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Co-valorization of agro-industry by-products: effect of citrus oil on the quality of soap derived from palm fatty acid distillate and spent bleaching clay

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ABSTRACT

This study deals with the co-valorization of spent bleaching clay (SBC) and palm fatty acid distillate (PFAD) –by-products of palm oil refining plants- through soap manufacture. Obtained SBC and PFAD samples show differing acidity and saponification values depending on fatty acids and acylglycerols content. Soaps are prepared using the stoichiometric amount of NaOH, under the varying proportion of water introduced through the basic solution. The mixing SBC and PFAD (ratio 1:3), the reaction completion (92.5%) is surprisingly higher than expected, indicating a synergistic effect on the course of the saponification reaction. The water is also a critical parameter, 30% w/w of added water allowing the highest yield. When testing for cleaning efficiency the products having the highest soap content, those from individual by-products give a low microbial count reduction after hand-washing (30-37%). But a much better score (74%) is obtained when using SBC:PFAD soap mixtures. This improvement could be due to abrasive and absorption effects of the clay, combined with the high soap content. The acceptability through a panel test is good for all soaps when formulated with citrus oil. The most active product corresponds to a SBC:PFAD ratio close to the production one in refining plants. Therefore these results provide an easy way for co-valorising these by-products, after further optimizing the saponification reaction in this complex triphasic medium (aqueous solution, oil, clay).

Keywords: *Palm fatty acid distillate, spent bleaching clay, palm oil by-product, citrus oil, soap, cleaning efficiency.*

1. INTRODUCTION

Crude palm oil (CPO) is extracted from the fibrous mesocarp of the oil palm fruit (*Elaeis guineensis*). Because of its high acidity and resulting in poor stability against oxidation, palm oil is usually refined prior to human consumption. Two by-products produced when refining CPO are spent bleaching clay (SBC) and palm fatty acid distillate (PFAD), respectively 0.9 Mt/year and 3 Mt/year worldwide (Fig. 1). These agro-industrial by-products hardly find uses; even disposal may be technically troublesome and costly. Regarding PFAD, despite attempts made for extracting high-value bioactive compounds like tocotrienols [1-3], these make only a minor fraction, and the free fatty acids (FFA) themselves are still to be valorised. In fact, PFAD find limited uses in the oleochemical industry [4, 5]. SBC contains up to 30% w/w of palm oil (called “waste oil”) which is discarded, due to low quality compared to food standard. Currently, oil-laden SBC is mainly disposed off in landfills [6, 7], whereas it could be a substrate for the synthesis of a wide range of bulk oleochemicals like detergents. Therefore, there is a need for innovation.

For example, soap is manufactured through the boiled kettle saponification process, by which triacylglycerols (fats or oils) and/or FFA are transformed into the corresponding alkali salt mixture (Fig. 2). For example the raw materials used for traditional black soap production in Thailand are fats and vegetable oils such as shea butter, palm-kernel oil and palm oil [8, 9]. This process could be applied to alternative feedstocks from agriculture like SBC or PFAD. The other necessary starting materials for soap production are usually potassium and sodium hydroxides, and potassium carbonate, which are imported, while ashes from agricultural wastes might be suitable substitutes to these imported chemicals. Indeed, soaps made from agricultural ashes display excellent solubility, consistency, cleansing and lathering abilities [10, 11].

Essential oils are obtained by distillation of by-products of the citrus processing chain and used as a flavor in many food products, including alcoholic and non-alcoholic beverages, candy, gelatin, but also in detergents, and in the pharmaceutical industry, to mask the unpleasant taste of drugs [12, 13]. Such essential oils are produced in Thailand and in other palm oil producing countries, and also used in soap and other cleaning products.

In addition, access to clean water being an important issue for human health, this is why an improved biodegradability of detergents -all ending in water streams- is a hot topic for researchers, governments and industry. This short bibliographical survey shows on the one side the need for renewable, safe and low- priced feedstocks for green chemistry, and on the other side several opportunities to use agricultural wastes or by-products (*i.e.* SBC and PFAD from palm oil refining, and possibly terpenics from citrus) to produce detergents.

