

*Full Length Research Paper*

# Deacidification of high acidic rubber seed oil by reesterification with glycerol

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Some studies have shown that rubber seed oil (RSO) from the seed of rubber tree (*hevea brasiliensis*) has potential technical applications. However, the high free fatty acid (FFA) associated with the oil may be a limiting factor in its applications. In this study, crude rubber seed oil (RSO) containing 37.69% FFA was deacidified using 4.3-5.6% of glycerol. The reactions were carried out at a pressure of 20mmHg in the presence of zinc dust and zinc chloride catalysts added separately at high temperature (150 – 250°C). The progress of the reaction was monitored by determining the FFA at various time intervals. The FFA content in the RSO was reduced to 1.5% in six hours when 4.3% glycerol was used with zinc dust at a temperature of 200°C while the triglycerides content of the oil increased from 40.32% in the crude oil to 80.62% in the deacidified RSO. The study showed that this process is effective in the deacidification of RSO without loss of neutral glycerides as in alkali neutralization.

**Key words:** Deacidification, free fatty acids, glycerol, esterification, rubber seed oil.

## INTRODUCTION

Vegetable oil is a major component of our diet. It is a source of energy, essential fatty acids and contains some fat-soluble vitamins such as vitamin A and E (Hay et al., 1980). Commercial sources of vegetable oils are oilseeds and fruit pulp. In 2004, about 380.3 million metric tons of the seeds were produced worldwide with a corresponding oil consumption of 105.6 million metric tons ([www.soystats.com](http://www.soystats.com), 2005).

The crude oil that is extracted from oilseeds consists of free fatty acids (FFA), monoglycerides (MG), diglycerides (DG), triglycerides (TG), phosphatides, pigments, sterol and tocopherols. It may also contain some amount of trace metals, tannins and glycolipids (Cheryan, 1998). Crude oils are usually subjected to purification (refining) process to remove the nontriglyceride fatty material. The conventional approaches to the purification process include degumming, alkali refining (deacidification), bleaching and deodorization. Of the stages of purification process, deacidification is the most delicate and difficult

step because it has the maximum economic impact on oil production (Rodrigues et al., 2007; Carr, 1976).

Deacidification is a process for the removal of FFA in the vegetable oil. FFA is virtually absent in fats/oils of living tissue. They can be formed by enzyme (lipase) action after the oilseed has been harvested (Bhosle and Subramanian, 2005). FFA is liberated by the hydrolysis of ester bonds in the lipid by the action of enzyme or heat and moisture (Nawar, 1996). The release of the short-chain fatty acids by hydrolysis is responsible for the development of undesirable rancid flavour in the oil. In addition, FFAs are more susceptible to oxidation than the glycerol esters of these fatty acids; and this lipid oxidation leads to oxidative rancidity in vegetable oils and fat-containing foods (Bhosle and Subramanian, 2005). In view of this, it is important to remove the FFA from the oil and avoid any action that would promote increase in the acidity of the oil.

Several approaches have been adopted to deacidify vegetable oil such as chemical, physical refining and etc (Bernardini, 1985). In the conventional chemical (alkali) deacidification, FFA is neutralized to form soaps which are removed by centrifuging. However, this method is not suitable for oils that contain more than 8 - 10% (wt) because of high oil losses due to saponification and

