



Research Article

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Esterification of stearic acid for biodiesel production in the presence of homogeneous milder organic acid as a catalyst

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ABSTRACT

To study fatty acid esterification process, stearic acid esterification with low aliphatic alcohols like methanol, ethanol etc. was studied in batch reactor using oxalic acid, homogeneous milder organic acid as a catalyst. Methyl stearate formation was observed by change in acid value. It was confirmed by FTIR analysis. The process parameters including recovery and reusability were studied and optimized.

Keywords: Esterification, Stearic acid, Oxalic acid.

INTRODUCTION

A conventional theory in process chemistry has been the optimization of the time-space yield. In modern perspective, this limited point of view must be enlarged, for example toxic wastes can destroy natural resources and especially the means of livelihood for future generations. In addition, many feedstocks for the production of chemicals are based on petroleum, which is not a renewable resource.

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 [1]. With diminishing natural resources, increase in petroleum waste and alarming global warming alters brought more attention towards biodiesel production. The biodegradability, low emissions such as CO, CO₂, similar flow and combustion properties over ride petroleum based diesel makes these renewable fuel a good alternative for transportation fuel. There are many additional advantages of biodiesel such as zero sulphur, ability to use as a blend with other petroleum resources and lengthening the lifetime of engine due to its lubrication property. Biodiesel can be used in existing oil heating systems and diesel engines without making any alteration [2-5]. With international trends swinging toward sustainable transportation, it seems like a good step toward cleaner and greener highways.

The successful implementation of greener chemical processes relies not only on the development of more efficient catalysts for synthetic chemistry but also as importantly on the development of processes and separation technologies which can deliver enhanced processing performance in a safe, cost-effective and energy efficient manner. The amplification of a process has shown potential which can effectively tackle the challenges of significant process enhancement, even as offering the probable to reduce the environmental impact presented by the chemical industry.

Biodiesel is synthesized by esterification of fatty acid as well as transesterification reaction of animal fats and vegetable oils with lower aliphatic alcohol like methanol, ethanol [6 -9]. There are many stumbling blocks for the production of commercialization of biodiesel. Many common crops could economically produce biodiesel in certain parts of the world. But in other regions, the same plants would be impossible or extremely costly to grow. Likewise the fertilizer, water and land required to produce enough biofuel to reduce fossil fuel consumption significantly can create other problems, ranging from increased pollution to decrease access to food [3].

The alkaline catalysts like KOH and NaOH are very cheap & readily available with fast reaction rate with high conversion (Up to 98%), process gives product with formation of soap, which is very difficult for separation. Whereas common acids like H₂SO₄, H₃PO₄ catalyzed process are slow and prolong to several hours with low conversion. This prolong processing has overcome by increasing higher acid catalyst loading. It includes neutralization process for product separation. This not only leads neutralization process cost with subsequent corrosion to material of construction but also generate high amount of processing waste and loss of catalyst as well [10-13].

In the present work oxalic acid, crystalline organic acid was successfully used as catalyst for esterification of stearic acid. The various known uses of oxalic acid are recovery of rare-earth metals, bleaching agent in textile, wood pulp, rust remover for metals, purifying agent in pharmaceutical industries. It has high solubility in water, alcohols [14, 15]. Oxalic acid has acidity (pKa =1.25) 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 90-95% which was reusable and recycled for several times.

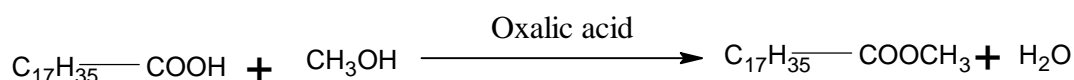


Fig.1: Reaction scheme

EXPREMENTAL SECTION

Materials:

Stearic Acid, (90%), Oxalic acid, Methanol, Hexane & Diethyl Ether of AR grade were obtained from M/s. s.d. fine chem. Pvt. Ltd., Mumbai., India.

Experimental procedure:

The laboratory experimental set-up consist 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 equal addition of water and n-hexane/diethyl ether under stirring. The two layers formed were separated by means of separating funnel. Each layer was washed thrice. The organic layer was passed through anhydrous sodium sulphite to remove moisture. Organic layer was evaporated to get the crude methyl stearate product. The aqueous layer was distilled and excess methanol followed by water was collected, oxalic acid catalyst was recovered as residue in the distillation flask. Thin layer chromatography was employed to indicate product formation. The percentage conversion of reactant was calculated by change in the acid value by simple titrimetric technique. Further product confirmation and characterization was done on FTIR technique.

