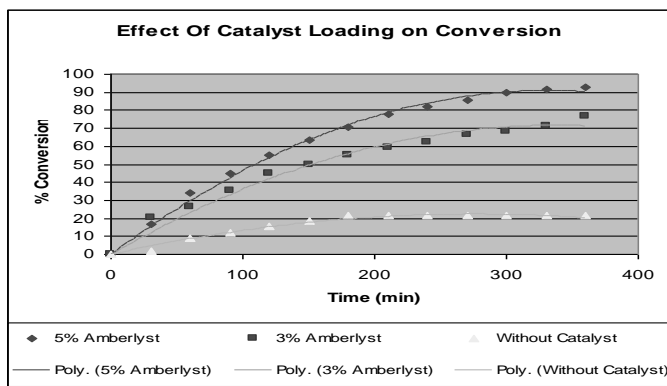

Fig. 9: Comparison graph of catalyst loading.

5.3 Effect of change in catalyst:

In this case we have taken two different catalysts such as amberlyst-15 and sulphonated zirconia without changing other parameter and it is observed from above graph that the sulphonated zirconia gives more conversion than amberlyst-15 comparatively. But due to powder form zirconia is difficult to separate from reaction mixture for the titration and HPLC analysis and also it is difficult to

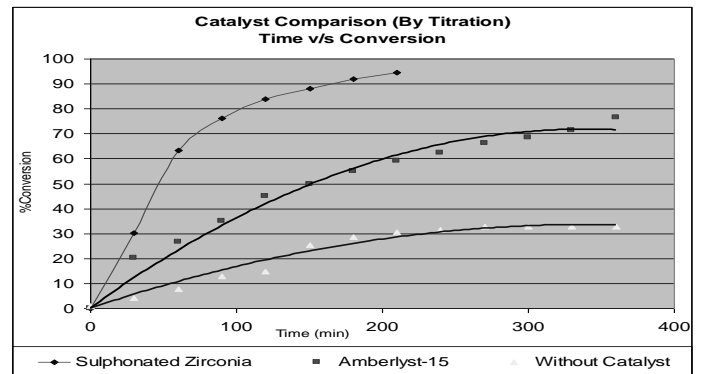regenerate. Hence, for the further runs amberlyst-15 is used as catalyst.

Fig.10 Comparison graph of different catalyst

5.4 Effect of heat load:

In heat load the different bath temperature such as 115°C,125° C,135°C where studied without changing other parameter, and it is observed that as heat load increases conversion goes on increasing. So from above graph maximum conversion is achieved at bath temperature of 135°C. But from above graph the optimum conversion is at 125°C. Hence, the rest of runs where taken with 1:4 mole ratio, 5%wt of catalyst and at bath temperature of 125° C.
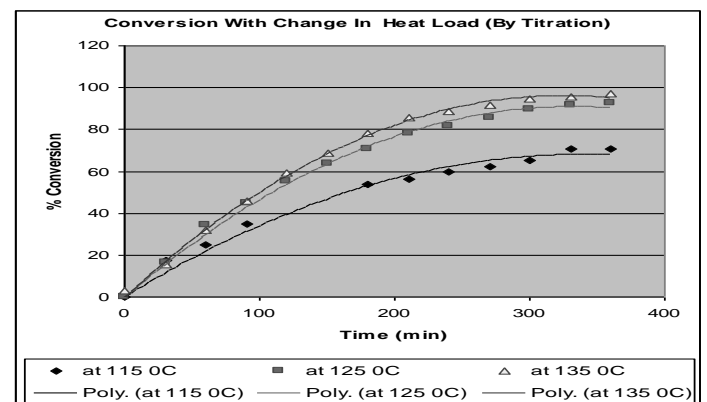

Fig. 11: Comparison graph of heat load.

5.5 Effect of agitation RPM:

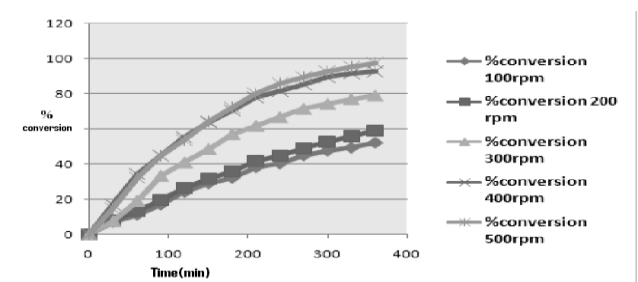Fig. 12 shows that conversion of studied reaction is optimum at 400rpm speed in reactor.

Fig. 12 Effect of agitation RPM

5.6 Effect of the presence of water:

To study the effect of presence of water in esterification of oleic acid ,the reaction was done using and 99% butanol in the presence of amerlyst-15 .The bath temperature was $125^0 C$, a molar ratio of 1:5 was used and the amount catalyst was 5% W/W.

