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SURFACE ACTIVE PROPERTIES OF PALM OIL WITH RESPECT TO THE PROCESSING OF PALM OIL

Keywords: Interfacial tension, surface tension, surface active, sludge, crude palm oil, refined oil, milling, refining.

CHOW, M C* and HO, C C**

* Malaysian Palm Oil Board, P.O. Box 10620, 50720 Kuala Lumpur, Malaysia.
** Chemistry Department, Universiti Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia.

The supernatant sludge from the palm oil mill was determined to be surface active from surface tension measurement. In crude palm oil (CPO)/sludge supernatant, the inter-facial tension was determined to be 3 mN m^{-1} which is favourable for the formation of oil droplets in the CPO slurry.

The refined oillwater systems have higher interfacial tension compared to the CPO/water system. Depending on whether the CPO is chemically or physically refined, the oil/water interfacial tension differs and can be as high as 25.6 mN m^{-1} and 12.7 mN m^{-1} respectively compared to an interfacial tension of 8.00 mN m^{-1} in the CPO/water system. The higher inter-facial tension value indicates more efficient removal of surface active compounds from the chemically refined oil. This may have great implications in the quality and utilization of palm oil in food processing.

The interfacial tension values of the partially refined oils as sampled from various points of refining were found to increase as the oil is processed. In view of this increase, interfacial tension could possibly be used as a process control parameter in the refining of CPO.

Lecithin and monoglycerides were determined to significantly reduce the interfacial tension at the refined palm oil /water interface. Some of the common minor constituents found in CPO such as carotene, diglycerides, fatty acids and cholesterol did not show surface activity at the refined palm oil/water interface.

INTRODUCTION

Palm fruits are harvested in bunches and sent to the mill for processing (*Figure* I). On arrival, the bunches are steam sterilized where the fruits soften and are easily detached from the stalk. These detached fruits are further softened with steam in digesters. The digester mash is then passed to the screw press where oil together with the juice from the fruits are expressed. The crude oil slurry which is expressed may contain approximately 48% oil, 45% water and 7% solids. Some of the water in this slurry is actually steam condensate from the sterilization, digestion and screw pressing where steam is injected into the respective machinery to maintain the high temperature required throughout the milling process. Hot water is further added to the crude oil slurry to reduce the viscosity so that the oil will cream to the surface in large clarification tanks. The underflow from the lower section of the clarification tank is centrifuged to remove as much of the heavier phase consisting of solids and water. This watery phase or sludge is discharged and any oil found here constitutes oil loss as it is discharged as effluent, The lighter phase from the centrifuge, which consists of oil and water, is recycled to the clarification tank. The creamed palm oil from the surface of the clarification tank is then skimmed and further purified, dried and sold as CPO to the refinery for further processing.

