# ADSORPTION OF PALM OIL MONOGLYCERIDES USING RICE HUSK ASH

**Keywords**: Monoglycerides, Adsorption, Monopalmitin, Rice husk ash, Palm oil

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*It is shown that monoglycerides can be selectively adsorbed on rice husk ash from crude palm oil-hexane miscella or crude palm oil. The adsorbed monoglycerides were identified by gas chromatography and GC/MS. The major fatty acids of the monoglycerides were found to be palmitic and oleic acids. In model experiments, 0.2%(w) of monopalmitin added to refined, bleached and deodorized palm olein could be removed completely using rice husk ash; about 48 µmol or 15.84 mg of monopalmitin were adsorbed by one gram of ash.*

## INTRODUCTION

The main object in refining crude palm oil is to remove objectional impurities and produce a bland, stable, light-coloured edible oil acceptable to consumers. One of the important steps in this process is adsorptive cleansing. The use of acid-activated clay of montmorillonite type for this step is widely acceptable in both the physical and chemical refining of palm oil (Bek-Nielson and Krishnan, 1976; Pritchard, 1975). The function of the clay is to remove colour, trace metals, phospholipids, soaps and products of decomposition and oxidation such as peroxides (Wiedermann, 1981; Liew *et al.*, 1982; Zchan, 1981; Shaw and Tribe, 1981). However, these activated bleaching earths are imported into Malaysia and are expensive. The present study was intended as a preliminary investigation of the effectiveness of treated rice husk ash as an adsorptive cleanser in crude palm oil refining, and of the identity of the components adsorbed by the ash, which is a silicate material composed of cristobalite and tridymite (Hsu and Luh,1980).

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Recently, Proctor and Palaniappan (1989) demonstrated that acid-treated rice hull ash is effective in binding the soy oil pigment lutein at 20°C. They also demonstrated that free fatty acids can be adsorbed from a soya bean oil-hexane miscella by inorganic rice hull ash (Proctor *et al.*, 1990). In this paper, our findings on the adsorption of monoglycerides from crude palm oil by rice husk ash are presented and discussed.

## MATERIALS AND METHODS

Materials: Crude palm oil and refined, bleached and deodorized palm olein were obtained from Lam Soon Oil and Soap Mfg Sdn.Bhd., Kuala Lumpur. The samples were stored at 4°C. Palm oil-hexane miscellas (1:5 w/v) were prepared by diluting palm oil with n-hexane.

Rice husk was obtained from a local rice processing mill in Kuala Selangor, Selangor, Malaysia. Monopalmitin and monoolein were purchased from Sigma Chemical Company, U.S.A. and were of approximately 99% purity. All the solvents used were of analytical grade.

### Ash Production

Unless stated otherwise, the adsorbents were prepared by heating the rice husk at various temperatures for two hours in a muffle furnace. The ashing temperatures studied were at 500°C, 600°C, 700°C and 800°C.

### TLC Analysis

In preliminary experiments, 2 g of ash sample was added to 10 g of crude palm oil or crude palm oil-hexane miscella (1:5 w/v) at 80°C and kept for one hour with constant stirring. The mixture were then filtered and the ash was washed with 3 × 30 ml hexane.

The adsorbed monoglycerides were recovered by extraction with chloroform. The solvent was then removed completely in a rotary evaporator at 40°C, followed by drying under a stream of nitrogen. The dried sample was then redissolved in 5.0 ml of chloroform.

Aliquots of solution were spotted on silica gel TLC plates (20 cm × 20 cm), Merck, and chromatography was carried out in the solvent system: n-hexane:diethyl ether:formic acid (60:40:1, v/v/v). Spots were visualized by spraying with 1% 2,7-dichlorofluorescein in absolute ethanol.

### Determination and Quantification of Monoglycerides

Monoglycerides were determined by gas chromatographic analysis using the following conditions.

| | |
|---|---|
| Gas chromatograph | : Shimadzu model 9 APTF |
| Column | : 3% OV–1 (dimethyl silicone) on 80/100 Supelcoport, 90 cm × 3mm i.d., glass |
| Column temperature | : Isothermal, 220°C |
| Injector and detector (FID) temperatures | : 260°C |
| Nitrogen carrier gas | : 50 ml/min |

Quantification of monoglycerides was done with an external calibration curve using various concentrations of authentic monopalmitin. The same conditions were used for the analysis of standards. 0.5μl samples were used for the analyses.

