

Trans-Esterification with Homogeneous Acid Catalyst - Linear Alkyl Benzene Sulfonic Acid for Biodiesel Production

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Abstract: *Trans-esterification process was studied using linear alkyl benzene sulfonic acid as catalyst. From various vegetable oils, coconut oil was trans-esterified with low aliphatic alcohols like methanol, ethanol etc. The process was studied in batch reactor; Linear alkyl benzene sulfonic acid (LABS) is used in catalytic amount for trans-esterification of coconut oil. Methyl ester derived from coconut oil is very interesting to study as coconut oil majorly contains medium carbon chain (C12 – C14), so the methyl ester obtained from its part can be a biodiesel. The product formed was tested using gas chromatography (GC) technique and was confirmed by GC-Mass Spectra analysis. The process parameters including recovery and reusability of catalyst were studied and optimized.*

Keywords: Trans-esterification, linear alkyl benzene sulfonic Acid (LABS), Coconut oil

1. Introduction

The utilization of fossil fuel still dominates energy consumption, especially in transportation sector and will go on increasing significantly years ahead. The vanishing natural resources will be a big challenge, many feed stocks for the production of chemicals are based on petroleum, and simultaneously the international price of petroleum is continually fluctuating. Further issue is the increase in petroleum waste and alarming global warming which made the international community think and search for alternate fuel sources.

The key question to address is, “what alternatives can be developed and used?” In addition, we must ensure that future generations can also use these new alternatives. Mother Nature has many such resource stocks like animal fat, vegetable oil and many more. An alternative energy like biodiesel is essential as the use of fossil fuel. One of alternative renewable energy that is being developed from vegetable oil – coconut oil to fatty acid methyl esters (FAME), also known as “Biodiesel” [1-3].

Biodiesel can be renewed, is non-toxic, has a higher cetane number, contains low sulfur, as well as reduces emissions of combustion, making it more environmental friendly.

The typical trans-esterification reaction is,

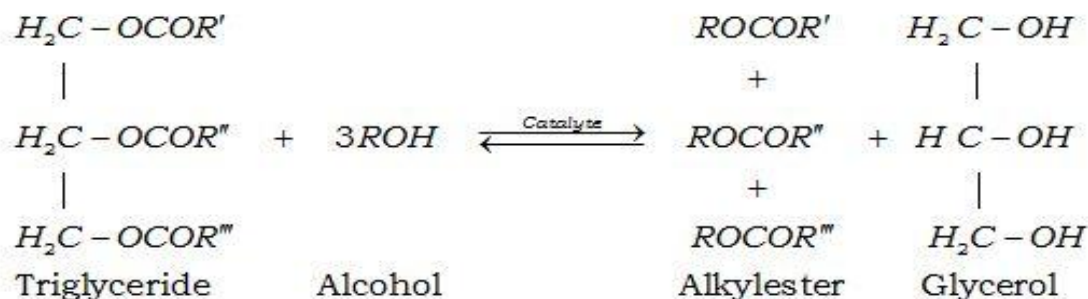


Figure 1

R', R'' and R'''- fatty acids chain from C-8 to C-18

Trans-esterification is widely used because it is quite simple and can produce high purity FAME. The trans-esterification process is a chemical reaction in which triglyceride reacts with an alcohol in the presence of a catalyst to produce alkyl ester as the main product and glycerol as a byproduct. Note that three moles of alcohol

are needed for each mole of coconut oil feed. However, since the reaction is reversible, excess alcohol is normally used to shift the reaction forward. Furthermore, in the case of coconut oil whose molecular weight typically is in about 660 *g/mole*, the balanced reaction, expressed in theoretical mass ratios, is,

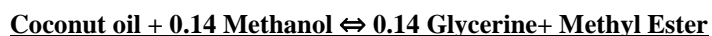


Figure 2

Therefore, each gram of coconut oil is expected to yield one gram of methyl ester [6]. The glycerol separates spontaneously from the biodiesel phase after the reaction. The latter phase contains the methyl ester as well as unreacted oil, whose molecular glycerol content can then be used to assess the extent of the reaction (pure methyl ester should be glycerol-free). Majority of excess methanol present dissolves in the glycerol phase.