This study is aiming at producing soap from waste products such as SBC, PFAD and SBC-PFAD mixtures, produced by palm oil refining plants, with NaOH. The final products were analyzed for soap content, cleaning efficiency, and tested for consumer acceptance.

2. EXPERIMENTAL SECTION

2.1. CPO, SBC and PFAD samples and oil analysis.

The samples of CPO, SBC and PFAD were collected at Oleen Palm Oil plant (Samut Sakorn, Thailand) and stored at room temperature (26±2ºC). Citrus oil was obtained from AG Trade Co. Ltd. (Thailand). Percent of waste oil in SBC was determined by AOCS method Ba 3-38 [14]. The waste oil was extracted SBC with hexane (1:1 w/v) in a 2 L flask. The mixture was shaken for 10 min at room temperature, the hexane phase was separated, and the solid extracted again with hexane. The two hexane extracts were joined and the oil was concentrated by evaporation under reduced pressure. The waste oil and PFAD were analyzed for FFA content (acidity) by AOCS Ca 5a-40 [14], saponification value by AOCS Cd 3-25 [14], and the fatty acid composition was determined by gas chromatography after derivatization into fatty acid methyl esters following AOCS Ce 1-62 [14].

2.2. Production of soaps from palm oil processing by-products.

Soap bars were prepared from SBC, from SBC waste oil and from PFAD, and also from mixtures of SBC and PFAD. Triacylglycerols and FFA were converted into soap using NaOH and different water contents. The starting amount of by-product was 200 g. Stoichiometric amounts of NaOH needed for the saponification were determined from the saponification values. Individual solutions of NaOH in water were prepared according to each selected reaction condition. Experiments were conducted with a laboratory-scale set. The mixture was stirred in a 500 mL glass beaker, heated with a hot plate, and kept for 15 minutes at 50 ºC. After the reaction, the mixture was poured into a mould, then placed in a closed plastic bag, and stored for one week at room temperature (26±2 ºC). The reaction yield was measured as the soap content according to AOCS Cc 17-79 [14]. Reaction runs and soap analysis were done in triplicate, and the results are expressed as mean value and standard deviation (SD). Results were analyzed statistically using SPSS software version 10.0. Data was tested by analysis of variance (ANOVA) and significant difference by evaluating least significant differences (LSD) at the P 0.05 level.

Then the product containing the highest percent of soap was prepared again under the corresponding suitable conditions. This soap was placed in a sealed plastic bag and stored for one week at room temperature (26±2ºC) before determining the cleaning efficiency. Other batches of soap were prepared under the same conditions as above (maximum soap content), and 1.25% v/w of citrus oil was added at the end of the heating step and mixed. Each prepared soap was then placed in a sealed plastic bag and stored for one week at room temperature (26±2 ºC) before testing the sensory acceptability by a panel.

2.3. Determination of cleaning efficiency.

The cleaning efficiency of prepared soaps (without added citrus oil), was measured by total microbial count before and after hand washing, following the hereafter method adapted from Larry and James [15]. Before hand washing with the soap, an area of 25 cm^2 of hand skin was swabbed with sterile cotton handled with clean pliers. The cotton was then immersed in a test tube containing 10 mL of a NaCl solution (0.85% w/v in distilled water), and vortexed for 2 min. Serial dilutions, 10-2; 10-4; 10-6; were done with same saline solution. For microbial count, 1 mL of above dilutions was pipetted and poured on the top of agar contained in Petri dishes (9.5 cm diameter). Dishes were then incubated for 48 h at 35±1°C. The total number of mesophilic microorganisms was calculated. The plate count agar was carried out for the total viable count (TVC) in triplicate. The above procedure was performed again after hand washing with the bar soap (hand humidified with distilled water, impregnated with soap from the soap bar, washed for 2 min and rinsed with distilled water).