### Fatty Acid Composition

Fatty acid methyl esters were prepared according to the AOCS standard method (1981), and analysed by gas chromatography.

### Effect of Ashing Temperature

In adsorption experiments, 1 g of ash sample was added to 10 g of refined, bleached and deodorized (RBD) palm olein containing 0.02 g of added monopalmitin and the mixture was kept for 1 hr at 50°C. The amount of monopalmitin adsorbed as determined by gas chromatography was then plotted against the ashing temperatures.

### Effect of Adsorbent Dosage

Doses at 0.5, 1.0, 1.5, and 2.0 g of the adsorbents were added to 10 g of RBD palm olein containing 0.02 g of added monopalmitin. The mixtures were agitated with a magnetic stirrer for 1 hr in a closed vessel at 50°C. The adsorbed monopalmitin was measured by gas chromatography as described previously. The adsorbent doses were then plotted against the amount of monopalmitin adsorbed.

### pH measurements

The pH of a 4% slurry of the ash in deionized water was measured with a pH meter.

## RESULTS AND DISCUSSION

The approximate yields of ash obtained by treating the rice husk in a muffle furnace at 500°C, 600°C, 700°C and 800°C for two hours were 18.6%(w), 14.8%(w), 12.9%(w) and 12.0%(w) respectively. The colour of the ash produced turned more greyish as the temperature was increased. The pH values of 4% suspensions of the ash sample in deionized water were found to be 9.61, 10.17, 10.20 and 9.93, respectively.

Our preliminary studies revealed that the rice husk ash adsorbed monoglycerides strongly from a 20% palm oil–hexane miscella at 80°C. It seems that diglycerides could also be adsorbed, but not as strongly as monoglycerides. The diglycerides adsorbed could easily be washed out by hexane solvent. This difference in adsorbability of mono- and diglycerides may be exploited to effect separation of these two classes of partial glycerides. It was also observed that free fatty acids in palm oil could be adsorbed from palm oil–hexane miscella by alkali-treated rice husk ash, consistently with the observation of Proctor and Palaniappan (1989) on the adsorption of free fatty acids from soya bean oil–hexane miscella. *Figure 1* shows the TLC analysis of the hexane and chloroform extracts of the rice husk ash.

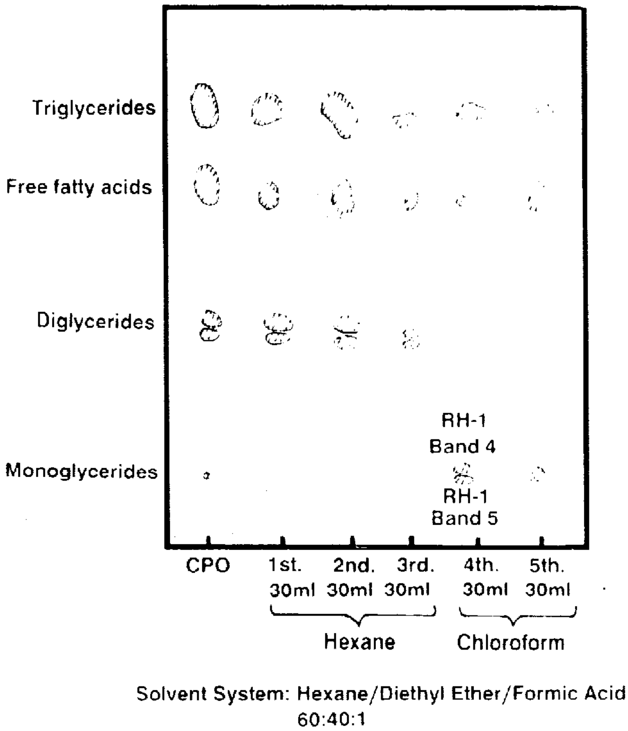



*Figure 1. Thin Layer Chromatogram of Chloroform Extract of Rice Husk Ash with Adsorbed Components from Crude Palm Oil–hexane Miscella. (The ash was mixed with the miscella as described in the text, then washed three times with hexane before extraction with chloroform).*