The reactions given in Equations 1 and 2 take place in the presence of a catalyst. Without a catalyst, the trans-esterification process runs very slowly, but with the addition of a catalyst, the reaction is very fast. Which can be acidic, basic or organic in nature, usually in molar excess of alcohol. The economy of the process depends on the type and quantity of catalyst used among other factors. The catalyst can be homogeneous or heterogeneous depending on whether it is in the same or different phase with the reactants; oils and alcohols [4-8].

The conventional alkaline catalysts like KOH and NaOH are very cheap and readily available with fast reaction rate with high conversion (Up to 90-98%), process giving product with formation of soap, which is very difficult for separation. Such side reactions impose three process cost penalties: first, a portion of the raw material is converted to an undesired product; second, additional processing effort and cost is incurred to remove the undesired product; finally, the side reaction consumes some of the catalyst that is needed for the main process reaction [7, 10].

Whereas common acid (like H_2SO_4 , H_3PO_4 acids) catalyzed processes are slow and prolong taking several hours with low conversion. The prolonged processing can be overcome by increasing higher acid catalyst loading. It includes neutralization process for product separation. This not only leads to neutralization process cost with subsequent corrosion to material of construction but also generates high amount of processing waste and loss of catalyst as well [7].

Hence the researchers focused their attention towards heterogeneous catalysts, that can be regenerated, thereby it can reduce the purchase cost of the catalyst and is easier to separate, so it can also reduce the production costs and the formation of waste makes them all more environmental friendly too; especially to produce high quality esters and glycerol. But now the use of heterogeneous catalysts in the production of methyl ester requires expensive catalyst with severe conditions (high pressure and high temperature), while low temperature and atmospheric conditions can make the yield of methyl ester relatively low[2-13].

Another catalyst-free alternative requires the use of supercritical methanol, methyl acetate at temperatures in the range of 200 – 400 °C. Supercritical plants can achieve high product yields even with low-grade feed stocks, but they involve high initial costs and are energy-intensive. Similarly in some processes co-solvent were used [6, 14].

Though we use any process, conversion and product yield quantification is must. It is also important to know feed composition, product formation in reaction mass and quality and quantity of product too. Various analytical methods, instruments has been used for evaluation of coconut oil composition, product formation in tran-esterification reaction mass, quality and quantity of isolated methyl esters product - Biodiesel and glycerol. Number of specified quality parameter of methyl ester has been tested and confirmed using different analytical instruments like Gas chromatography (GC), GC-Mass spectra, Viscometer, Density meter, etc. Biodiesel have number of parameters with its specification's, the product –methyl ester need to pass it before its commercial application. That's the reason trans-esterified - Methyl ester product essentially need to characterize completely using various analytical method. The typical compositions of Coconut oil and tran-esterified methyl ester – Biodiesel parameters with its specification's are as following tables [2, 3, 14-17].

Table 1: Physicochemical properties of the produced coconut oil

Properties	Values
Specific gravity	0.912
Density (kg/m ³)	912
Viscosity at 40°C (mm ² /s)	23
Free fatty acid (mg/g)	28.025
Saponification	191.89
Iodine	121.1
Peroxide (mol/kg)	8
Acid (mgKOH/g)	14.025

Table 2: Typical Coconut oil composition

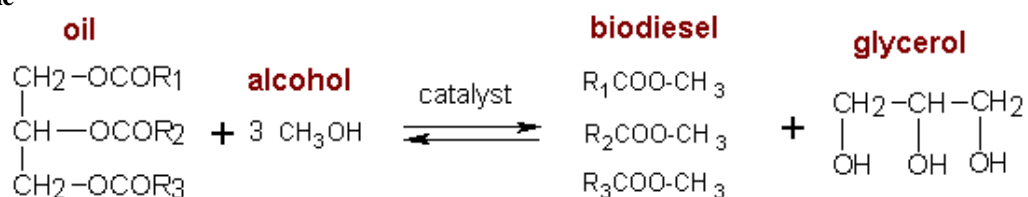
Fatty Acid		Form	Coconut Oil Composition	
			% Range	(Mass %)
Caproic acid	Hexanoic	C6:0	0.4 - 0.6	0.5
Caprylic acid	Octanoic	C8:0	6.9 - 9.4	7.8
Capric acid	Decanoic	C10:0	6.2 - 7.8	6.7
Lauric acid	Dodecanoic	C12:0	45.9 - 50.3	47.5
Myristic acid	Tetradecanoic	C14:0	16.8 - 19.2	18.1
Palmitic acid	Hexadecaonoic	C16:0	7.7 - 9.7	8.8
Stearic acid	Octadecanoic	C18:0	2.3 - 3.2	2.6
Oleic acid	9Z-octadecanoic	C18:1	5.4 - 7.4	6.2
Linoleic acid	9Z, 12Z-octadecadienoic	C18:2	1.3 - 2.1	1.6

