Bleachability and the DOBI

Ringkasan

Kemudahan meluntur minyak sawit mentah adalah satu-satunya ciri mutu yang paling penting bagi penghasilan minyak tulen gred satu. Proses kimia mengenai tindakbalas kerosakan yang mempunyai kesan ke atas keluntūran dan kaedah-kaedah analisis untuk menentukan keluntūran diḥuraikan. Kegunaan perincian perdagangan terhadap ujian ke atas minyak sawit mentah, yang dikenali sebagai DOBI, dibincangkan.

Introduction

Quality of a high and consistent standard must be the objective of the palm oil industry. For international trade not only are certain specifications included in the contract but the palm oil must be of "good merchantable quality". *Chapman (1981)*, at a meeting of the Federation of Oils, Seeds and Fats Associations in England, defined three main quality criteria that the average buyer is seeking.

Firstly he requires an oil with the normal and expected characteristics of palm oil as to melting point or solid fat content; secondly he requires an oil that will bleach easily and to pre-determined levels whether during a conventional refining process or by the more modern physical method; thirdly he requires the oil to have good stability and to enable him to produce an end-product which does not suffer from flavour reversion.

The criterion of bleaching easily and to a pre-determined level in the physical refining process is one that is also of importance to the Malaysian refining industry. Thus the identification of the factors responsible for difficulty and variability in bleaching is one of the major research themes of the Chemistry and Technology Division of PORIM.

Certain end-uses for processed palm oil have very stringent colour specifications; these can be as low as 1 Red, 10 Yellow Lovibond colour units as measured using a 5.25 in. cell *(Oh & Berger, 1981)*. However the common trading specification is a maximum of 3 Red units *(PORAM, 1981)*. No modification of the physical refining process can consistently give darker colours than this; but refining of bad quality crude certainly does.

The DOBI

DOBI is the acronym for an analytical procedure intended for quality control which is described as the "Deterioration Of Bleachability Index". It was proposed as a simple and hopefully relevant spectrophotometric measurement to be made on crude palm oil in an attempt to predict ease of bleaching during refining *(Swoboda, 1981)*. Deterioration by oxidation is a most important chemical change affecting bleachability *(Swoboda, 1980)* In addition the intrinsic content of trace impurities of crude palm oil as produced at the oil mill are of importance, and this aspect is also under investigation at PORIM.

Bleaching at the Refinery

The purpose of refining palm oil is to produce a bland, pale coloured product of good stability. Indeed the commercial product is described as "refined, bleached and deodorised" (RBD). During physical refining the crude palm oil (CPO) is first subjected to "pretreatment" and then to "deodorisation and deacidification". The "pretreatment" comprises of a "degumming" step and an "earth bleaching" step, together yielding the bleached palm oil (BPO). The final colour of the fully processed product (RBDPO) is dependent on the efficient operation of all these unit operations at the refinery and the quality of the CPO being processed.

Chemistry of Refining Technology

"Degumming" should be more correctly described as gum conditioning by the addition of acid, since the removal of any undesirable minor constituents and impurities does not occur until filtering after "earth bleaching". These steps of "pretreatment" should therefore be considered as a process for adsorptive cleaning. Impurities have to be removed which at the high temperature of the "deodorisation and deacidification" could give rise to coloured products, colours which are often described as "fixed" since they are even difficult to remove by further re-refining. Phosphorus containing gums are an example of minor constituents in oils, not only palm oil, which have to be so removed, and a maximum of 4 ppm phosphorus in the BPO feedstock to the deodoriser has been recommended by *Young (1981).* Oxidation products are another example of impurities which have to be removed by adsorptive cleansing if they are not to cause colour problems in the RBDPO.