RESULTS AND DISCUSSION

Various processing parameters were studied such as effect of reaction time, temperature, catalyst concentration, stearic acid to alcohol mole ratio. Percentage conversion of reactant was titrimetrically analyzed and change in acid value was tabulated.

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, 45°C, 55°C and 65°C. All other parameters were kept constant i.e. stearic acid: alcohol 1:20, catalyst concentration 10% w/w and reaction time 8 hrs. It was observed that optimum % conversion was at 65°C. Figure 2 also indicated that reaction rate was temperature dependent. Hence further parameters were studied at 65°C.

Effect of Reaction Time:

The effect of reaction time on rate of conversion was studied. The reaction condition was stearic acid: alcohol 1:20 mole ratio, temperature 65°C, with catalyst concentration 10% w/w was maintained and the reaction was monitored for 8 hrs. Intermediate samples were tested for percentage conversion. The experimental observations are shown in figure 3. Percentage conversion was much faster but as time progresses conversion rates slows down due to accumulation of water of reaction which hinders forward reaction.

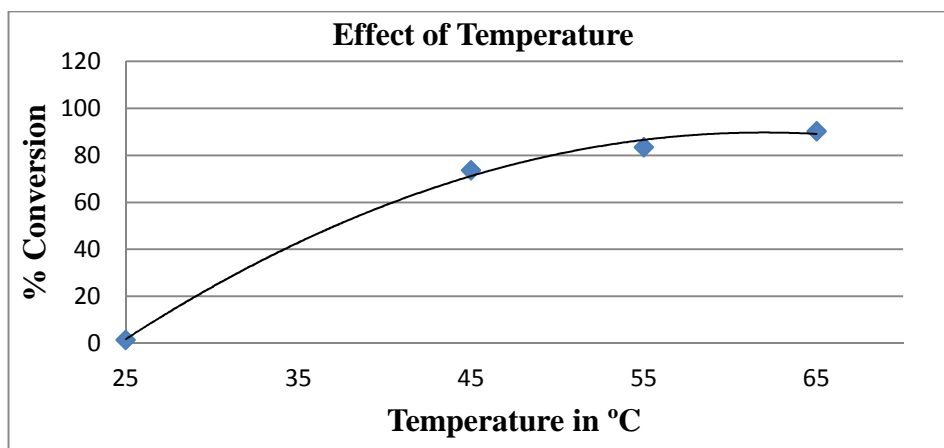


Figure 2: temperature versus percentage conversion
Stearic acid: Alcohol mole Ratio-1:20, catalyst Conc. -10%w/w, time- 8 hrs.

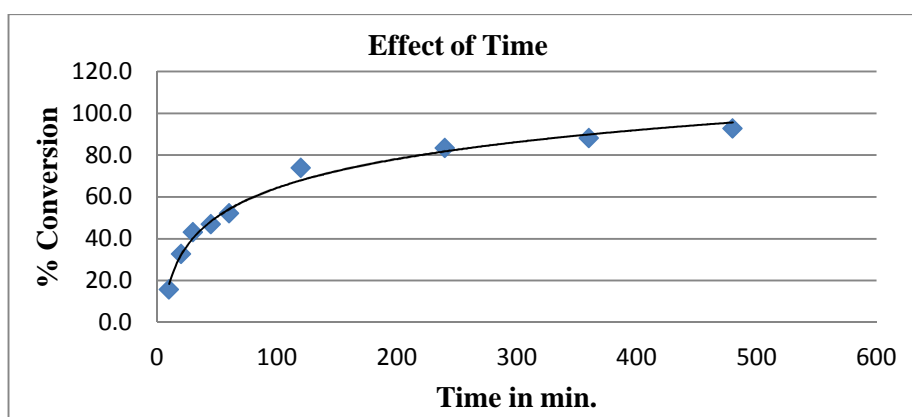


Figure 3: Reaction time versus percentage conversion
Stearic acid: alcohol mole ratio- 1:20, temperature: 65°C, catalyst Conc.-10%w/w

Effect of Catalyst concentration:

The effect of catalyst - oxalic acid concentration was studied with 5, 10, 20 and 30 w/w % of stearic acid & alcohol. The reaction conditions were kept at stearic acid: alcohol 1:20 mole ratio, temperature 65°C and reaction time 8 hrs. The percentage conversion was monitored and as figure 4, Percentage conversion is directly proportional to reactive site. The formation of water limits conversion rate.

