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# Pre-Treatment of High Free Fatty Acids Oils by Chemical Re-Esterification for Biodiesel Production—A Review

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## ABSTRACT

Non edible oil sources have the potential to lower the cost of biodiesel. However, they usually contain significant high amounts of free fatty acids (FFA) that make them inadequate for direct base catalyzed transesterification reaction (where the FFA content should be lower than 3%). The present work reviews chemical re-esterification as a possible method for the pre-treatment of high FFA feedstock for biodiesel production. The effects of temperature, amount of glycerol, type and amount of catalyst have been discussed. Chemical re-esterification lowers FFA to acceptable levels for transesterification at the same time utilizing the glycerol by product from the same process. Further researches have been proposed as a way forward to improve the process kinetics and optimization so as to make it more economical.

**Keywords:** Chemical Re-Esterification; High Free Fatty Acid; Glycerolysis; Biodiesel Feedstock

## 1. Introduction

The worldwide worry about the protection of environment and the dependence on fossil fuel has given rise to development of alternative energy sources as substitute for traditional fossil fuels. Fossil fuel sources are nonrenewable, and will be exhausted in the near future. According to Alekett [1] the world's oil reserves are up to 80% less than predicted, which calls for alternative sources of energy. Biodiesel is one of the renewable energy fuel sources alternatives to the conventional petroleum diesel. It is simply produced by transesterification process whereby the vegetable oil or animal fat (Triglyceride) reacts with alcohol in presence of catalyst or without catalyst to give the corresponding alkyl esters of the fatty acid mixture that is found in the parent vegetable oil or animal fat [2,3]. Transesterification reaction can be uncatalyzed, base-catalyzed, acid-catalyzed or enzyme-catalyzed.

Research on biodiesel production has captured the attention of different researchers with focus on heterogeneous catalysts which have received considerable attention [4-9]. Unfortunately these studies did not lead to the development of catalysts with high activity, good reusability and stability in order to replace the homogenous catalysts, such as the sodium methoxide or hydroxide [10-12]. Today, homogeneous base-catalyzed transesterification process is widely used industrially due to the fact that, it is kinetically much faster and it has been proven to be economically viable [13]. According to the report by Bacovsky, Körbitz, Mittelbach and Wörgetter [14] on the status of biodiesel production technology, most of the commercialized biodiesel production technology utilizes homogeneous base-catalyzed transesterification. However, the main drawback of this technology is its sensitivity to the purity of feedstocks, especially water and free fatty acid content [15-17].

The use of edible grade oils as feedstocks competes with food supply in the long-term [18] and accounts for the higher price of biodiesel, since the cost of raw materials accounts for 60% to 80% of the total cost of biodiesel fuel [19-22]. One way of reducing the biodiesel production costs is to use the less expensive feedstocks

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mostly containing fatty acids such as inedible oils, animal fats, waste food oil and by-products of the refining vegetable oils [23-25]. However, feedstocks high in free fatty acid are not easily converted by homogeneous base transesterification, because of the concurrent soap formation of the free fatty acids with the catalyst. The excessive amount of soap formed significantly interferes with the washing process by forming emulsions, thus leading to substantial yield losses [26-30]. The reaction can only tolerate FFA content up to 3% in the feedstock without affecting the process negatively as suggested by Knothe, Van Gerpen and Krahl [31]. The free fatty acid (FFA) value lower than 3% is recommended for higher conversion efficiency [32]. The pre-treatments of non-edible oils for lowering the FFA in feedstock for base catalyzed transesterification are therefore inevitable.

The pre-treatment of high FFA with acid catalysis followed by base catalyzed transesterification has been proposed by several authors [2,23,33,34]. The process can lower a high FFA feedstock to ≤0.5% quickly and effectively. However, depending on the amount of FFA in the oils or fats; one-step pre-treatment may sometimes not reduce the FFA efficiently because of the high content of water produced during the reaction [35]. In this case, a mixture of alcohol and sulphuric acid can be added into the oils or fats three times (three-step pre-esterification) and the water must be removed before transesterification [36]. Van Gerpen, Shanks, Pruszko, Clements and Knothe [37] suggested the use of high molar ratios of alcohol to oil as high as 40:1 to dilute the water formed during pre-treatment, yet this will require more energy to recover the excess alcohol used. The water formed during the pre-treatment phase requires removal and the use of corrosive nature or catalysts commonly $H_2SO_4$ which requires high capital intensive reactors, has limited the application of the process.