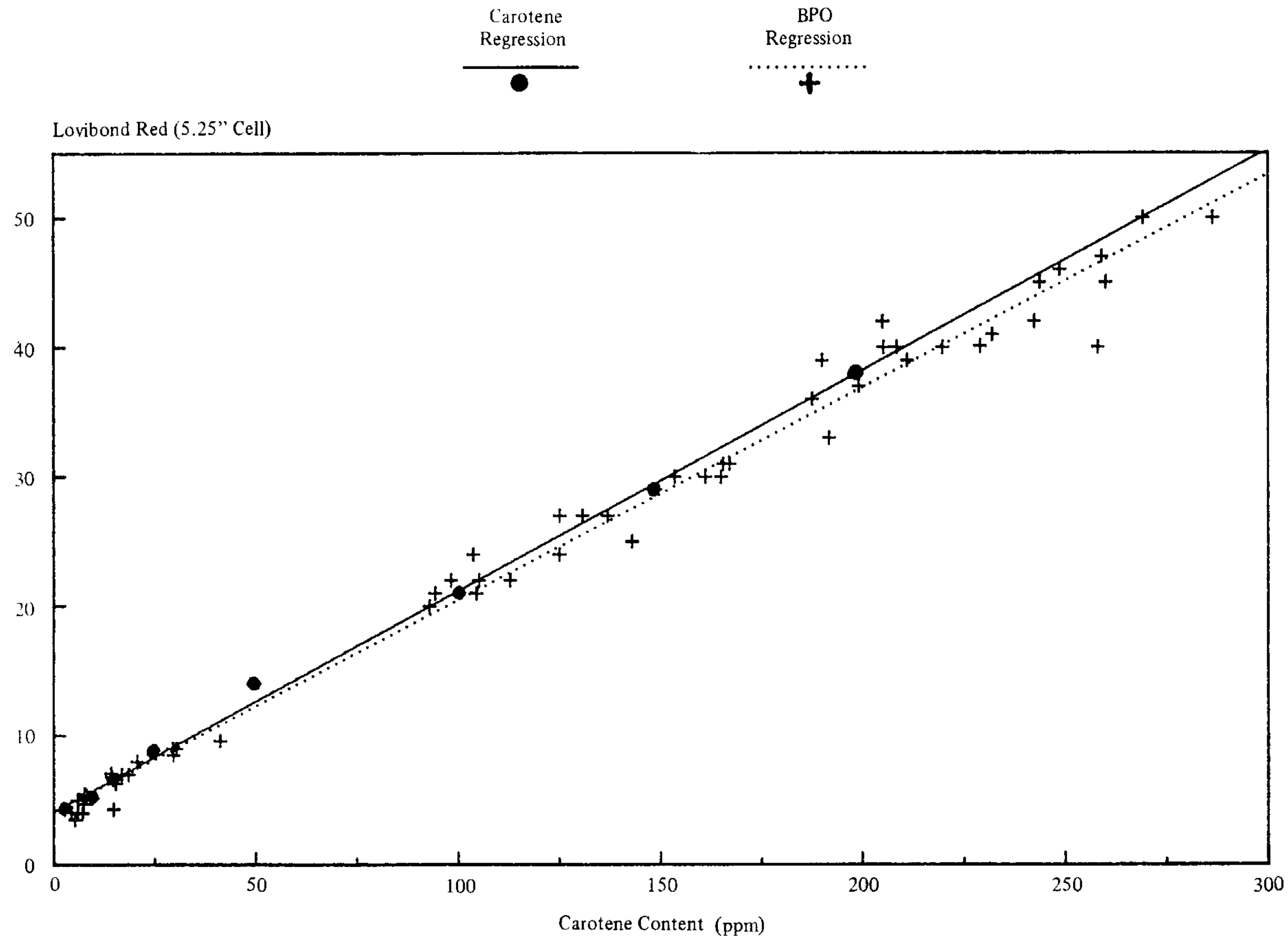
Of course the unique feature of CPO which makes it so different from other vegetable oils is its orange-red colour due to a carotenoid content of between 500 and 700 ppm for the Malaysian oil derived from *Elaeis guineensis.* This colour is removed during refining. The high temperature-time exposure during "deodorisation and deacidification" is sufficient to thermally bleach the carotenoids present in fresh CPO. There is no need for any colour reduction at the "earth bleaching" step, only an efficient adsorptive cleansing of impurities is required. Indeed the Malaysian refining industry now uses conditions for "earth bleaching" that roughly only halves the natural carotenoid level of CPO. Thermal bleaching alone, when other colour forming impurities have been removed, will reduce the orange-red colour of crude to a final product colour of 1 Red, 10 Yellow in a 5.25 in. Lovibond cell. This has been shown both in commercial practice and in laboratory experiments.