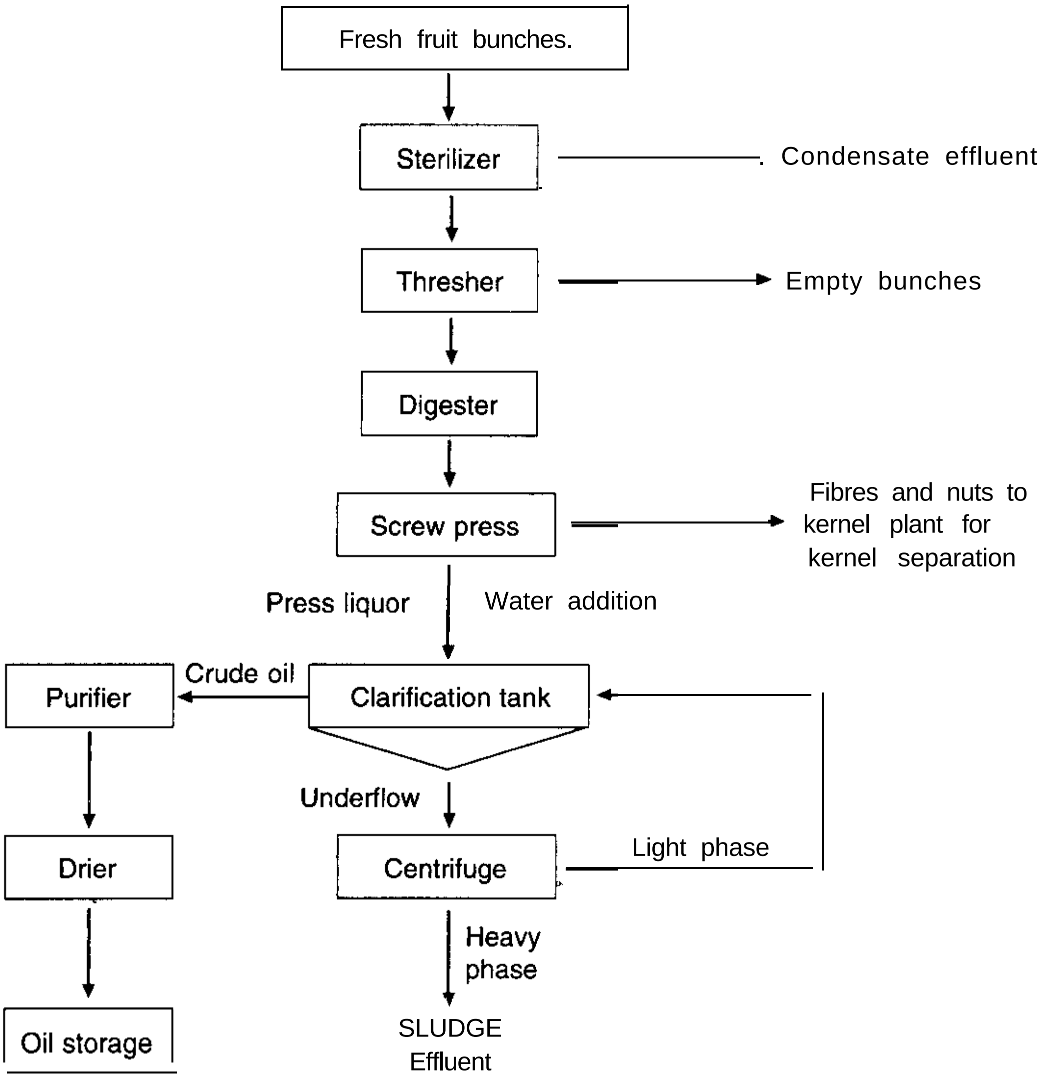


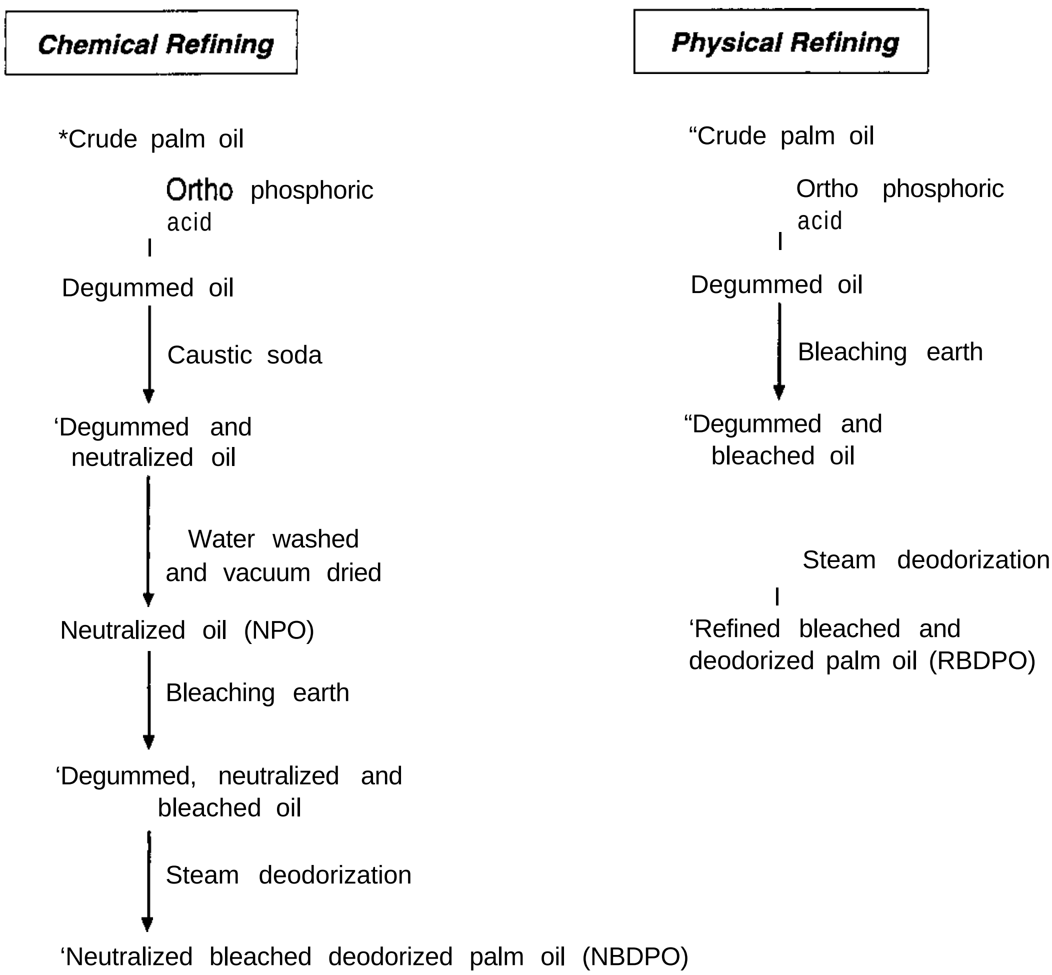
Figure 1. Flow diagram of palm oil extraction.