The chemical re-esterification (glycerolysis) process has the capability of converting the free fatty acid back to their respective glyceride molecule. This technique involves adding glycerol to the high FFA feedstock and heating it to temperature of about (200˚C), with a metallic catalyst such as zinc chloride and zinc dust or without catalyst. The glycerol reacts with the FFAs to form monoglycerides, diglycerides and triglycerides [38]. It produces a low FFA feed that can be processed to methylesters using traditional homogeneous base transesterification technique. The advantage of this approach is that no alcohol is needed during the pre-treatment and the water formed from the reaction can be immediately vaporized and vented from the reaction mixture. The process has also the potential of utilizing glycerol, a by-product from transesterification and thereby lowers the cost of biodiesel. However, the drawbacks of this method are its high temperature requirement and relatively slow reaction rate [37]. Although chemical re-esterification has a potential to lower the high FFA feedstock for homogeneous base catalyzed transesterification. The re-esterification method has not been studied from the standpoint of the extent of de-acidification for biodiesel production. The literatures on the applicability of this process as a high FFA pre-treatment for biodiesel are hard to find. It is the purpose of this paper to review the applicability of the glycerolysis process as a pre-treatment method for lowering the FFA to the acceptable level of 3% for Biodiesel production using homogenous base catalyzed transesterification.

## 2. Background of Chemical Re-Esterification

The chemical re-esterification process is one of the old high FFA pre-treatment methods for food grade products. It has been in existence for more than centuries [39]. It converts the free fatty acid into neutral glycerides by reesterification with the free hydroxyl groups remaining in the oil (or with added hydroxyl groups from glycerol) at a high temperature, with or without catalyst [38]. The reaction starts with the formation of monoglycerides, which is further esterified to diglycerides and then to a triglyceride [40]. Contrary to loss of oils during pre-treatment by other FFA pre-treatment processes, the re-esterification increases the yield of neutral oil. The water formed during reaction lead to the establishment of equilibrium between the reactants under the experimental conditions and it should therefore be removed. Several approaches have been proposed to remove water in the reaction mixture. The use of an inert gas or air and to maintain vacuum have been suggested to eliminate water from the reaction mixture [39].

## 3. Factors Affecting the Chemical Re-Esterification Reaction

The reaction temperature, amount and type of catalyst, and amount of glycerol are the main factors that are said to affect the yield of the chemical re-esterification process in converting free fatty acid into triglycerides.

### 3.1. Effect of Temperature on Chemical Re-Esterification

Literatures show that chemical re-esterification can occur at different temperatures, depending on the type oil used. Variable temperatures of 180˚C, 220˚C and 230˚C were used by Felizardo *et al.* [41] in pre-treating acidulated soap stock of 50% FFA. It was found that temperature increase favors the reaction kinetics considerably faster at 230˚C. However, more significant difference in FFA drop seems to occur when the temperature increases from 180˚C to 220˚C. The FFA content of the acidulated soapstocks was reduced from 50% to 5% after 3 h of reaction at 200˚C. Similar temperature trend were also observed by [39,42,43] in re-esterification of high FFA rice bran oil whereby the rate at which raw rice bran oil re-esterifies was maximum between 180˚C and 200˚C. De and Bhattacharyya [44] show that the reaction temperature of 210˚C was more effective than temperature below 200˚C in re-esterifing rice bran oil containing high FFA (9.5% to 35.0%) with monoglycerides.

The reaction temperature was also found to influence the rate of re-esterification process by Ebewele, Iyayi and Hymore [45], in chemical re-esterification of high acidic rubber seed oil with 37.69% FFA. At low temperature of 150˚C the FFA was lowered to about 7.03% in 6 h. While at 200˚C, the FFA dropped to 1.5% over the same period. On increasing temperature further to 250˚C, the reduction in FFA was fastest within the first two hours. However, the FFA dropped to 3.88% after 6 h of the reaction time. It is supposed that there was a small degree of fat splitting at this elevated temperature after being held for 6 h. The rate at which FFA re-esterifies was at its maximum between 200˚C and 250˚C.