Bleaching in the Laboratory

Bleachability tests in the laboratory may be carried out using earth bleaching or thermal bleaching or both. In a review of current technology the *MOPGC (1981)* state that there are a number of bleaching tests available for palm oil. However, none has been given universal recognition. The technical committees of the MOPGC and of PORAM have been considering this problem and the Chemistry and Technology Division of PORIM proposes to organise collaborative trials.

A laboratory test, to be acceptable to all sections of the industry must be predictive, in that it should correlate with bleaching at the refinery. Also it must be reproducible between laboratories. To achieve this the United Kingdom refiners feel that a palm oil bleachability test must measure bleaching by a heat bleach process in addition to an earth bleach stage. Accordingly a two-stage bleachability test has been derived which includes a preliminary degumming step. The Seed Crushers and Oil Processors Association of the United Kingdom (SCOPA) set up a bleachability test sub-committee in 1978 and by 1980 their final report contains a recommended procedure and the claim that the variability between laboratories is no greater than that involved in colour measurement by the Lovibond technique *(SCOPA, 1980).*

Fig. 1. Effect of Earth Bleach On Colour BPO & Carotene Calibration



The SCOPA Palm Bleachability Test

The procedure comprises of an initial "degumming" of the sample of crude palm oil (100 g) by mixing with 0.5 ml of a 20% aqueous solution of citric acid at 90°C for 10 minutes. Then at 105°C "earth bleaching" is simulated by treatment with 2 g Tonsil Standard FF bleaching earth for 15 minutes. Both these steps of "pretreatment" are carried out under a nitrogen blanket. After filtering, 90 g of this earth-bleached oil is further heat-bleached at 260°C for 20 minutes under vacuum (1 to 3 mm Hg). With the vacuum still applied, the oil is cooled to 60°C and the final colour measured.

Several staff of the Chemistry and Technology Division of PORIM have been successfully using the SCOPA test since 1980, not only to compare the bleachability of palm oil samples but also to study the effect of variations in pretreatment and adsorptive cleansing by different clays.

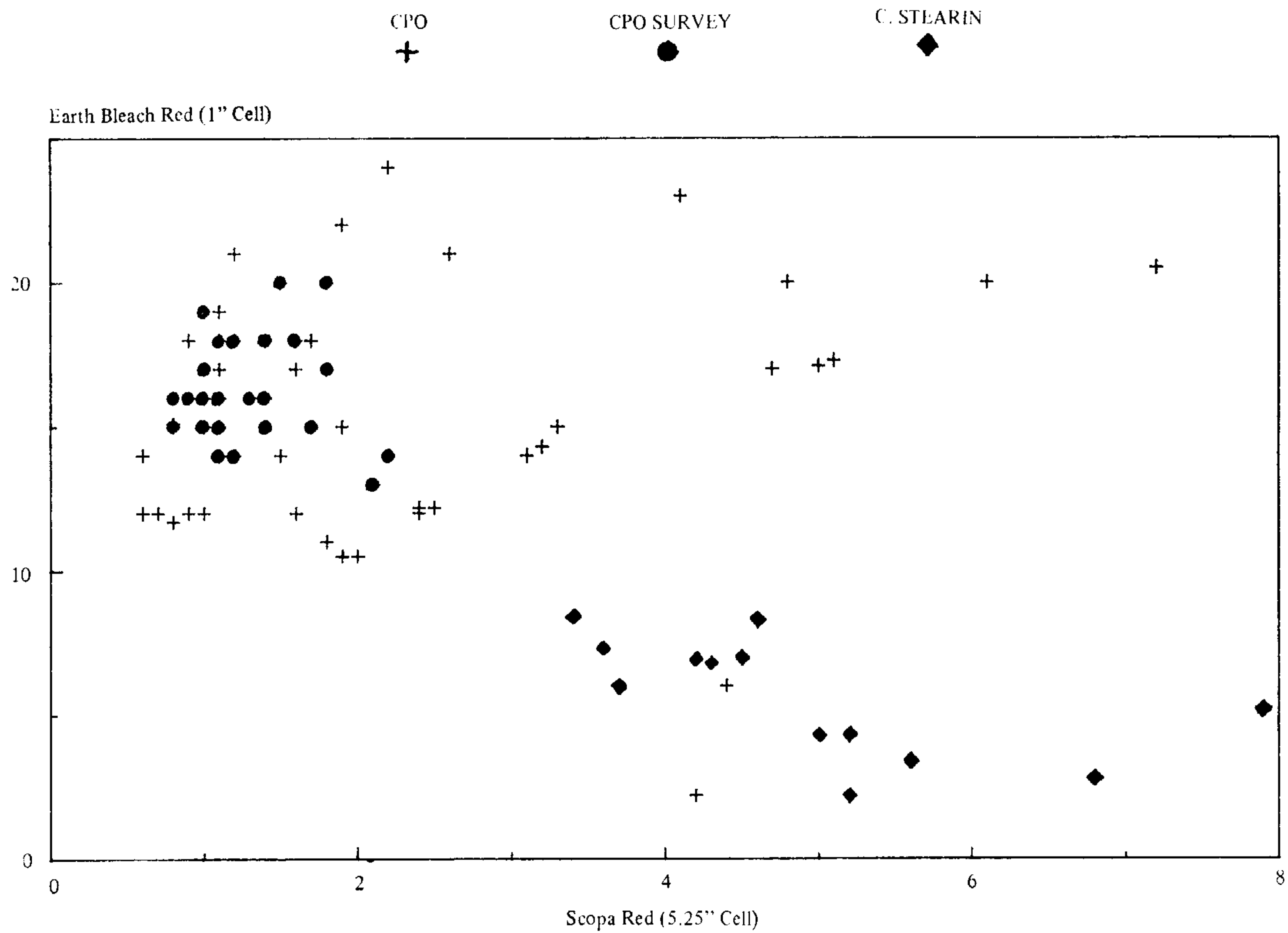
A modification of the SCOPA test using phosphoric acid (0.1%) instead of citric, and slightly different time temperature treatments, has been used with good repeatability at Guthrie Research, Chemara *(Chooi & Koh, 1981)*.