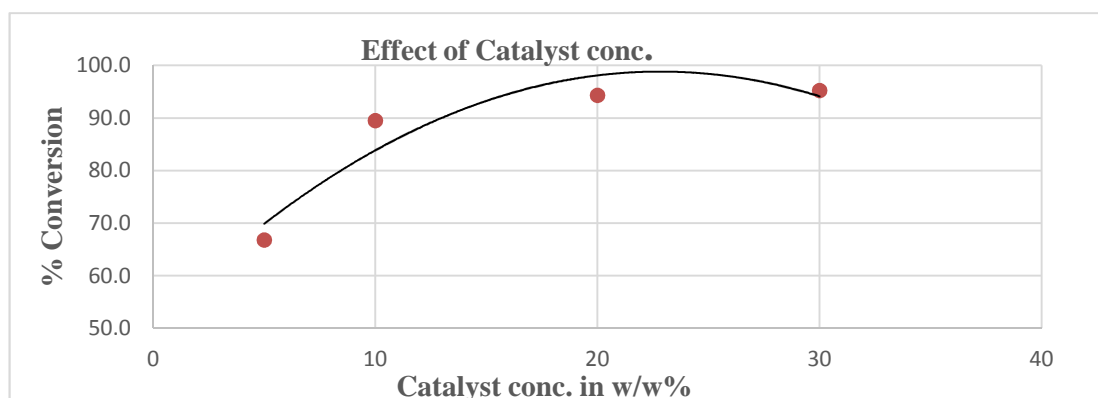


Figure 4: Catalyst concentration versus percentage conversion
Stearic acid: alcohol mole ratio - 1:20, temperature :65°C, time - 8 hrs.

Effect of mole ratio of stearic acid to alcohol:

In reversible reaction, forward reaction will be possible only when one of the reactant is in excess. The effect of mole ratio of stearic acid to methanol 1:6, 1:10, 1:14 and 1:20 mole ratio was studied, The figure 5 clearly indicates increase of conversion with respect to increase in methanol concentration.

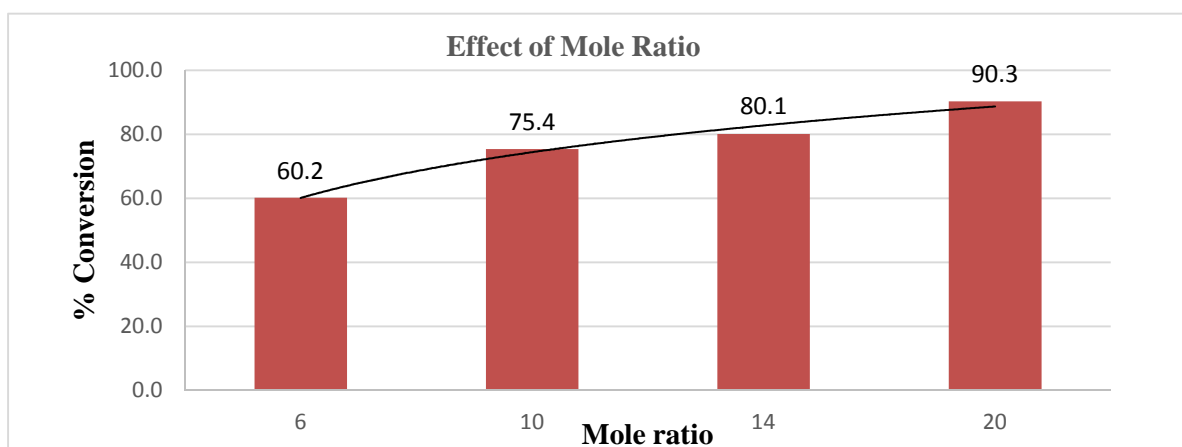


Figure 5: Mole ratio versus percentage conversion
% catalyst concentration – 10 w/w%, temperature: 65°C, time - 8 hrs.