Table 3: Methyl Ester – Biodiesel Product Composition with Specification's

Property	Units	lower limit	upper limit	Test-Method
Ester content	% (m/m)	96.5	-	EN 14103
Density at 15°C	kg/m ³	860	900	EN ISO 3675 / 12185
Viscosity at 40°C	mm ² /s	3.5	5.0	EN ISO 3104 / EN 14105
Flash point	°C	> 101	-	EN ISO 2719 / 3679.
Sulfur content	mg/kg	-	10	EN ISO 20846 / 20884
Centane number	-	51, 0	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0, 02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability, 110°C	hours	6	-	EN 14112
Acid value	mg KOH/g	-	0, 5	EN 14104
Iodine value	-	-	120	EN 14111
Linolenic Acid methyl ester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) methylester	% (m/m)	-	1	EN 14103
Methanol content	% (m/m)	-	0, 2	EN 14110
Monoglyceride content	% (m/m)	-	0, 7	EN 14105
Diglyceride content	% (m/m)	-	0, 2	EN 14105
Triglyceride content	% (m/m)	-	0, 2	EN 14105
Free Glycerine	% (m/m)	-	0, 02	EN 14105 / EN 14106
Total Glycerine	% (m/m)	-	0, 25	EN 14105
Group I metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109 / EN 14538
Group II metals (Ca+Mg)	mg/kg	-	5	EN 14538
Phosphorus content	mg/kg	-	4	EN14107

In the present work linear alkyl benzene sulfonic acid, organic acid, was successfully be used as catalyst for trans-esterification of coconut oil. The well-known use of linear alkyl benzene sulfonic acid is Anionic surfactant in salt form, to make liquid detergent, powders, bar cakes, unique property of biodegradability. It has high solubility in water, alcohols. Linear alkyl benzene sulfonic acid has acidity (pKa<1) which permits to use as catalyst in this type of reaction. All the important effects of process parameters were studied. Solubility in water, methanol was also helped to recover the catalyst up to 95% which was reusable and recycled for several times.

Reaction Scheme



R₁, R₂, R₃ are hydrophobic rest of fatty acids

Figure 3

2. Experimental Section

Materials

Coconut oil was purchased from local Vendor, (90%) Linear alkyl benzene sulfonic acid was procured from M/s. Radha Madhav surfactant Pvt. Ltd., Surat, Gujarat, India., Methanol, Hexane and Diethyl Ether of AR grade were obtained from M/s. S.D. fine chem. Pvt. Ltd. Mumbai., India.

R_1 , R_2 and R_3 will be fatty acids chain from C8:0 (Caprylic), C10:0 (Capric), C12:0 (Lauric), C14:0 (Myristic), C16:0 (Palmitic), C18:0 (Stearic), C18:1 (Oleic), C18:2 (Linoleic). Coconut oil majority contents lauric acid (48%) and myristic acid (17%)

Experimental Procedure

The laboratory experimental set-up consists of 250 ml three neck round bottom flask, submerged in an oil bath and equipped with condenser, circulated with cooling / chilled water to reflux, a thermometer and a graduated addition funnel. This assembly kept on a magnetic driven hot plate. All the raw materials and catalyst weight accurately and placed into the round bottom flask. Reaction conditions sets as per required parameter, started stirring and considered as initiation of reaction time. These reactions were carried out as per reaction plan and separation of product was done by adding n-hexane under stirring. The two layers formed were separated by means of separating funnel. Each layer was washed thrice with n hexane. Organic layer was evaporated to get the crude coconut oil methyl ester product. The aqueous layer was distilled and excess methanols followed by Glycerin were collected, linear alkyl benzene sulfonic acid catalyst was recovered as residue in the distillation flask. Thin layer chromatography was employed to indicate product formation. Coconut oil methyl ester product formation confirmation and characterization was done by Gas chromatography using UV and Mass spectra detectors.