Chemistry of Laboratory Bleaching

The effect of "degumming" and "earth bleach" only is best illustrated by the results of a survey of the relative activity of different commercial bleaching earths *(Siew & Berger, 1980)*. After treatment with citric acid at 90°C for 10 minutes, 0.5, 1, 1.5 or 2% of each bleaching earth was added and allowed to react for half an hour at 150°C before filtering for colour measurement of the BPO. Fourteen commercial earths of widely different activity were thus evaluated for their adsorption isotherms. *Figure 1* shows that quite independent of the type of earth or of the amount used there is a good linear relationship (R^2 = 0.988 for 56 tests) between the Lovibond red colour of the BPO and its carotene content as measured by absorbance at 446 nm. Superimposed on this plot are the same measurements made on dilutions of synthetic β-carotene concentrate (30%) prepared by weight in RBDPO. Again a good linear relationship (R^2=0.996 for 7 tests) is observed and in fact there is no significant difference between the results for carotene dilutions and partially-bleached palm oils. It is reasonable to conclude therefore that the dominant effect of "earth bleaching" on colour is due to the residual carotenoids.

The next question that arises is whether there is a relationship between the colour of BPO and the RBDPO produced by thermal bleaching? *Figure 2* suggest that the answer is no! All results plotted are from SCOPA bleachability tests where the colour after the earth bleach step was measured in a 1 in. cell and the final colour after the thermal bleach measured in a 5.25 in. Lovibond cell. The results of three sets of tests are shown. Those labelled CPO survey refer to 32 tests made on production CPO sampled at an estate oil mill throughout the year and always treated with the SCOPA test as described. The other CPO set of samples varied both in their origin and also in modification of the SCOPA test; some had phosphoric acid substituted for citric and some used different and varying amounts of commercial activated bleaching earths. Finally a set of crude stearin samples have been included as this product of fractionation is often found to be difficult to bleach during physical refining; here the standard SCOPA test procedure has been used. The absence of any correlation is not surprising when the colour of BPO is due to residual carotenoids, which are efficiently destroyed by the thermal bleach, and leave a final colour in RBDPO due

Fig 2. Scopa to Earth Bleach Comparison
Lovibond Red Units for 80 Tests



to inefficient adsorptive cleansing.