## 3.2. Effect of Amount and Type of Catalyst

The chemical re-esterification of free fatty acid is affected by the type and amount of catalyst used, although reaction can also proceed without catalyst [39]. An extensive research on different types of catalysts was done by Feuge, Kraemer and Bailey [46] whereby $AICl_2·6H_20$, $Al_2O_3$, $SnO_2$, $SbCl_3$, $HgCl_2$, FeO, $NiCl_2·6H_2O$, NaOH, $MgCl_2·6H_2O$, MgO, $MnCl_2·4H_2O$, $PbCl_2$, ZnO, $FeCl_3·6H_2O$, $CdCl_2·2.5H_2O$, PbO, $MnO_2$, $ZnCl_2$, $SnCl_2·2H_2O$, $SnCl_4·5H_2O$ and HCl were tried by chemical reesterification of the mixed fatty acids obtained by saponification of peanut oil with 90.3% FFA under reduced pressure (20 mmHg) and at the temperature of 200˚C. Only $SnCl_2·2H_2O$, $SnCl_4·5H_2O$ and $ZnCl_2$ were found to be excellent in catalytic activity and the FFA of oil drop from 90.3% to 2.8%, 2.4% and 3.5% respectively for 6 h. When the reaction was uncatalyzed, the FFA drops to 5.34 after 8 h and at an elevated temperature of 241˚C.

The rate of re-esterification was observed to be slow in the absence of catalyst by Ebewele, Iyayi and Hymore [45]. In this reaction, FFA was reduced to 15.38% from 37.69% in 6 h without catalyst. However, on using zinc dust (0.25% by weight of oil) and zinc chloride (0.15% by weight of oil) significant reduction in FFA was achieved. Zinc dust lowered the FFA of rubber seed oil from 37.69% to 1.50% while Zinc chloride lowered the FFA to about 1.27% within 6 h of reaction time. No significant reduction of FFA was observed when the two catalysts were combined.

Felizardo *et al.* [41] tried metallic zinc and dehydrated zinc acetate as chemical re esterification catalysts. The catalysts concentrations used were 0.1%, 0.2% and 0.3%w/w of the acidulated soap stock. Both metallic zinc and dehydrated zinc acetate catalysts showed almost the same effect on reaction kinetics. On increasing catalyst dose the reaction kinetic was also increasing until a reaction time of 1 h, however the final acidity did not seem to be affected after 1 h. It was also shown that 2 h will be required to achieve the same drop of FFA without catalyst. The effect of the catalyst dose on re-esterification of rice bran oil with 50% and 70% excess glycerol was also investigated by Singh and Singh [43] with 7 h of reaction time. $SnCl_2$ catalyst concentrations of 0.1%, 0.15%, 0.2%, 0.25% and 0.3%w/w were used. At the stated conditions, 0.2%w/w catalyst concentration was found to be optimum in lowering the acid value of the rice bran oil in both 50% and 70% excess of glycerol. Bhattacharyya and Bhattacharyya [42] investigated the effect of two catalysts namely stannous chloride and an aromatic sulphonic acid (p-toluene sulphonic acid) on the extent of re-esterification of FFA in rice bran oil with added glycerol. The catalysts were shown to influence the re-esterification rate only during the initial 2 h. The p-toluene sulphonic acid was found to be more effective by lowering the rice bran oil with 15% - 30% FFA to low levels (1.6% - 4.0%) by reesterification with glycerol.

Wang, *et al.* [47] tried the super acid solid catalyst $SO_4^2$ -/$ZrO_2$-$Al_2O_3$ in the chemical re-esterification before homogeneous base transesterification. The FFA in the waste cooking oil with an acid value of 88.4 mg KOH/g was lowered to 1.414 mg KOH/g. The re-esterification efficiency was found to be 98.4%. The catalyst showed good activity in catalyzing the re-esterifying waste cooking oil by glycerol. Their work also shows the advantages of easy separation of excess glycerol and less catalyst loading (0.3%w/w).

## 3.3. Effect of Amount of Glycerol

The effects of amount glycerol on the re-esterification reaction was studied by Felizardo *et al.* [41]. The experiments were performed at 220˚C with a glycerol excess of 4%, 11% and 52%. The use of more than 10% (molar ratio glycerin/FFA = 1.10) excess glycerol did not show any improvements in the reaction kinetics at a temperature of 220˚C.

In their study, Ebewele, Iyayi and Hymore [45], the stoichiometric amount of glycerol (4.3%w/w of oil) in re-esterifing rubber seed oil of 37.69% FFA was shown to be significant in FFA reduction as compared to when no glycerol was used in the reaction. However, using 5.6%w/w of oil that is 30% excess of glycerol there was no significant improvement in FFA reduction as compared to the stoichiometric amount of glycerol. With 30% excess of glycerol, the rate of FFA reduction was rapid during the initial 2 h of reaction and thereafter decreases considerably. This could possibly due to high re-esterification reaction occurring between the hydroxyl groups from the added glycerol and FFA at the initial stage which leads to an increase in triglycerides content. A reduction in FFA from 37.69% to 1.5% was achieved in a reaction time of 6 h with 4.3% glycerol (stoichiometric amounts) at 200˚C while under the same reaction condition and time the FFA dropped from 37.69% to about 15% when no glycerol was used. In this case reduction in FFA content is thought to be the reaction between FFA and the free hydroxyl groups remaining in the oil (Bhosle and Subramanian, 2005).