In the refinery, the CPO is processed to remove most of the undesirable impurities thus making the oil bland, colourless and chemically stable according to trade specifications and consumer requirements, There are basically two types of refining practiced by the Malaysian palm oil refiners. They are chemical and physical refining. The two processes differ in treatment of the oil and result in differently labelled oils as illustrated in *Figure 2.*

In the mill, as the CPO is extracted there is no continuous on-line monitoring of quality but the impurities present are only of botanical origin from the palm fruits. In the final quality assessment when sold to the refineries, only certain contractual specifications are measured. They are free fatty acid, moisture and impurities, and, in some mills, the peroxide value, which determines the degree of oxidation.

Similarly, in the trading of refined palm oil, the same set of contractual specifications are required with the additional requirement of colour. These parameters are used to assess not only the initial quality of CPO but also the amount of bleaching earth required which is one of the major costs incurred in CPO relining. No form of continuous monitoring is known in palm oil relining.

This study reports an alternative qualitative parameter, interfacial tension, which can possibly be used to assess the effectiveness of each stage of the refining process. The significance



Notes: * Samples of partially processed oil.

Adapted from *Selected Readings* on *Palm Oil and its* Uses. Ministry of Primary Industries, Malaysia, 1993, p. 150-174.

Figure 2. Refining processes for *CPO.*

and importance of this parameter in causing oil loss in the milling process is also discussed.

MATERIALS AND METHODS

Materials

Sludge from the centrifuge of a palm oil mill was collected and analysed the following day. High speed centrifugation at 10 000 G was used to separate the suspended solids and the oil droplets in which a clear brown supernatant was obtained. This sludge supernatant was used in subsequent interfacial tension and surface tension measurements.

CPO was collected from various palm oil mills in Peninsular Malaysia. Some samples of CPO and partially processed palm oils were obtained from various refineries in Peninsular Malaysia too. Commercial monoglyceride, PVP, consisting of 90% monopalmitin and 10% monoolein of 90% purity, was supplied by Grindsted Products A/S, Denmark. The lecithin was type IV-S: (soyabean lecithin containing approximately 40% phosphatidylcholine) supplied by Sigma Chemical Co. Diglycerides of dipalmitin and diolein, fatty acids palmitic and stearic and cholesterol palmitate were also supplied by Sigma Chemical Co. Carotene concentrate was an extract from CPO.

Commercial chemical refined palm oil (NBDPO) was used as the standard palm oil in which other components were added in all the interfacial tension measurements. The NBDPO used contained 95.97% triglycerides, 3.99% diglycerides and 0.04% monoglycerides. The fatty acid composition and some quality parameters are as shown in *Tables* la and *b.*

TABLE la. FATTY ACID COMPOSITION OF NBDPO

Fatty Acid	wt. (%)
12:o	0.2
14:o	1.0
16:0	43.9
18:0	4.0
18:1	40.6
18:2	9.6
18:3	0.3

TABLE lb. QUALITY OF NBDPO

Free fatty acid (as palmitic acid)	0.02%
Peroxide value	2.41 meq kg-'
$UV^{1\%}_{233}$	1.55
$UV^{1\%}_{269}$	0.36
carotene	1 ppm
Anisidine value	1.31

Methods

The Kruss Digital Tensiometer Model KT 10 was used for the measurement of surface tension and interfacial tension in the systems studied. All water and oil samples were placed in a 60°C oven before transferring to the tensiometer for measurement. All measurements were also carried out at 60°C.

Surface tension measurement. The tensiometer with the attached ring in air was tared. The sample was then brought up until the ring was submerged. The system was allowed to stabilize for half an hour and measurement began by slowly lowering the sample stage. The ring pulled a collar of liquid into the air. The maximum force necessary to break the film in air was taken as the surface tension of the liquid. The ring was cleaned with methanol, acetone and finally flamed after every measurement before the next.

Interfacial tension measurement. The tensiometer was tared in the lighter phase (oil) by submerging the ring completely in it. Zero adjustment in the oil was necessary to compensate for buoyancy and surface tension which acted on the shaft of the ring. The ring was cleaned as described above.

After that, a new sample container was half filled with the heavy phase (water, 12.5 g) and the cleaned ring submerged into it. The lighter phase (oil, 12.5 g) was added carefully to the top of the water. The system was allowed to stabilize for half an hour before the ring was pulled through the oil/water interface. The maximum force necessary to break the film in the oil was taken as the interfacial tension of the system.