Just to confirm the similarity between the SCOPA test and physical refining, the Lovibond measurements of the final colour are shown in *Figure 3*. The characteristic relationship of 10 Yellow units for 1 Red unit is observed whatever crude or whatever variation of the conditions of the SCOPA test. This relationship does not exist for partially earth-bleached only samples nor for dilutions of carotene, where lower and variable ratios are observed.

Chemistry of CPO Affecting Bleachability

Having established the importance of adsorptive cleansing it is now necessary to consider why it can become inefficient. There appear to be two factors. The first is intrinsic in the composition of certain fresh CPO samples, in that their contents of trace constituents and impurities overload the bleaching earth's capacity to remove them. The second factor is a much more dramatic effect caused by the accumulation of oxidation products during deterioration of CPO in storage and transport.

Figure 4 illustrates the first type of factor. The analyses are of 32 samples from the survey of production CPO sampled at an estate oil mill twice each month in duplicate from June 1981 to February 1982. As the FFA increases through the year so a higher colour is observed after the standard SCOPA test procedure. There is also a correlation in these samples between increasing FFA and increasing phosphorus and iron content. The changes in carotene content and oxidation parameters are not significant.

Similarly *Chooi, Koh and Goh (1981)* comment on the correlation between phosphorus with moisture, total iron, bleachability and FFA content from a survey of 119 fresh crude oil samples from five mills taken both at production and despatch. Peroxide value was not related to bleachability.

There appears to be an indirect relationship between bleachability and FFA in fresh oils. Maybe FFA helps to solubilise important trace constituents and impurities in CPO. The isolation and chemical identification of these causes of poor bleachability is part of the research program at PORIM.

Deterioration of bleachability of CPO due to oxidation during storage and transport is a well known phenomenon — and the adverse effects of iron and copper contamination have been well documented.

Studies at PORIM on model systems of CPO with added iron, and on CPO from different oil mills have identified a deterioration of bleachability on storage which is associated with high iron content. These stored samples undergo a dramatic destruction of carotenoids and tocopherols as well as showing an increase of secondary oxidation products as measured by the ultraviolet absorbance at 269 nm *(Swoboda & Gapor, 1981)*. *Chooi, Koh and Goh (1981)* on ageing their crude oil samples find that copper is a more significant pro-oxidant, but also report their best correlation for poor bleachability is with the absorbance at 269 nm. That a CPO which does not have the full orange-red colour and has a brownish tint will be difficult to bleach is a traditional criterion in the refining industry *(Chapman, 1981 and Young, 1981)*.

Thus as an indicator of this type of deterioration of bleachability the DOBI analytical procedure was proposed *(Swoboda, 1981)*. The "Deterioration of Bleachability Index" or DOBI is defined as the numerical