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occlusion of oil in the soap stock (Anderson, 1962). Besides, large quantities of water are used to wash the oil after caustic soda treatment which leads to contaminated discharges and high disposal costs (Raman et al., 1996). A refining loss of three times the FFA content has been reported in chemical deacidification of soybean and cottonseed oil (Norris, 1982). Physical refining process (Cvengros, 1995) removes the FFA and other odoriferous compounds by sparging the oil with saturated steam at high temperature and under vacuum thereby eliminating soap stock and a reduction in neutral oil losses. Darkening of the oil may occur if it is not pre-treated to remove impurity such as gums (Mishra et al., 1988). Other methods which have received attention in vegetable oil deacidification include solvent extraction (Rodrigues et al., 2007, Kale et al., 1999), miscella refining (Chan et al., 1996, Turkey and Civelekoglu, 1991), and the most recent developments such as membrane deacidification (Raman et al., 1996), chemical reesterification (Bhattacharyya and Bhattacharyya, 1987; De and Bhattacharyya, 1999; De, 2006) biological reesterification (Bhattacharyya and Bhattacharyya, 1989; Cho et al., 1990) and super critical fluid extraction (Dunford et al., 2008, Brunetti et al., 1989; Favati et al., 1991) each with advantages and disadvantages (Bhosle and Subramanian, 2005). Among these, membrane and reesterification processes are more attractive owing to their inherently lower oil losses. In fact, with reesterification process, oil yield is increased especially triglycerides (TG) content (De, 2006). Reesterification involves the conversion of FFA into neutral glycerides with the free hydroxyl groups remaining in the oil or with the added hydroxyl group from glycerol at high temperature under high vacuum or inert atmosphere with or without catalyst (Anderson, 1962). Bhattacharyya and Bhattacharyya, 1987 carried out the reesterification of crude rice brand oil containing FFA (15 - 30%) using glycerol with acid catalyst and metal salts and achieved a reduction of FFA content to 2 - 6%.

Rubber seed oil (RSO) from the seed of rubber tree (*hevea brasiliensis*) has potential applications in the manufacture of some consumer goods (Iyayi et al., 2007). However, the incidence of high FFA in the oil may be a limiting factor in its application in the synthesis of some compounds such as vulcanized oil (Fernando, 1971). Attempt to deacidify the oil by using the alkali refining resulted in high refining losses (UNIDO, 1989). The purpose of this study was therefore to ascertain conditions under which the high-acidic RSO could be deacidified by reesterification with glycerol.

## EXPERIMENTAL PROCEDURES

### Materials

Rubber seeds from which the oil was extracted were obtained from the plantation of Rubber Research Institute of Nigeria during the harvest period of August to September. The seeds were dried in a

batch dryer operating at temperature of 65-70°C to a moisture content of about 7% and were thereafter subjected to mechanical extraction process using hydraulic press. The crude rubber seed oil obtained was first degummed with citric acid and subsequently by water degumming according to the method described in UNIDO (1989) report on Rubber Seed Processing. Thereafter it was used in the deacidification process.

Ethyl alcohol, hydrochloric acid, citric acid, potassium hydroxide, iodine trichloride, potassium iodate and sodium thiosulphate were products of BDH, Poole, England and were of analytical grade. Glycerol, zinc chloride and zinc dust were products of CVI, U.K.

### Analysis of rubber seed oil

The physicochemical properties of the oil such as specific gravity, FFA, saponification value and iodine value were determined following standard AOCS methods (Firestone, 1998).

### Chemical reesterification

The degummed RSO (ca. 200 g) was placed into a 400-ml conical flask with a ground-glass B-24 joint. A predetermined amount of glycerol was added to the oil as shown in Table 1. The reactions were carried out at temperatures from 150-250°C and at a constant pressure of 20 mmHg. The reaction mixture was heated in the flask by temperature controlled heating mantle and stirred with a Teflon magnetic stir bar (2.54cm). The catalysts used, zinc dust and zinc chloride were at 0.25 and 0.15% by weight of the oil respectively. Samples were withdrawn at 1-hour interval and the FFA determined until there was no significant change in the FFA. The triglycerides, diglycerides and monoglycerides contents of the initial and final samples were determined using high performance liquid chromatograph (HPLC) by Waters Associates, Milford, MA; Model 510 equipped with a UV detector (Model 441) and data module (Model 740) in accordance with the procedure of Foglia et al (1997).

### Experimental setup

A total of three experiments were carried out to determine the effect of glycerol on the deacidification at a constant temperature of 200°C and pressure of 20 mmHg with zinc dust as catalyst as shown in Table 1. Furthermore, three other experiments were carried out at different temperatures (Table 1) while keeping both the glycerol and pressure constant at 4.3% and 20 mmHg respectively using zinc dust as catalyst. The last set of four experiments were carried out with zero catalyst, zinc dust, zinc chloride, zinc dust/zinc chloride at constant temperature and pressure as shown in table 1.