The mean interfacial tension of the NBDPO against water was 20.6 mN m^{-1} at 60°C based on measurements of 10 samples of the same batch of oil. The measured values ranged from 19.2 to 21.6 mN m^{-1} with a standard deviation of 0.72 mN m^{-1}.

RESULTS AND DISCUSSION

Surface Activity

Surface activity is manifested by groups of compounds called surface active agents or surfactants, commonly known as emulsifiers in foods. The structures of these molecules are such that they consist of two moieties; a hydrophobic chain linked to a hydrophilic functional group. In view of the amphiphilic nature of the emulsifiers irrespective of the phase in which they are dispersed, they will tend to become located at the interface be it the air/water, air/oil or water/oil interface. The hydrophilic head-group will tend to locate itself in the aqueous phase while the lipophilic hydrocarbon chain orientates towards the oil phase, this situation being thermodynamically more favourable than complete dissolution in any particular phase. This phenomenon of lowering the energy level at the interface between the two phases is measurable and is termed surface tension if one of the phases is air while that which occurs at two liquid phases such as oil/water is termed interfacial tension. Through such determination, the surface activity caused by the presence of the surface active compounds can be detected and determined by a surface tensiometer. Further lowering of the energy at the interface will result in a lowering of the surface or interfacial tension which will be conducive for emulsification or droplet formation when mixing. At extremely low interfacial tension, spontaneous emulsification will result in the formation of microemulsions and when the interfacial tension is negligible complete miscibility or dissolution of the two phases takes place.

Milling

In the mill, the liquid discharged (sludge) contains only botanical residues from the mesocarp or fleshy part of the fruit. It is not possible to measure the surface tension in the presence of solids and thus the sludge had to be centrifuged. On centrifugation, a clear brown supernatant was obtained while the solids settled to the bottom and the oil droplets which creamed were separated. The supernatant obtained from sludge was determined to have a surface tension of 30 mN m^{-1} at 60°C compared to water which has a surface tension of 66 mN m^{-1} indicating the presence of surface active agents in the sludge.

The surface activity of the sludge supernatant decreased linearly when plotted against the logarithmic concentration of sludge diluted with water (Figure 3). However, at the same concen-

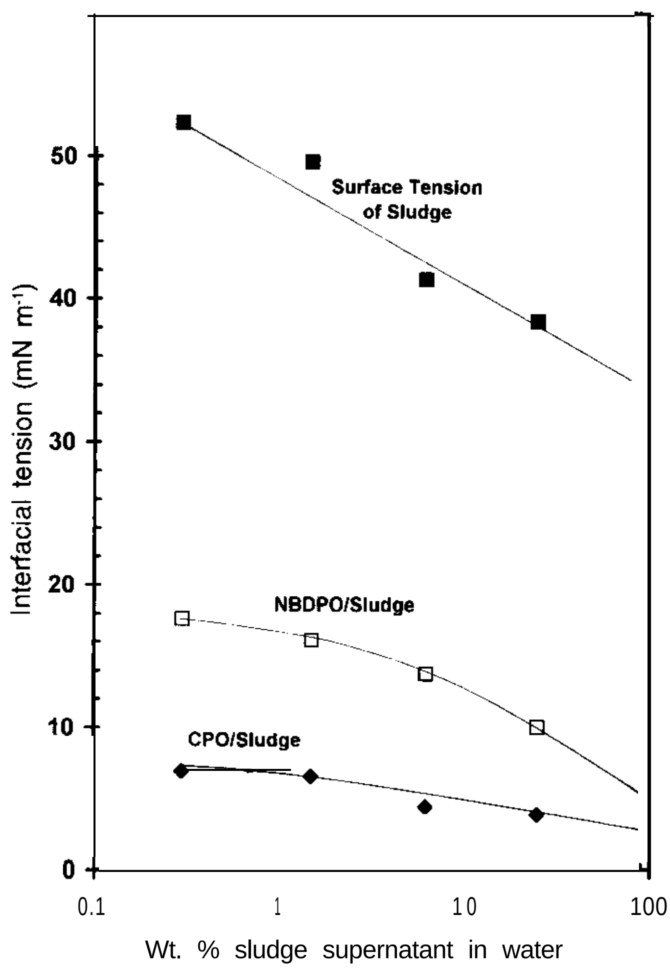


Figure 3. Effect of dilution with water at 60°C on the surface tension of sludge supernatant and interfacial tension of palm oil (NBDPO) and CPO/sludge supernatant interface.

tration of sludge supernatant in water when different types of palm oil was present at the interface, there was a further reduction in the interfacial tension but the decrease was not as sharp when compared to the surface tension of the supernatant only (Figure 3).