Fig. 3. Scopa Bleaching Test Results
Ratio of R to Y for 80 Tests

LINEAR
1:10 RATIO

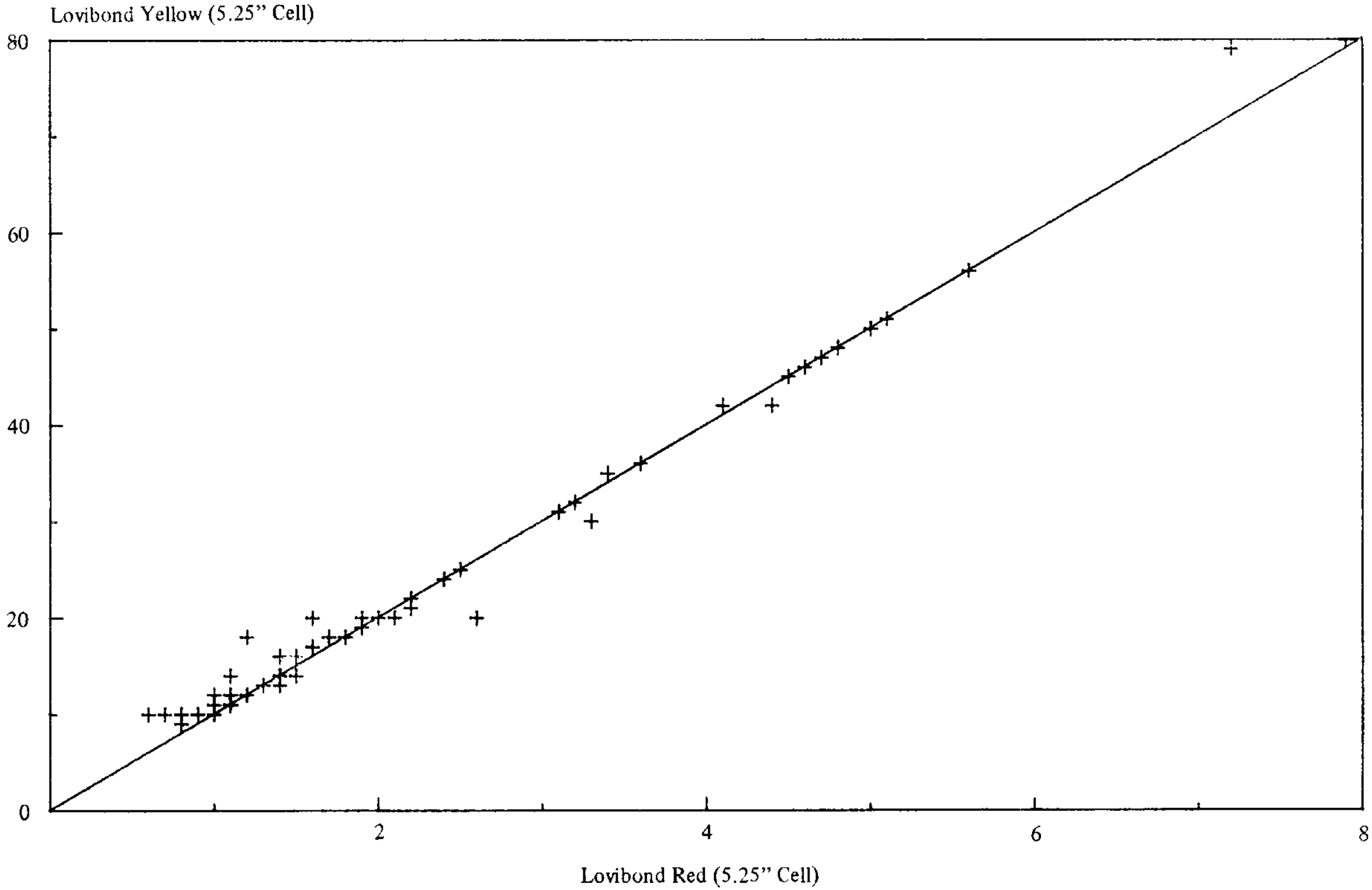