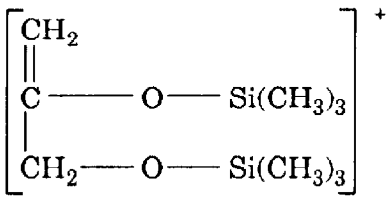
*Table 1* shows the percentage fatty acid composition of the monoglycerides. The major fatty acids present are palmitic and oleic, which are also the main fatty acids in palm oil. The results also suggest that α-monoglycerides are preferentially adsorbed as compared with β-monoglycerides. This supposition is based on the observation that the $R_f$ value of the monoglycerides adsorbed corresponded to that of α-monopalmitin. In the interpretation of mass spectra from GC/MS analysis, it is observed that

TABLE 1. FATTY ACID COMPOSITION (%) OF MONOGLYCERIDES ADSORBED BY RICE HUSK ASH

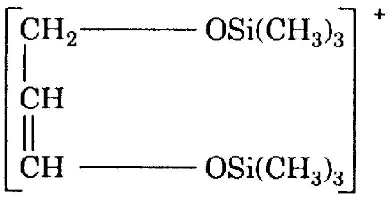
| | C12 | C14 | C16 | C18:0 | C18:1 | C18:2 | OTHERS |
|---|---|---|---|---|---|---|---|
| Crude Palm Oil | 0.4 | 1.0 | 43.6 | 4.4 | 40.8 | 8.8 | 1.0 |
| RH-1 BAND 4 | 0.9 | 1.5 | 51.6 | 10.1 | 27.7 | 5.3 | 2.9 |
| RH-1 BAND 5 | 0.7 | 2.1 | 49.2 | 11.8 | 24.6 | 4.4 | 7.2 |

(RH-1 BAND 4, RH-1 BAND 5 – refer to *Figure 1.*)

the two major monoglycerides adsorbed yielded a very weak ion at m/z 218 which is due to



β-monoglycerides usually yield a strong m/z 218 ion which is due to



However, the idea that α-monoglycerides are preferentially adsorbed as compared with β-monoglycerides should be further studied. It could be that there was very little of the β-isomer in the sample since α-monoglycerides are much more stable than β-monoglycerides, and α-monoglycerides predominate at 80°C (the temperature of the adsorption studies).

The amount of monoglycerides adsorbed by rice husk ash from palm oil–hexane miscella varied with the method of ash preparation.

Adsorption of monoglycerides was also observed when undiluted crude palm oil was used. This again indicates clearly that genuine adsorption has taken place and not simply precipitation of the monoglycerides. *Figure 2* shows the TLC analysis of the hexane and chloroform extracts of the rice husk ash which had been put into crude palm oil. Small amounts of partial glycerides are present in palm oil, usually as a result of hydrolysis. The content of monoglycerides in palm oil, in which they are soluble, is usually below 1% while that of diglycerides can be as high as 6% to 8%. The presence of monoglycerides together with free fatty acid is reported (Berger, 1977) to promote an increase in solubility of water in the crude palm oil. This will affect the solubility of glycerides in solvents and hence the solvent fractionation process, and will also promote hydrolysis (Berger, 1977). The presence of diglycerides is even more important than that of monoglycerides, and

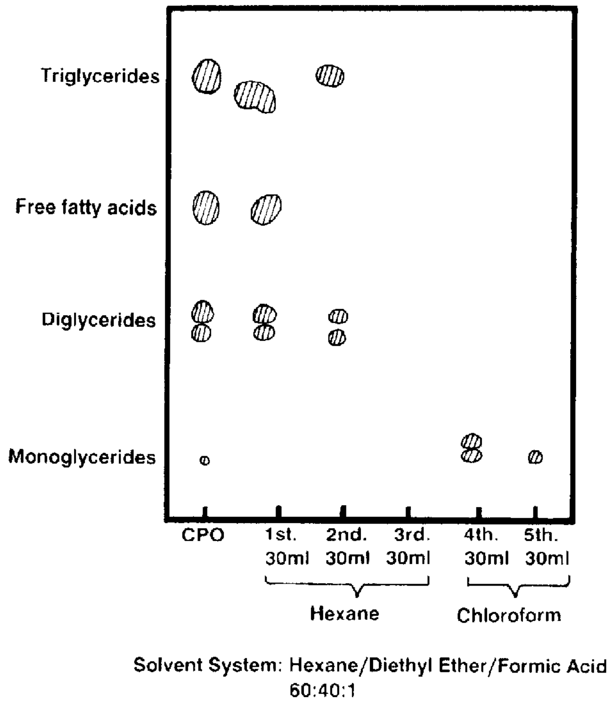
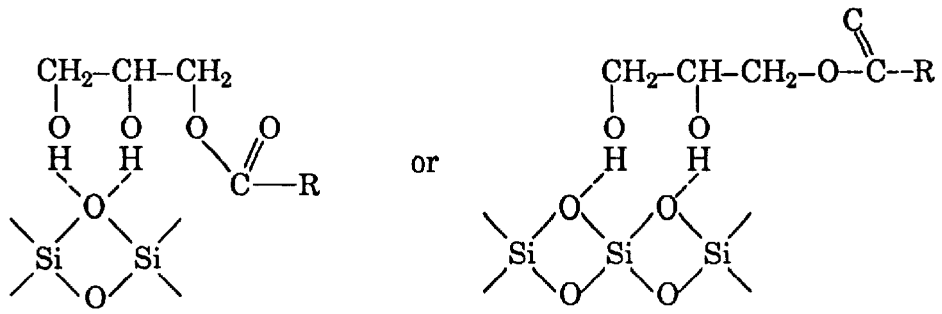