The reduction of interfacial tension of the NBDPO/sludge supernatant system compared to the surface tension of sludge supernatant at the same concentration indicated that the oil/supernatant system had a lower free energy than the supernatant/air system. This could possibly be due to more favourable orientation of surface active agents from the supernatant preferentially absorbed by the oil phase. However, the interfacial tension of the CPO/sludge supernatant was further depressed compared to the NBDPO/sludge supernatant system. This could possibly indicate that there were also surface active agents in the CPO. In the undiluted sludge supernatant/CPO system, the interfacial tension was reduced to 3 mN m^{-1} which was sufficiently low for emulsification to occur.

The CPO/sludge supernatant system is a close simulation ofthe clarification station ofthe milling process where there is intimate contact of the two liquid phases. Together with the intensive agitation of pumping and high temperature, the conditions are ideal for undesirable emulsion formation. Optical microscopy showed that these oil droplets are indeed present in sludge (Chow, 1987). As much as 30% of the total oil found in the sludge is actually in the form of minute droplets.

In emulsification, once the droplets are formed, subsequent stabilization of the oil droplets must occur otherwise the droplets may rapidly flocculate and coalesce separating into the respective original phases. The stability of these newly formed droplet interface may depend on the interaction of the various surface forces of the molecules at the interface (Bergenstahl and Claesson, 1990). Mixed emulsifiers at the surface of the droplets may form stable complexes which stabilize the droplets (Boyd et al., 1972). Monoglycerides, diglycerides, glycolipids and phospholipids are natural. biosurfactants and are known to be present in CPO (Goh and Timms, 1985; Kulkarni,1991;Goh et *al.*,1982). Glycolipids at as high as 3.8% are found in oil from spent earth discarded in the refining process (Yamaoka et *al.*,1989). These molecules can act as natural biosurfactants in the CPO/sludge supernatant interface and further stabilize the droplet surface as even when these droplets from the sludge are concentrated they do not coalesce easily to form a homogenous layer.

Evidence ofsurface active agents in the CPO is further illustrated in the decrease of interfacial tension at the NBDPO/water system (Figure 4) when CPO is added to the NBDPO which is a relatively purified commercial palm oil. Other known commercial vegetable oils such as olive, corn, canola and olive oils have interfacial tension ranging from 19.0-23.0 mN m^{-1} and when purified through Florisil had their interfacial tension increased to 30532.0 mN m^{-1} (Goankar, 1989).

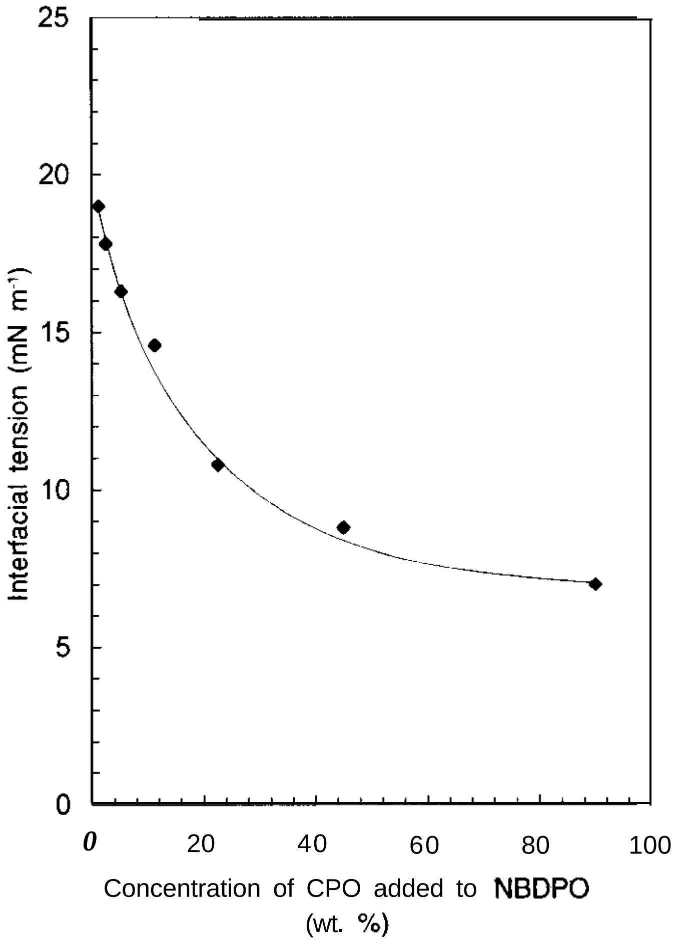


Figure 4. ***The effect of** CPO **on the interfacial tension of NBDPO/water** interface.*

Refining

The surface tensions of various commercial palm oil products had been measured previously at specific temperatures but no significant variations were found (Oh and Chong, 19921. The present study also showed that at 60°C, the surface tension of palm oil at various stages of refining were very similar within a narrow range of 30.6-31.7 mN m^{-1} but that their interfacial tensions varied and decreased differently as the oil was processed (*Table* 2). The presence of surface active agents in CPO and its products was clearly manifested in their low and varied interfacial tension values but not in the surface tension values. This also indicated that the surface active compounds present in the oil were thermodynamically more favourably absorbed at the oil/water interface than at the oil/air interface. The surface active agents present in the oil had greater affinity for water or are relatively polar.