## RESULTS AND DISCUSSION

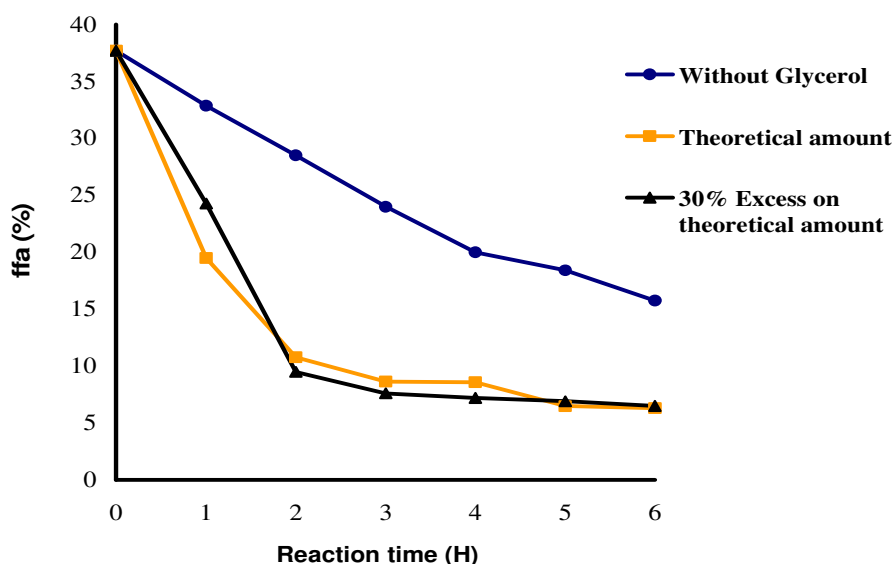
The physico-chemical characteristics of crude rubber seed oil used as feed material for the deacidification experiments are shown in (Table 2). It can be seen from the presence of high FFA of 37.69% that the conventional deacidification process of alkali refining will lead to high refining loss (Kale et al, 1999). Initial experiments carried out in our laboratory using this process confirmed this whereby the caustic soda completely turned the oil to soap. Thus chemical reesterification process was thought more feasible for deacidifying RSO of high acidity

**Table 1.** Deacidification conditions during experiments.

| Experimental runs | Glycerol (%) | Temperature (°C) | Pressure (mmHg) | Catalyst used  |
|-------------------|--------------|------------------|-----------------|--|
| 3                 | 0, 4.3, 5.6  | 200              | 20              | Zinc dust  |
| 3                 | 4.3          | 150, 200, 250    | 20              | Zinc dust  |
| 4                 | 4.3          | 200              | 20              | 0, zinc dust, zinc chloride, zinc dust/zinc chloride |

**Table 2.** Characteristics of crude RSO.

|                                      |        |
|--------------------------------------|--------|
| S.G. (25 °C)                         | 0.943  |
| FFA (wt %)                           | 37.69  |
| Saponification value (mgKOH/g)       | 226.12 |
| Iodine value (gI <sub>2</sub> /100g) | 142.45 |
| <b>Glyceride composition (wt %)</b>  |        |
| Triglycerides (TG)                   | 40.32  |
| Diglycerides (DG)                    | 18.44  |
| Monoglycerides (MG)                  | 2.32   |

**Figure 1.** Variation of FFA with the time of reesterification with glycerol.

(De and Bhattacharyya, 1999).

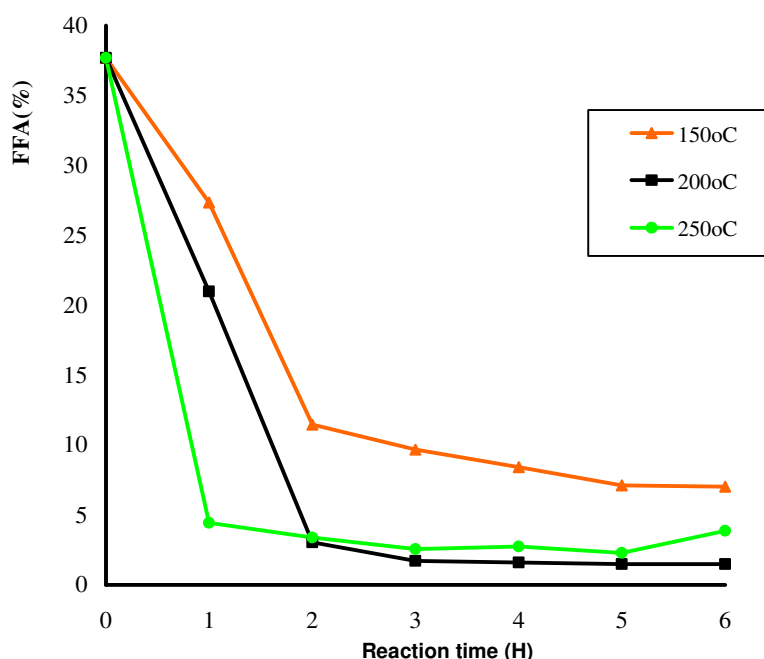
#### Effect of glycerol on the extent of deacidification of rubber seed oil