Recovery & recyclability of catalyst:

The objective of this study was to screen a new catalyst which is not only recoverable but also reusable, recyclable too. While studying various parameters, the product separation and recovery of catalyst, diethyl ether and water were added into warm reaction mixture. Separating funnel was used to separate organic and aqueous layers. The product carrying organic layer was further washed thrice with water. These water washes were collected and distilled in rotavac distillation unit, methanol followed by water was collected and oxalic acid catalyst was recovered as residue. It was recovered in crystalline form at the bottom of the distillation container and precaution was taken not to overheat.

Recovery of oxalic 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 esterification reaction. As figure 6, 7 shows, after every cycle no significant losses of catalyst with just about same % conversion were observed.

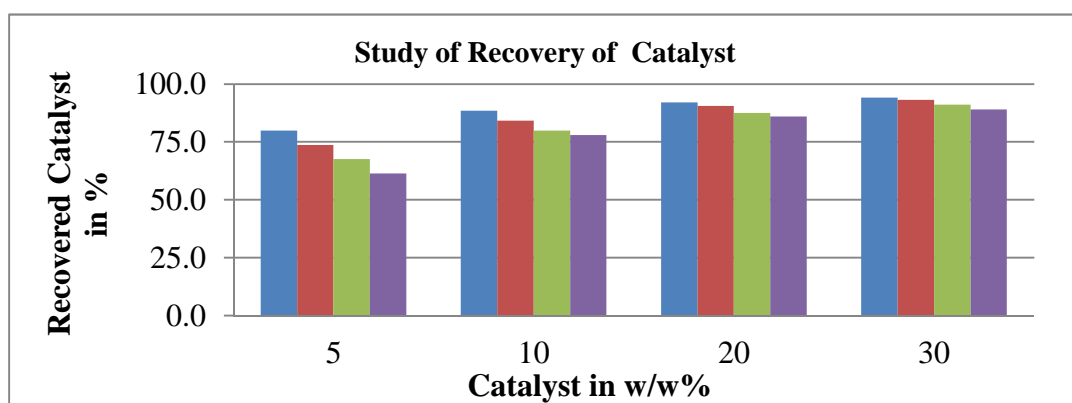


Figure 6 Recovery of catalyst with every cycle
Stearic acid: alcohol mole ratio - 1:20, temperature: 65°C, time - 8 hrs.

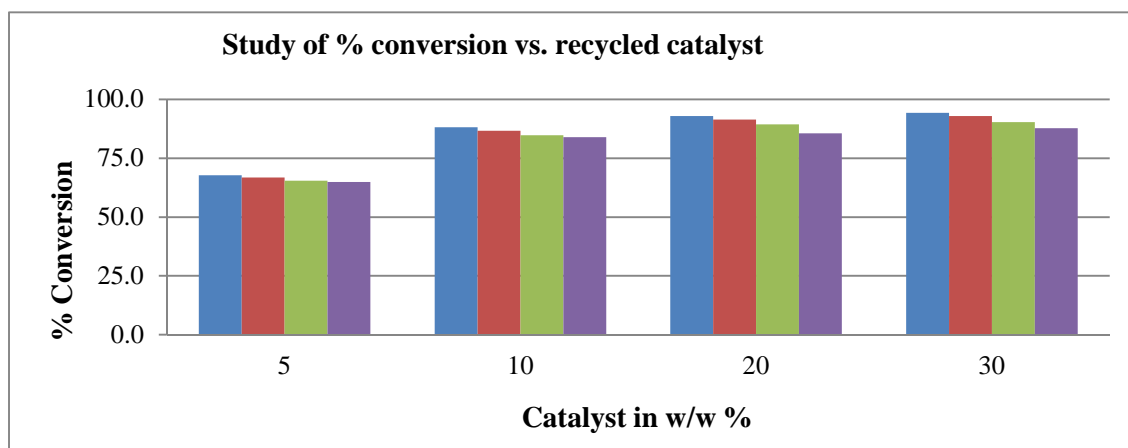


Figure 7: Catalyst in w/w versus percentage conversion
 Stearic acid: alcohol mole ratio - 1:20, temperature: 65°C, time - 8 hrs.

CONCLUSION

The esterification of stearic Acid with methanol in presence of homogeneous milder organic acid, oxalic acid was tested successfully. The study implies reaction rate is directly proportional to reaction temperature, stearic acid to alcohol mole ratio, catalyst concentration and reaction time. This milder organic acid catalyst over rides the processing and separation problems arises in present process using mineral acids like H_2SO_4 , H_3PO_4 . Also recoverability and reusability of catalyst has made cost effective and greener process.

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