The interfacial tension of CPO/water interface ranged from 6.0-9.6 mN m^{-1}. As the oil is processed, the interfacial tension is increased. Chemically refined oils were determined to have higher interfacial tension ranging from 25.0 to 26.4 mN m^{-1} compared to physically refined oil with interfacial tension ranging from 10.6 to 12.9 mN m^{-1} (Table 2) indicating that chemical refining was capable of removing more impurities that were surface active. The presence of such substances in the oil may have great implications in the quality and utilization of palm oil in food manufacturing.

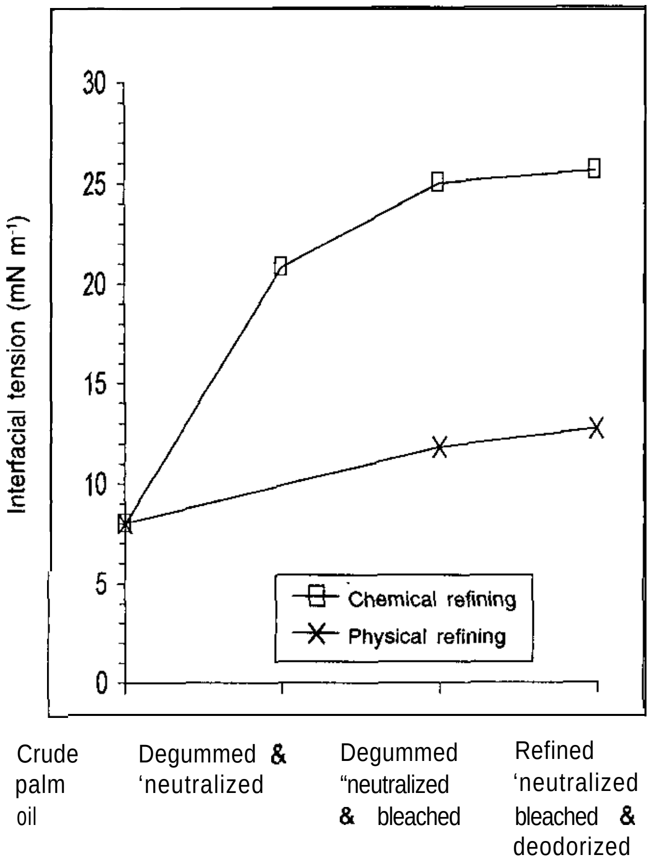
Surface active agents in palm oil may include monoglycerides, glycolipids and phospholipids. Hydrolysis products such as fatty acids, aldehydes, ketones, hydroperoxides and peroxides are some of the impurities removed in the refining process. Carotene breakdown products are also subsequently removed in the refining process. These minor by-products could possibly play a role in affecting the properties of the bulk phases and thus affect the interfacial property. At each stage ofdegumming, neutralization and bleaching of the oil, more surface active substances are removed as shown graphically (Figure 5) by the increase in interfacial tension of the oil against water. In chemical refining, the degumming and neutralization seemed much more effective than bleaching in the removal of

TABLE 2. SURFACE TENSION OF PALM OIL AND INTERFACIAL TENSION OF PALM OIL/WATER INTERFACE AT VARIOUS STAGES OF REFINING MEASURED AT 60°C

Oil*	Interfacial tension against water (mN m-9			Surface tension (mN m^{-1})		
	Range	Mean	S.D.	Range	Mean	S.D.
[a] Crude palm oil	6.0- 9.6	8.0	1.2	30.6-30.9	30.8	0.1
[b] Degummed and bleached palm oil	10.1-15.6	11.8	1.7	30.8-31.0	30.9	0.1
[b] Refined, bleached and deodorized palm oil (RBDPO)	10.6-12.9	12.7	1.1	30.8-31.1	30.9	0.1
[c] Degummed and neutralized palm oil	18.9-24.2	20.8	1.8	31.0-31.7	31.2	0.1
[c] Degummed, neutralized and bleached	24.7-25.4	25.0	0.3	30.7-31.0	31.0	0.1
[c] Neutralized, bleached and deodorized palm oil (NBDPO)	25.0-26.4	25.6	0.5	30.8-31.1	31.0	0.1

Notes: [a] Based on 18 samples.
[b] Based on 11 samples (physical refining from four refineries).
[c] Based on seven samples (chemical refining from two refineries).
Five hourly samples from one refinery and another two from another refinery.