Fig. 4. Production CPO Survey from Mill FFA & Bleachability for 32 Test

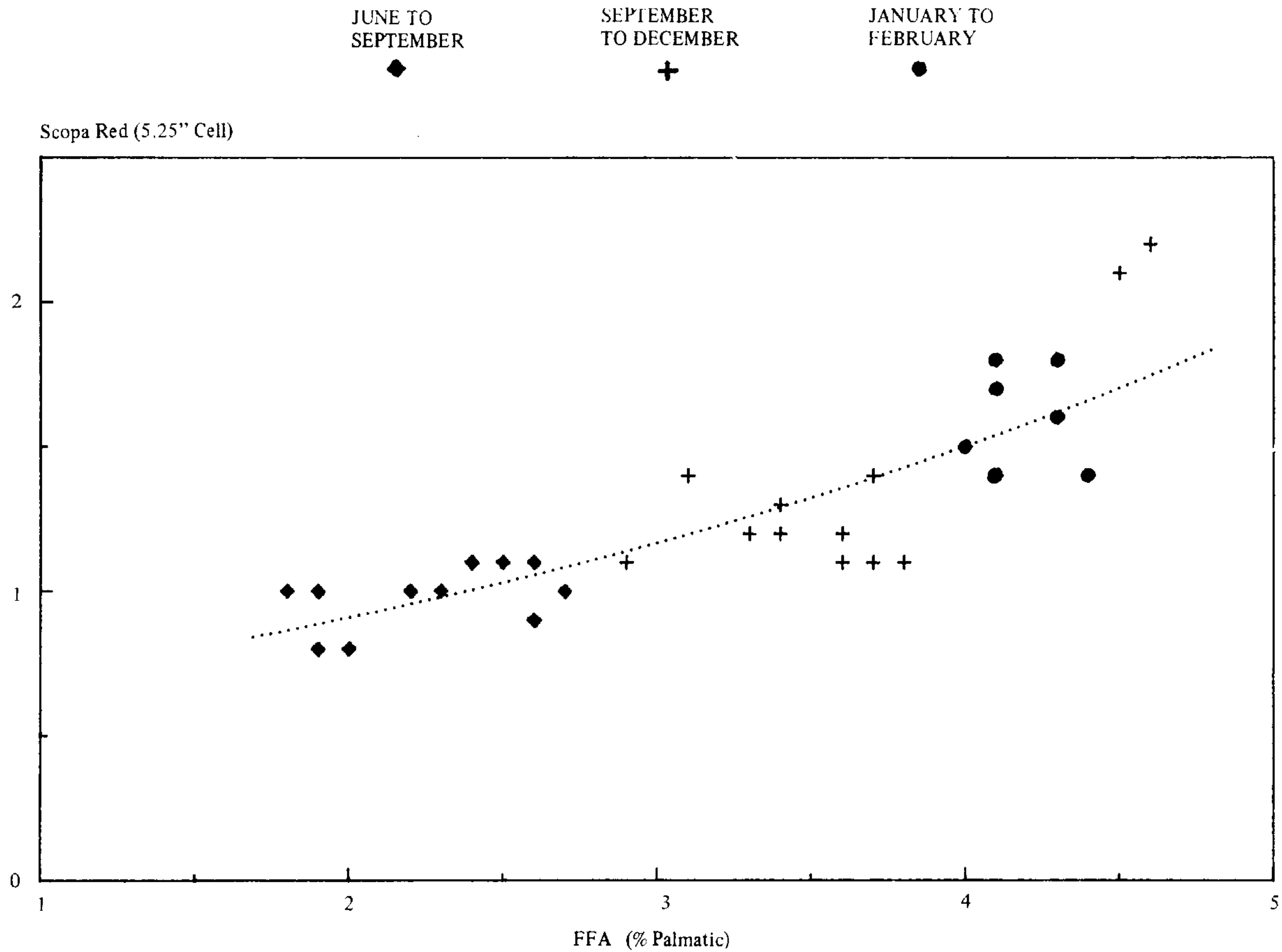
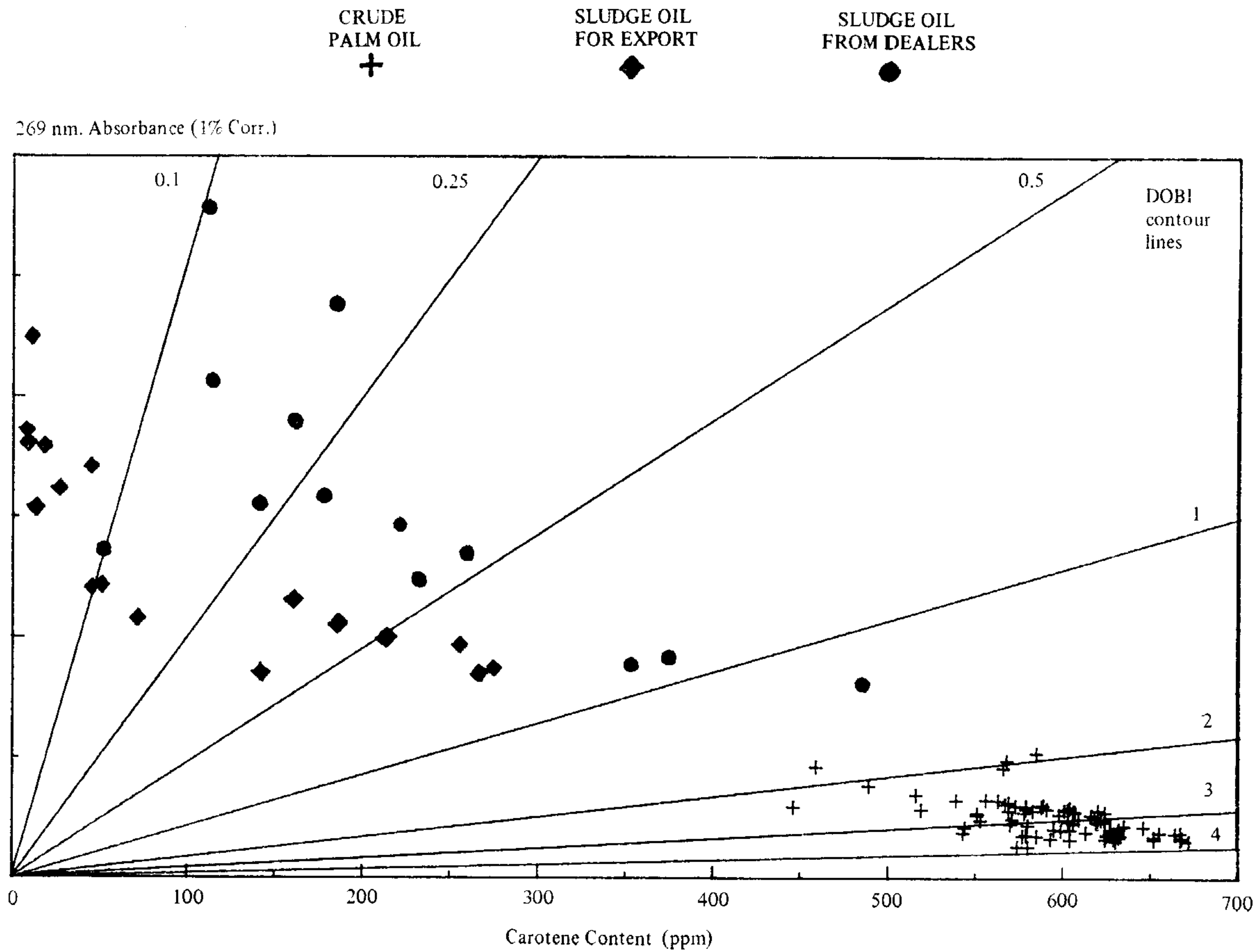