The results of the effect of glycerol on the deacidification of RSO are presented in Figure 1. The results show that by using the stoichiometric amounts (4.3% wt oil) of glycerol, there was a significant reduction in FFA level compared to when no glycerol was used during the reesterification reaction. However, using (5.6%) that is

30% excess of glycerol did not show any appreciable improvement in FFA reduction compared with the use of stoichiometric amount of glycerol. It was observed that the rate of reduction in FFA was rapid during the initial two hours of the deacidification reaction and thereafter it decreased considerably. This may be as result of high reesterification reaction occurring between the hydroxyl groups from the added glycerol and FFA at the initial stage leading to increase in triglycerides content. In reaction kinetics, this is expected as increase in the concentration of product should lead to a reduction in the reaction rate. In the case of deacidification without

**Table 3.** Effect of different reaction conditions on glycerides content of RSO.

| Parameter                 | MG   | DG    | TG    |
|---------------------------|------|-------|-------|
| Without glycerol          | 2.34 | 29.45 | 51.49 |
| 4.3% glycerol             | 0    | 16.35 | 76.26 |
| 5.6% glycerol             | 0    | 15.88 | 76.96 |
| 150 <sup>o</sup> C        | 0.64 | 16.47 | 73.11 |
| 200 <sup>o</sup> C        | 0    | 14.52 | 80.62 |
| 250 <sup>o</sup> C        | 0    | 14.31 | 80.53 |
| Without catalyst          | 0.76 | 21.52 | 61.40 |
| Zinc dust                 | 0    | 14.52 | 80.62 |
| ZnCl <sub>2</sub>         | 0    | 15.88 | 79.23 |
| Zn dust/ZnCl <sub>2</sub> | 0    | 17.53 | 77.48 |

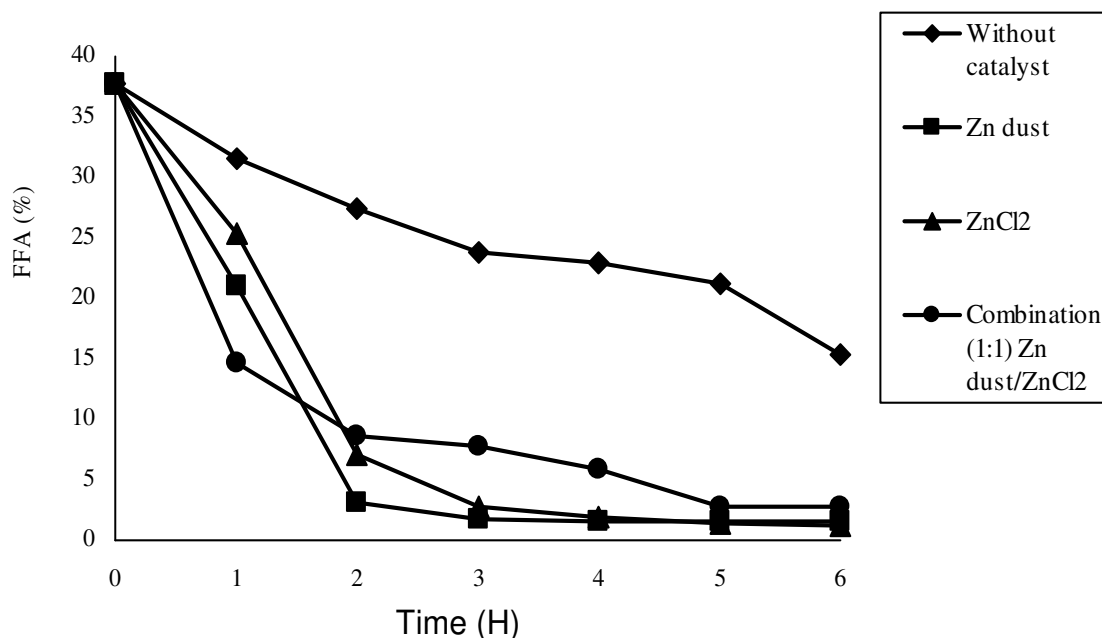
**Figure 2.** Variation of FFA with time due to changes in temperature in the deacidification of RSO.