The cleaning efficiency was computed according to the following formula:

$$\text{Cleaning efficiency (\%)} = [(a-b) \cdot 100] / a$$

Where a : Pre hand washing TVC (log cfu/cm^2)
b : Post hand washing TVC (log cfu/cm^2)

2.4. Sensory acceptability by a panel.

Sensory acceptability was carried out by a 30 member panel (12 men and 18 women) consisting of Faculty members and Bachelor of Science students (Prince of Songkla University, Suratthani campus, Thailand). All samples were coded with a three-digit random number and served in random order. The product was tested for colour, lathering ability, odour, consistency and overall acceptability (modified method of Prescott and Bell [16](. A nine-point hedonic scale was used to determine acceptability: 9 = like extremely, 7 = good, 5 = neither like nor dislike, while a rating less than 5 corresponds to unsuitability of each tested property (i.e. 3 = poor, 1 = dislike extremely).

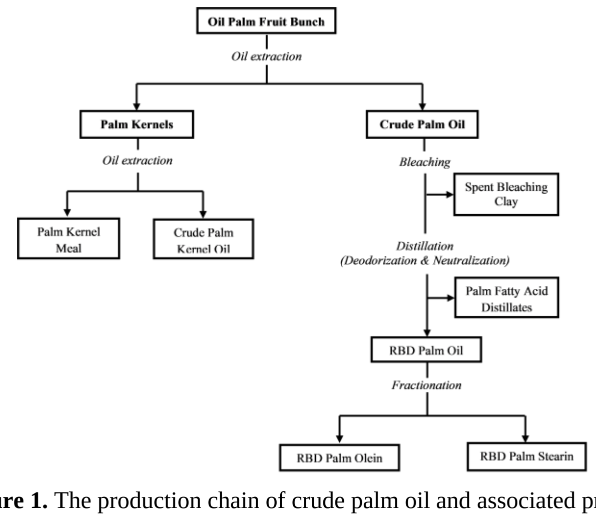

Figure 1. The production chain of crude palm oil and associated products and by-products (RBD: Refined bleached deodorized).

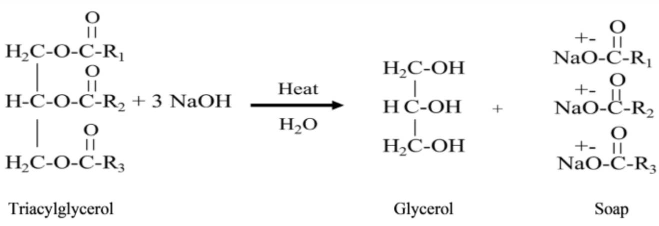

Figure 2. Saponification reaction of a triacylglycerol.

3. RESULTS SECTION

3.1. Composition of SBC and PFAD samples.

SBC contains mainly clay, and of course species taken from the crude palm oil (CPO, Fig. 1) adsorbed at clay inner surface, but also acylglycerols (bulk oil) absorbed within the interlayers of the clay. For analysis purpose, the mixture of lipids called "waste oil" was extracted from SBC by hexane at room temperature: the yield was 22.4+0.2%. Waste oil and PFAD were then analysed for acidity (free fatty acids, FFA) and saponification number, respectively 60.5+0.4% and 182+1 mg KOH/g oil, for SBC waste oil, and 88.4+0.1% and 204+1 mg KOH/g oil for PFAD. As expected the acidity of SBC waste oil is much higher than that of the corresponding CPO from the refining plant taken as reference, because FFA adsorbs at the surface of the clay together with other unwanted components in the refined oil like phospholipids. The acidity of PFAD is even much higher because the aim of the distillation step is to withdraw all FFA in order to yield neutral palm oil. Accordingly, the saponification value of PFAD is higher than that of waste oil and of CPO, as the result of the decrease of the triacylglycerol portion in these samples, which is acting in favour of lower molecular weight compounds like FFA [17].