*Figure 2. Thin Layer Chromatogram of Chloroform Extract of Rice Husk Ash with Adsorbed Components from Crude Palm Oil. (Procedure as in* Figure 1, *except that in the first step the ash was mixed with undiluted crude palm oil).*

they are fairly difficult to be removed by refining because of their low volatility. Their presence will result in the formation of eutectic mixtures with the triglycerides, causing a reduction in the yield of high-melting triglycerides (the stearin fraction) in the fractionation process. The diglycerides will slow down the transformation of the crystals from the α-form to the β'-form and to the β-form. This leads to mixed crystals, resulting in a poor separation of the various fractions of the oil (Berger 1977).

The mechanism for the adsorption of the monoglycerides by the rice husk ash can possibly be represented as follows:




Molecular size and shape are important factors in adsorption because steric hindrance can prevent hydrogen bonding and hence adsorption on the silica surface (Iler, 1979). Thus, a diglyceride molecule possesses only one OH group and being more bulky than a monoglyceride is possibly more sterically hindered in respect of hydrogen bonding. This could be the reason for its weak adsorption by the rice husk ash. The stronger the tendency for hydrogen bonding, the stronger the adsorption. Furthermore, the number of molecules adsorbed per unit area of silica decreases as the molecular size increases.

Quantification of monoglycerides adsorbed from palm oil was also one of our primary interests. It was done using the external calibration curve of monopalmitin plotted in *Figure 3*. The effect of the ashing temperature on the adsorption of monopalmitin from RBD palm olein onto the ash was then studied. *Figure 4* shows the amount of the monopalmitin adsorbed versus the temperature at which the rice husk ash was prepared. It was found that ash prepared at 500°C had the highest adsorptive capability for monopalmitin. Proctor and Palaniappan (1990) also found that the most effective ashing temperature was 500°C