glycerol, the observed 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) under the reaction condition. There is evidence, as seen in Table 3, that the reactions seem to have favoured the increase in the content of triglycerides (TG) and the reduction of monoglycerides (MG) and diglycerides (DG) indicating that by the addition of glycerol, the FFA in the oil was converted mostly to TG. The variations of FFA with reaction time are graphically illustrated in figure 1. There was an initial rapid reduction in FFA which was followed by a period of gradual reduction of FFA content in the oil samples. As already suggested above, this pattern of FFA reduction could be attributed to the reactivity of the hydroxyl groups

of the glycerol with the later portion being due to the depletion of the reactants.

#### Effect of temperature on the extent of the deacidification of RSO

The reaction temperature during the reaction was found to influence the rate of deacidification (Figure 2). Thus at 150°C the FFA was lowered to about 7.03 from 37.69% in 6 h. While at 200°C, the FFA dropped to 1.5% over the same period. When the reaction was carried out at 250°C, the reduction in FFA was fastest within the first two hours. However, the FFA dropped to 3.88% which is a little higher than that at 200°C over the same reaction



**Figure 3.** The variation of FFA with time due to the effect of catalyst in the deacidification of RSO.

time. It is suspected that there was a small degree of fat splitting at this elevated temperature after being held for 6 h. Figure 2 clearly illustrates this phenomenon. It does appear that at the temperatures investigated, the rate at which RSO reesterifies is at its maximum between 200 and 250°C. The yield in triglycerides content of 80.62% at a temperature of 200°C was not significantly different from that at 250°C (80.53%) except at 150°C when TG was found to be 73.11% (Table 3). The result shows that an operating temperature below 200°C does not reduce FFA content sufficiently and incapable of producing the higher TG that is mostly desired in vegetable oils.

#### Effect of catalyst on the extent of deacidification of RSO at 200°C

The influence of catalyst on the rate of deacidification was also studied. Without catalyst, the rate of deacidification was observed to be slow (Figure 3). In this reaction, FFA was reduced to 15.38 from 37.69% in 6 h. However, on the introduction of catalyst such as zinc dust, zinc chloride and a combination of the two, significant reduction in FFA is achieved as illustrated in Figure 3. While FFA dropped to 1.50% when zinc dust was used, it was lowered to about 1.27% on using zinc chloride. The use of the combination of both catalysts did not appear to present any improvement from when the catalysts were used separately. Again, there was a significant increase in the TG and reduction in MG and DG with the introduction of catalyst (Table 3). The catalyst is seen to facilitate the reaction between the

glycerol used and the FFA or between the DG and MG and the FFA to form TG (Nawar, 1996).

#### Conclusions

The study shows that rubber seed oil could be deacidified by chemical reesterification process using glycerol in the presence of a catalyst and under vacuum. With this process, there is almost no loss of oil since the process involves the addition of glycerol to the free fatty acids (FFA) in the oil to produce more triglycerides.

A reduction in FFA from 37.69 to 1.5% was achieved in a reaction time of six hours while operating at a pressure of 20 mmHg, with 4.3% glycerol and a temperature of 200°C. Operating at higher or lower temperature than this did not produce better result. Under this condition, which is regarded as the optimum, the deacidified RSO contained zero monoglycerides, 10.52% diglycerides and 80.62% triglycerides compared to the crude oil which contained 40.32% TG, 18.44% DG and 2.32% MG.

Two catalysts, zinc dust and zinc chloride were both effective in the reduction and the rate of reduction of FFA in the crude RSO. However, while zinc chloride gave the lowest FFA in the final product, it was zinc dust that produced the highest yield in the triglycerides.

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