3. Results and Discussion

Various processing parameters were studied such as effect of reaction time, temperature, catalyst concentration, coconut oil to alcohol mole ratio. Percentage conversion of reactant was calculated by analyzed formation of methyl ester product using as chromatography technique. Three point calibration was done for each product component's using authentic methyl ester on GC instrument. Methyl ester of coconut oil was confirmed by measuring mass of each product using gas chromatography MS.

Effect of Temperature

In every reaction, it is necessary to know at what temperature reaction will give optimum conversion. It was investigated by varying the reaction temperature from room temperature i.e. 25°C, 40°C and 60°C. All other parameters were kept constant i.e. Coconut oil: alcohol 1:8 (effectively its 1:24), catalyst concentration 5% w/w and reaction time 6 hrs. It was observed that optimum % conversion was at 60°C. Figure 4 also indicated that reaction rate was temperature dependent. Hence further parameters were studied at 60°C.

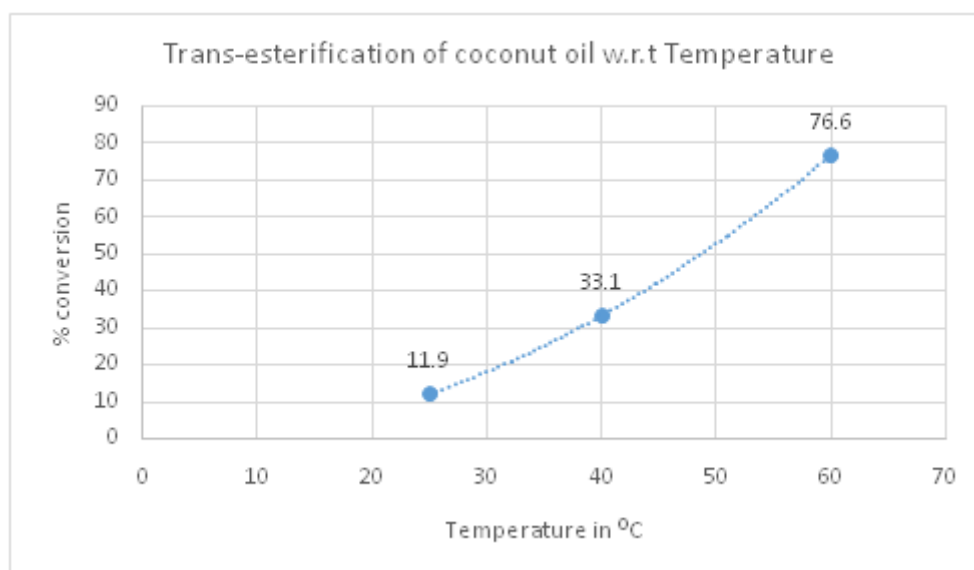


Figure 4: Coconut oil: Alcohol mole Ratio-1:24, catalyst Conc. -5% w/w, time- 6 hrs.

Effect of Reaction Time

Coconut oil has triglyceride get converted to diglyceride and to its monoglyceride forms and subsequently gives ester product which prolongs the reaction rate. The rate of reaction was studied with reaction time. The reaction condition was Coconut oil: alcohol 1:8 (effectively its 1:24), mole ratio, temperature 60°C, with catalyst

concentration 5% w/w was maintained and the reaction was monitored for 6 hrs. Intermediate samples were tested for % conversion. The intermediate samples drawn were tested on well three point calibrated GC. Percentage, conversion of reactant was calculated by analyzed formation of methyl ester product. The experimental observation shown in figure 5.