The initially reaction rate seems higher when there is a small presence of water in reaction mixture. The presence of water in the reaction mixture might have two negative effect: one towards the catalyst, a fast interaction between the water and the catalyst might produce deactivation: and the second one toward the reaction itself .Since this is an equilibrium reaction the presence of a product from the beginning of the reaction could shift the reaction towards the reactant and therefore achieve a lower final conversion. In the esterification reaction by removing water it gives better conversion than without removing the water.
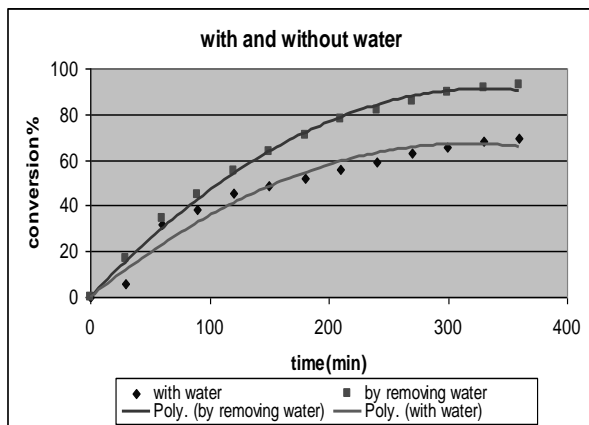

Fig.13: Comparison between SBR & BRD.

5.7 Determination of rate constant k(26):

Table 4- reaction rate data

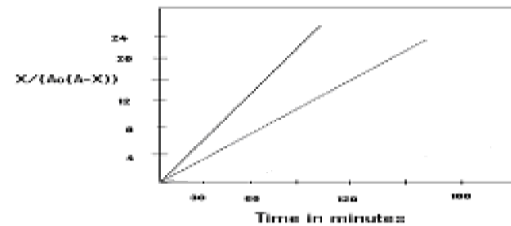| Time (min)	Run A $X/(A_0(A-X))$	Run B $X/(A_0(A-X))$
0	0	0
10	0.05	3.29
20	0.14	6.47
30	0.17	9.61
60	0.37	19.52
90	0.54	28.26
120	0.69	...
180	1.03	...

Fig. 14: Determination of rate constant k

Type of equation: the equation governing the rate may be determined by trial & error. A no. of equations are generally assumed as expressing second order reactions, and these were tested in the usual graphical ways by plotting various functions against time to find which gives a straight line relation. The one which did, is,

$$kt = X/(A_0(A-X)) \quad \ldots \ldots (1)$$

Where A_0= oleic acid originally present, moles/liter

A= oleic acid originally present, moles/100grams

X= amount of oleic acid transformed in the time

Interval, t(same unit as A)

k= rate constant.

When $X/(A_0(A-X))$ was plotted against t, straight lines were obtained for all runs.

The reaction rate constant, k, of each individual run was evaluated from the slope expressed by above relation. The data are in table 4 & fig.14(26).

Table 5- Comparison between C.D., B.R.D., S.B.R.D., C.R.D.

Sr. no.	Name	Conversion in %
1.	Conventional distillation	68
2.	Batch reactive distillation	94
3.	Semi- Batch reactive distillation	93
4.	Continuous reactive distillation	72

6. CONCLUSIONS:

The method for the development for the reactive distillation processes is applied for the esterification of oleic acid and butanol. Here, the reaction kinetics has been investigated. We have observed that BRD gives more conversion than simple batch reactor. Also we have come to conclusion that optimum molar ratio of feed is 1:4. and the best conversion is obtain by using sulphonated zirconia but zirconia gives problem in separation from reaction mixture for analysis by titration and HPLC so the amberlyst -15 is easy to separate

out from reaction mixture. Hence, we use amberlyst -15 as catalyst.

Also we observed that the optimum heat load for estrification of oleic acid and butanol is 125^{0}C (bath temperature). By analyzing different catalyst loading we observed that 5% catalyst (amberlyst-15) gives maximum conversion that means as % of catalyst increases conversion goes on increases.

In SBRDC and CRDC the residence time was less as compare to BRD, but we got optimum conversion in less residence time which is good enough.

7. FUTURE WORK:

We have performed experimental work on CRDC and observed that we get optimum conversion for the respective feed, catalyst, and feed location. But if one wants to increases the conversion from column then there are many options such as:

- By selecting different oils we can increase the conversion.

- By applying simulation to column we can improve the conversion.

- Also by inducing feed at various feed stages in column the conversion can be improved.

- By changing the catalyst in column one can check the conversion.

Nomenclature:

BD   = Biodiesel.
BRD   = Batch reactive distillation.
CRDC   = Continuous reactive distillation column.
FAAE   = Fatty acid alkyl ester.
FAME   = Fatty acid methyl ester.
FFA   = Free fatty acid.
HPLC   = High performance liquid chromatography.
IPA   = Isopropyl alcohol.
R   = Run (experiment).
RD   = Reactive distillation.
RDC   = Reactive distillation column.
SAC   = Solid acid catalyst.
SBR   = Simple batch reactor.
SBRDC   = Semibatch reactive distillation.
VOC   = Volatile organic compound.
O.A.   = Oleic Acid.
BuOH   = butanol.
RPM   = Revolutions per minute.

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