*Point of sampling. Refer to *Figure 2*.



Note: *Neutralization is only carried out in chemical refining.

Figure 5. *Changes in interfacial tension at the palm oil/water interface as the oil is chemically /physically refined.*

surface active substances from the oil as the changes in interfacial tension increased from a mean of 8.00 to 20.8 mN m^{-1} (difference of 12.8 mN m^{-1}) after degumming and neutralization while there was an increment from 20.8 to 25.0 mN m^{-1} (difference of 4.2 mN m^{-1}) after bleaching. Variation in the interfacial tension of the bleached oil may depend not only on the prior process of degumming and neutralization but may also be dependent on the type (surface activity) and dosage of bleaching earth used as well as the duration and temperature of the respective treatment (Krishnan, 19831. A larger variation in the interfacial value of bleached oil is expected (compared to a standard deviation ± 0.3 mN m^{-1} obtained) if samples from more refineries could be obtained. A higher standard deviation of il.7 mN m^{-1} was obtained in the bleached oil samples from the four physical refineries. This low standard deviation of the interfacial values could possibly be because a rather limited number of samples (from only two refineries) were analysed. Only five hourly samples were collected from one refinery and another two from the second refinery as chemical refining was usually carried out infrequently and increasing the samples size during the study was not possible.

Finally, deodorization at high temperature has a strong influence on the amount of volatile impurities removed but not so much on the removal of the associated surface active compounds, since the interfacial tension was not significantly changed in both the physically and chemically refined oils before and after the deodorization process. In chemically refined oil, deodorization only increased the interfacial tension by 0.6 mN m^{-1} from 25.0 to 25.6 mN m^{-1}. In physical refining after deodorization, the interfacial tension increased by 0.9 mN m-i from a mean of 11.8 to 12.7 mN m^{-1}.

Effect of Additives

Since the interfacial tensions ofthe CPO and NBDPO are so different, an attempt was made to study this parameter by individually adding to NBDPO some common constituents that are known to be present in CPO. These include fatty acids, carotene, cholesterol, phospholipids and partial glycerides of mono and diglycerides.

The effects of various additives on the interfacial tension of the NBDPO/water system are shown in *Figure* 6. Palmitic and stearic acid changed the interfacial tension only marginally *even* when as high as 5% w/w was added separately to the refined oil. In fact, the interfacial tension was increased slightly with the addition of palmitic acid. A very slight reduction in interfacial tension was observed when cholesterol was added to the oil. Similar findings were reported by Ogino and Onishi (1981) on oleic acid and cholesterol which were shown to have insignificant effect on the corn oil/water interface. Carotenes up to as high as 10 000 ppm added to NBDPO did not have any effect on the interfacial tension of the NBDPO/water system. Neither did diglycerides of dipalmitin or diolein at as high as 3% w/w affect the interfacial tension of the NBDPO/water interface.