Fig. 5. DOBI Contour Plot for 110 Tests
Comparison of Crude & Sludge Oil



ratio of the spectrophotometric measurement of absorbance at 446 nm divided by that at 269 nm for a solution of the CPO in a hydrocarbon solvent. The values for absorbance are measured against solvent but not corrected in any other way. Although spectroscopic grade iso-octane is the usual solvent, any hydrocarbon solvent sufficiently pure, so as not to have an absorbance different from water by more than 0.05, may be used. A solution of between 0.5 and 1% concentration is appropriate for CPO but, as the DOBI is a ratio of two measurements on the same solution, for convenience this can be very roughly prepared.

Figure 5 shows the relationship between the measurement of secondary oxidation products and the carotene content for contour lines of different DOBI values. Plotted on this graph are the experimental results for CPO samples which lie mainly between DOBI values of 2 and 4. On the other hand sludge oils, which are so difficult to bleach, show such a dramatic deterioration that their DOBI values are less than 1. Indeed the specification of a DOBI value less than unity should be the criterion for technical uses of coloured palm oil crudes as it also applies to acid oil recovered from soap stock, and the oil recovered from spent bleaching earth *(Tan, Ong, Swoboda, Gapor, Siew and Chow, 1982)*. A CPO with DOBI less than 2 is likely to be of poor quality for refining. For the common good quality CPO with DOBI around 3, it should be noted that the contour lines indicate a minimal effect of biological variation in the carotenoid content of CPO. However the main value of the DOBI is identifying conveniently those CPO batches that will be really difficult to bleach because of extensive deterioration.

Conclusion

A better understanding of the factors affecting the bleachability of crude palm oil and the efficiency of the refining process should lead to better quality. For physical refining the concept of adsorptive cleansing and not carotenoid bleaching is pertinent for pretreatment.

More relevant specifications based on simple analyses need to be developed for CPO quality. Then the refining unit operations have to be improved so that RBDPO of a better and more consistent colour is produced.

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