Bhattacharyya and Bhattacharyya [42] studied the effect of the amount glycerol on the extent of re-esterification of raw rice bran oil. The addition of glycerol was shown to increase the rate of reaction. The excess theoretical amounts of glycerol used were 10%, 30% and 50%. After 6 h of reaction, the FFA was reduced from 15.3% to 4% by using 50% excess amount of glycerol while the drop in FFA was from 15.3% to 6%, 5.6% and 4.8% for 10%, 20% and 50% excess glycerol, respectively.

Singh and Singh [43] tried to use 50%, 70% and 100% in excess of the theoretical amount of glycerol required in re-esterification of rice bran oil with acid value of 24.3 mg KOH/g. When using 50% excess glycerol, the drop in acid value was about 19.3% at 200˚C for 6 h. On increasing the excess glycerol up to 70%, the re-esterification rate was faster and the maximum reduction in acid value was 20.2% at 200˚C within 4 h. The use of 100% excess glycerol followed similar trend to that of 70% excess glycerol. However, the impact of increasing the amount of glycerol was not encouraging as the maximum drop in acid value was only 20% after 5 h.

## 4. Applicability of Chemical Re-Esterification in Biodiesel Production

The chemical re-esterification can lower the high FFA content in biodiesel for homogeneous base catalyzed transesterification technology as shown in **Table 1**. It is possible to lower the FFA of the oil to less than 3%, which is an acceptable requirement for efficient production of biodiesel with homogeneous base transesterification. Sousa, Lucena and Fernandes [48] use the glycerol by product from transesterification to re-esterify castor oil with an FFA of 2.36%. The high solubility of castor oil in glycerol due to hydroxyl group on the castor fatty acid glycerol makes it possible to lower the FFA to 0.22% for 2 h at 120˚C without catalyst. Their results confirmed that glycerol (produced during the transesterification reaction) can be used to re-esterify the oil before its use in the production of biodiesel. In most of the reviewed literatures, the process has been used mostly in producing edible grade products whereby sensory properties and colour are of importance and therefore limit further exploration of different catalysts which are not good for edible grade product. Therefore, more researches in understanding the kinetics, application of different catalysts and optimizing process are still required.

## 5. Conclusion

The reviewed literature proved that the chemical re-esterification can be used as a pre-treatment method for high FFA feedstock for biodiesel production. In fact, the process shows the potentiality of reducing FFA to less than 3% which is required for homogeneous base catalyzed transesterification. This process can also utilize the glycerol from the transesterification process and would therefore lower the cost of biodiesel. There is a need for further research on this area, since little is still known on the optimization of the process especially for processing biodiesel feedstock whereby sensory properties and color are not important. The chemical re-esterification can be more easily implemented than acid esterification and thereby avoids the need for neutralization and alcohol

**Table 1. The effect of chemical re-esterification on the final amount of FFA.**

| Oil type | Time (h) | Temperature (˚C) | Catalyst | Amount of excess ycerol | Initial FFA (%) | Final FFA (%) | Sources |
|---|---|---|---|---|---|---|---|
| Rice Bran oil | 6 | 200 | p-toluene sulphonic acid | 50% | 15.3 | 1.6 | [42] |
| Rice Bran oil | 6 | 200 | p-toluene sulphonic acid | 50% | 20.5 | 3.1 | |
| Rice Bran oil | 4 | 200 | $SnCl_2$ | 70% | 24.3 | 3.0 | [43] |
| Rice Bran oil | 6 | 200 | $SnCl_2$ | 0% | 64.7 | 0.9 | [39] |
| Rubber seed oil | 6 | 200 | $ZnCl_2$ | 4.3% | 37.69 | 1.5 | [45] |
| Mixed fatty acids obtained by saponification of peanut oil | 4 | 200 | $SnC1_4{\cdot}5H20$ | Stoichiometric amount | 90.3 | 1.8 | [46] |
| Waste cooking oil | 4 | 200 | $SO_4^2/ZrO_2\text{-}Al_2O_3$ | 70% | 44.42 | 0.707 | [47] |
| Castor oil | 2 | 120 | No catalyst | 100% | 2.36% | 0.22% | [48] |

removal steps.

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