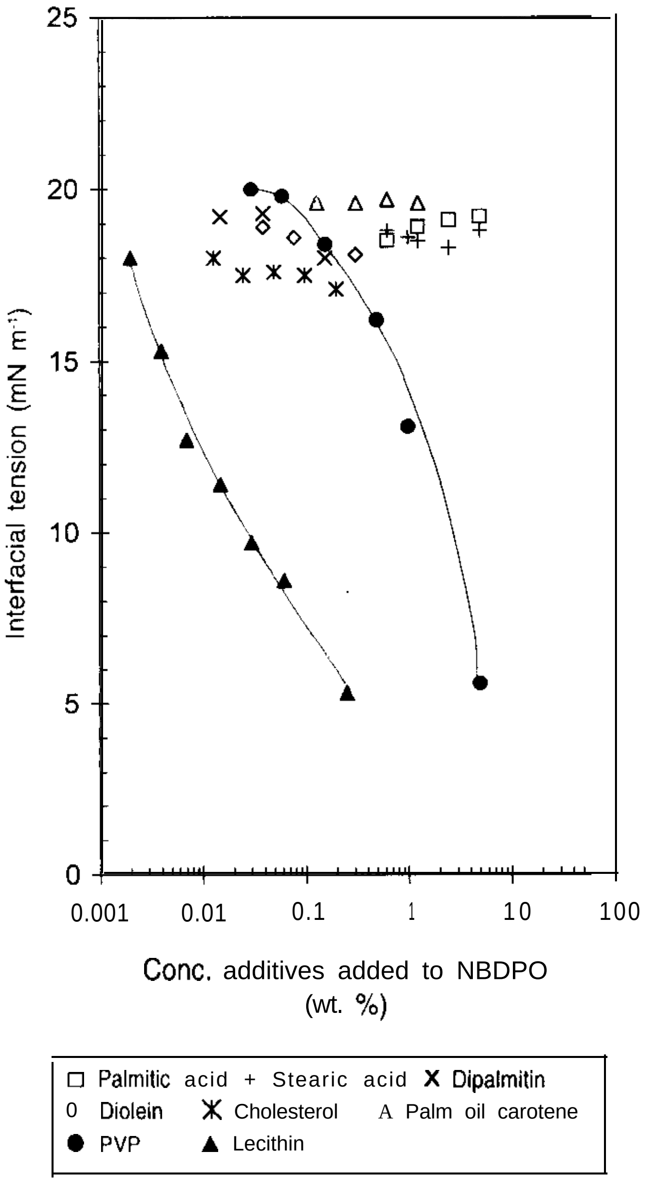


Figure 6. Effect of various additives on the interfacial tension of NBDPO/water interface.

When commercial monoglycerides PVP, a mixture of 90% monopalmitin and 10% mono-olein, was added to NBDPO, the decrease in interfacial tension at the NBDPO/water interface was gradual up to 0.2% w/w (*Figure 6*). Above 0.2% w/w, a rapid decrease in interfacial tension with PVP concentration was noted. The interfacial tension was reduced from 19 to about 6.5 mN m^{-1} at 1.25% w/w PVP. The NBDPO used contained 0.04% monoglycerides and additional monoglycerides further decreased the interfacial tension. CPO is known to have a monoglyceride content ranging from 0.26%-0.31% (Gob and Timms, 19851 and thus, most probably, monoglyceride is the surface active agent removed as the oil is refined whereby interfacial tension of the NBDPO/water system is raised. Various extent of lowering the interfacial tension of purified corn oil/water interface by mixtures of monoglycerides has also been reported (Goankar, 1989).

When soya lecithin was added to the NBDPO, there was a rapid decrease in interfacial tension at the oil/water interface (*Figure* 6). At 0.25% w/w, the interfacial tension was reduced to about 5 mN m^{-1}. At the same concentration of lecithin or monoglycerides in NBDPO, the decrease in interfacial tension at the oil/water interface caused by lecithin was much greater compared to the monoglycerides. However, phospholipids are only present in the range of 20-80 ppm in CPO (Goh et al., 1982). Although phospholipids are more surface active compared to monoglycerides, they probably are not as significant as monoglycerides in increasing the interfacial tension as the CPO was refined. Phospholipids and monoglycerides may have synergistic effect in reducing the interfacial tension of the palm oil/water system. In view of the phospholipids being so low in concentration in the CPO, its removal from the oil could not have increased the interfacial tension as significantly as the monoglycerides. Similarly lecithin has been found to be surface active in corn oil and safflower oil/water system too. At a concentration of 0.1% w/w lecithin in the oil, the interfacial tension was reduced to as low as about 2 mN m-i (Ogino and Onishi, 1981).

CONCLUSION

The aqueous supernatant from the palm oil mill sludge was determined to be surface active and to have a synergistic effect in lowering the interfacial tension of a CPO/water system. This resulted in the formation of undesirable stable oil droplets in the sludge discharge. Further studies had been carried out to determine the quantity of such surface active agents that contribute to the surface activity at the palm oil/water interface (Chow, 1997).

Under current practice, refining of palm oil is not intensively monitored except for colour and free fatty acid content. These parameters are more for trade specification and quality control purposes than for process monitoring. In this study, the surface active properties of palm oil refined to various extents of purity was investigated using interfacial tension measurement. It was found that interfacial tension could potentially be used to monitor the efficiency of each stage of refining as it indicates the level of 'impurities' removed. A simple interfacial measurement may be useful as a test to determine how efficiently the oil has been refined.

As the interfacial tensions of chemically and physically refined oils have been found to be very different, this simple physical measurement may be an appropriate indicator to be used to differentiate between the two oils. At present, there is no standard method to differentiate the two types of processed oils. The residual soap in the neutralization process of chemical refining was initially speculated to reduce the oil/water interfacial tension but this study showed that chemically refined oils have higher interfacial tension at the oil/water interface compared to the physically refined. Simultaneously this parameter could also be employed by end users to determine the suitability of any particular oil in product formulation where interfacial tension is one of the factors affecting manufacturing process such as emulsification.

Fatty acids, carotene, cholesterol and diglycerides when added in the concentration related to the amount found in CPO to relined palm oil did not exhibit significant surface activity at the NBDPO/water interface. However, monoglycerides at 0.1%-1.0% and phospholipids at 0.002%-0.2% concentration in NBDPO were found to be able to reduce the inter-facial tension significantly in the NBDPO/water system.

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