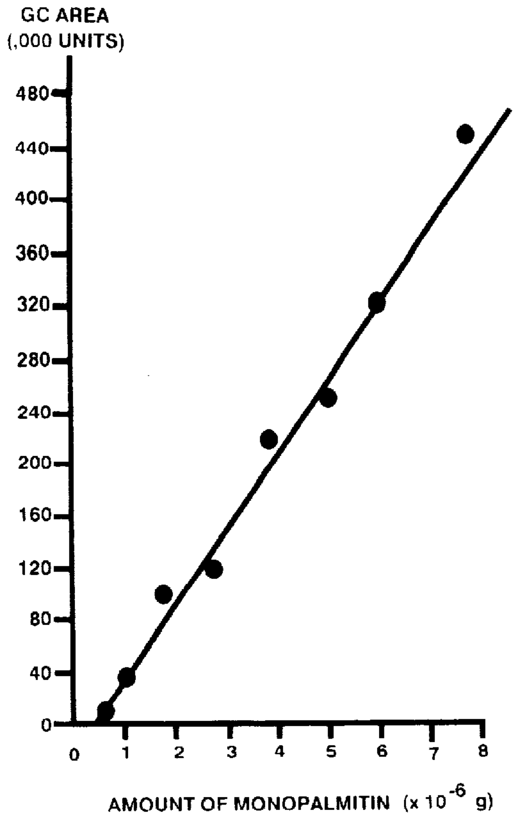



*Figure 3. GC Area versus Amount of Monopalmitin*

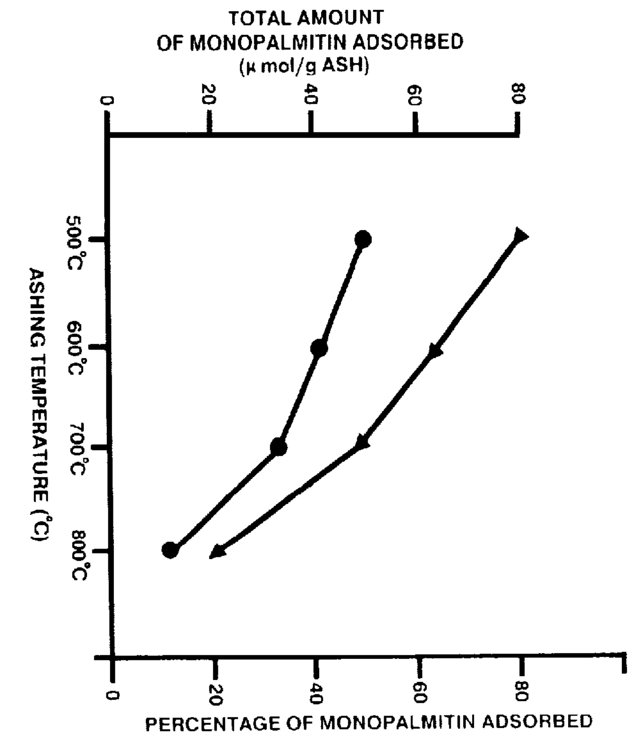



*Figure 4. Effect of Ashing Temperature on Adsorption of Monopalmitin (●—● total amount percentage ▲—▲ percentage adsorbed)*

for the adsorption of soya bean oil lutein, albeit our ashing time was only two hours while theirs was 10 hours. Liu (1963) offered some evidence from solubility studies that a part of the silica might be tied up with organic groups. Thus, the ashing at 500°C could have removed some of those organic groups and hence created the sites of adsorption. When the ashing temperature was greater than 500°C, the adsorption of monopalmitin on the ash decreased. This might be attributed to the breakdown of the crystal structure.

The amount of monopalmitin adsorbed as a function of the amount of adsorbent was also studied, using the one ashed at 500°C. The results (*Figure 5*) show that the adsorption of monopalmitin increased as the ash dosage was increased. Adsorption of monopalmitin from the RBD palm olein was found to be about 48 µmol or 15.84 mg per gram of ash.

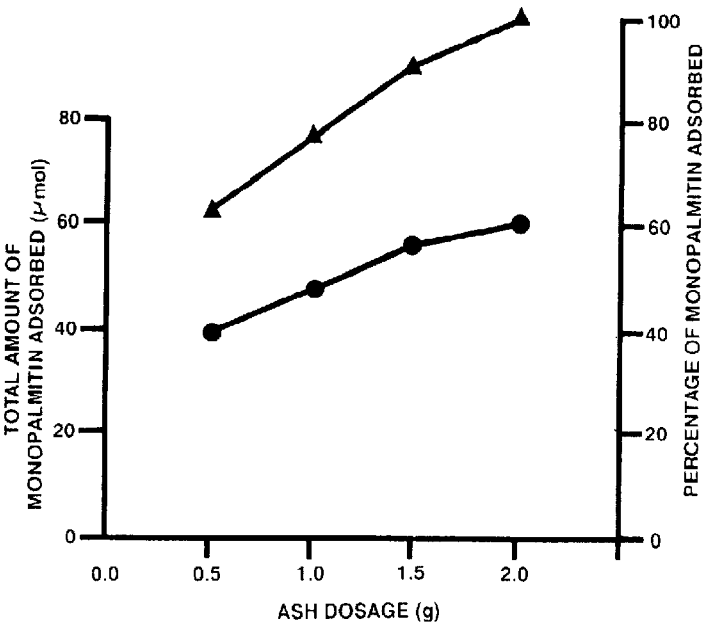



*Figure 5. Effect of Ash Dosage on Adsorption of Monopalmitin (●—● total amount absorbed ▲—▲ percentage adsorbed).*

## CONCLUSION

Our results indicate that rice husk ash can be used as an effective and selective adsorbent for monoglycerides. The preferential adsorption of monoglycerides by rice husk ash is interesting and it seems that this is the first report on this phenomenon.

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