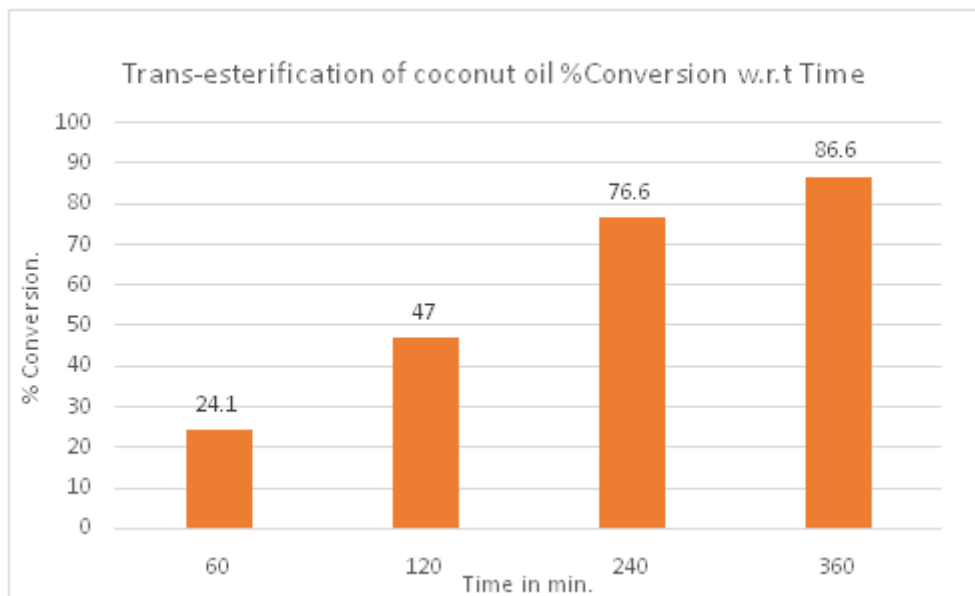


Figure 5: Coconut oil: alcohol mole ratio- 1:24, temperature -60°C, catalyst Conc.-5 % w/w

Effect of Catalyst Concentration

The effect of catalyst – Linear alkyl benzene sulfonic acid concentration was studied with 1, 5, 10 and 25 w/w % of Coconut oil and alcohol. The reaction conditions were kept at Coconut oil: alcohol 1:8 (effectively its 1:24), mole ratio, temperature 65°C and reaction time 120 min. The

formation of coconut oil methyl with respect to catalyst concentration was measured by established gas chromatographic method. Increases in catalyst concentration increase the product formation. The experimental observation shown in figure 6, is clearly indicative that conversion is directly proportional to reactive site.

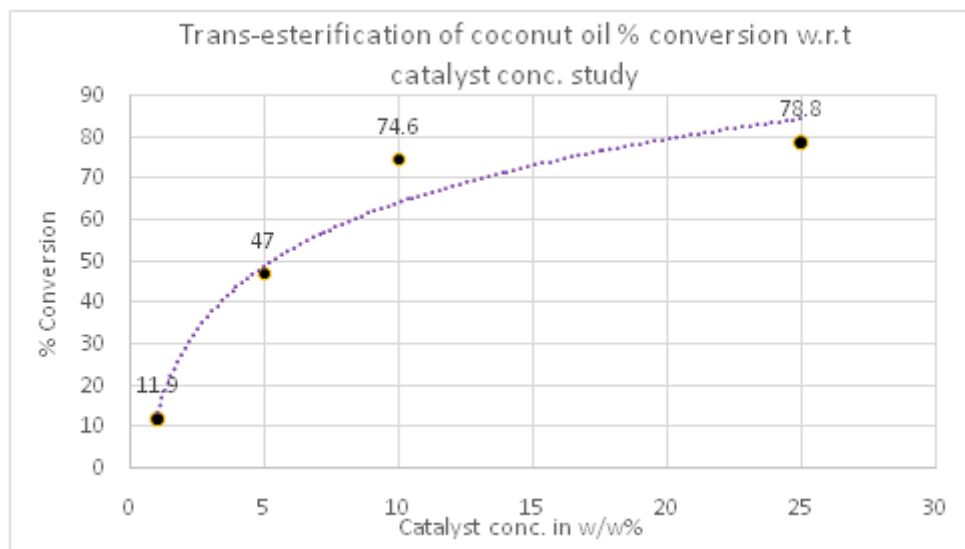


Figure 6: Coconut oil: alcohol mole ratio - 1:24, temperature – 60°C., time - 2hrs.

Effect of mole ratio of Coconut oil to alcohol

Trans-esterification reaction is a reversible reaction, will take forward path when one of the reactant has to be in excess. So alcohol was kept in excess. In trans-esterification each oil molecule requires three molecules of

alcohol to form coconut oil methyl ester. Coconut oil has triglyceride which follows the reaction path during reaction with alcohol triglyceride – diglyceride and to its forms monoglyceride and subsequently gives ester product along with glycerol as shown in figure 7.

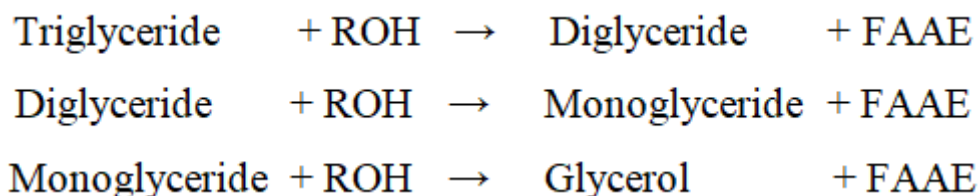


Figure 7

So the mole ratio of coconut oil to methanol 1:2, 1:5, 1:7 and 1:8 (effectively its 1:6, 10, 14 and 24 respectively), was studied, The figure 8 clearly indicates increase in

conversion of coconut oil to its methyl ester with respect to increase in mole ratio of methanol.

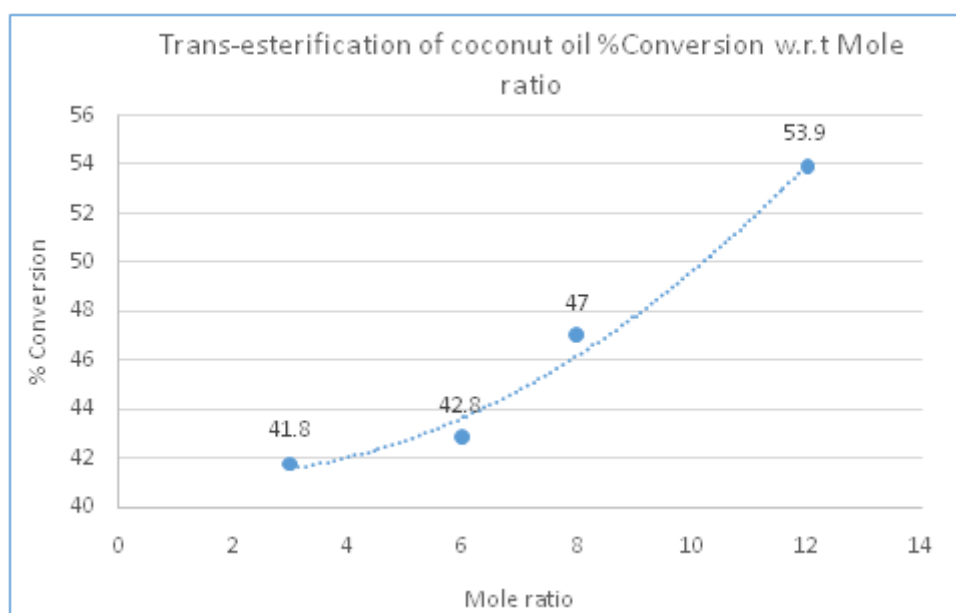


Figure 8: % Catalyst concentration – 10w/w%, temperature – 60°C, time - 2 hrs.

Recovery and recyclability of catalyst

The objective of this study was to screen a new catalyst which is not only recoverable but also reusable and recyclable. While studying various parameters, Product along with n Hexane was separated whereas lower layer contents alcohol, glycerol and catalyst. This lower layer was separated using distillation in rotavac distillation unit, where methanol followed by crude glycerol was separated and catalyst was recovered as liquid residue.

Recovery of catalyst, linear alkyl benzene sulfonic acid catalyst was observed nearly 95 % after every experiment. The loss of recovered catalyst was make up with fresh catalyst and reused, recycled several times for trans-esterification reaction. After each cycle around 2-5% losses of catalyst was observed with just about 75 % conversion was observed. Further the spent catalyst (inactive catalyst) was converted to its sodium salt to make use for detergent making which is biodegradable.

4. Conclusions

The trans-esterification of coconut oil with methanol in presence of homogeneous milder organic acid, linear alkyl benzene sulfonic acid was tested successfully. The study shows reaction rate is directly proportional to reaction temperature, coconut oil to alcohol mole ratio, catalyst

concentration and reaction time. This milder organic acid catalyst not only sort out the processing but also separation problems arises in present process using base catalyst like NaOH, mineral acids like H₂SO₄, H₃PO₄. The approach to make greener and coast efficient process was achieved because of recoverability and reusability of catalyst. Furthermore the spent catalyst (inactive catalyst) can be converted to its sodium salt to make use for detergent making which is biodegradable. In future the greener concept of zero effluent discharged can be achieved.

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