The fatty acid composition of the samples PFAD and SBC waste oil are sources of saturated and monounsaturated fatty acids, just like CPO, as expected. The waste oil, PFAD and CPO contain palmitic (16:0) and oleic (18:1) acids as main components. Waste oil and PFAD, as well as CPO, show a higher proportion of total saturated fatty acids (54.8; 56.9; 48.0, respectively) compared to unsaturated fatty acids. But CPO contains less palmitic acid (41.5%) than waste oil and PFAD (47.5 And 49.5%, respectively). CPO contains 41.7% of monounsaturated fatty acids including 40.2% of oleic (18:1) acid. The content of oleic acid in waste oil and in PFAD is lower than in CPO, and the same remark applies to polyunsaturated fatty acids. Subsequently, low but significant amounts of a trans-fatty acid (C18:1-trans, elaidic), are found in waste oil, and to a lower level in PFAD, compared to CPO, 2.95%, 0.67%, 0.11%, respectively. The slight increase noted in the case of PFAD is the result of harsh thermal processing conditions applied during the last step of physical refining (distillation). Indeed, the temperature is in the range of 240°C –or even higher-, and the trans-isomer is thermodynamically favored [2, 17]. But the thirty-fold increase noted for the waste oil, which was not processed at a temperature higher than 95°C, could also be the result of the known cis-trans isomerization catalytic effect of phosphoric acid added prior to contacting with the bleaching clay, and/or that of the clay itself. In addition, the selectivity of adsorption on the clay could also play a role. The found fatty acid composition of the oils and derived samples used in this study is consistent with published data [4, 17, 18].

3.2. Soap production from SBC, waste oil, PFAD.

Before applying the procedure detailed in section 2.2, the stoichiometric amount of NaOH, was computed for each by-product, based on its saponification value. During this study no excess of NaOH was used, only the stoichiometric amount (Fig. 2) to avoid highly basic final products: 3.0, 13.4 and 14.6 % w/w, respectively for SBC, waste oil and PFAD; and the corresponding final products are named SBC-soap, waste oil-soap and PFAD-soap, respectively. The soap content, expressed as soap weight percentage based on the weight of the final product (soap bar), is not shown in Table.

In the case of waste oil, the soap content increases until a plateau at ~86%, when increasing the water content. PFAD falls in the case of waste oil, probably owing to the same physicochemical nature of these reaction media (an oil dispersed in an aqueous solution), the maximum soap content being ~92%. Thus, the soap content is similar in PFAD and in waste oil bars, although slightly lower in the former. This could be explained by the lower saponification value of about 10% in the first case. Actually, this high soap content results from the soap yield (%) computed as the ratio of the contained soap to the theoretical amount of soap that can be expected (Theoretical maximum soap content). The conversion is 99.9% in both the cases, meaning that the saponification reaction (and FFA neutralization, known to be a quick reaction) is nearly complete. Thus, the reaction conditions at plateau are suitable for the purpose. In addition, worth noting that there is a minimum proportion of water which is required to reach the plateau, although quite low, being in the range of 20-25% w/w. This could be due to a lower interfacial area, under this threshold, less favourable to the contact between sodium hydroxide and oil, in this biphasic reaction medium, especially after consumption of the major part of the base, under these stoichiometric reaction conditions. Regarding the case of SBC, we find a bell-shaped curve, the maximum soap content of ~12% being located in a narrow range of water percentage (30-40%), then the soap content decreases substantially to 8.2% with 50% of water. With SBC, the highest saponification yield is 56.1%, thus much lower than the 99.9% found in the case of pure fat substrates. The tested reaction conditions are thus not suitable for high conversion of the lipids retained within the SBC, probably because of the consumption of sodium hydroxide by other adsorbed -or absorbed- compounds, and also because of possible ion exchange at clay surface [17]. Further optimizing reaction conditions was out of the scope of this explorative work.

3.3. Soap production from mixtures of SBC and PFAD.

It appeared then useful to investigate mixtures of SBC and PFAD, in an attempt to valorize the two by-products in a single operation, and also to combine properties of both the by-products. For example, the high soap content of PFAD could be complemented by the abrasive and adsorbent effect of the clay. In addition, SBC brings more glycerol produced during the saponification reaction, owing to the high content of acylglycerols. Using SBC, instead of its contained oil, avoids a costly extraction step. The percentage by weighing of soap content obtained from SBC-PFAD mixtures is not given in Table, as a function of SBC:PFAD weight ratio, and with different amounts of introduced water. As already noted in case of SBC and PFAD alone, the soap content increases when increasing the water content, but here only to a lower extent. In the cases of SBC:PFAD ratio of 1:1 and 1:2, there is little or no influence of the proportion of water on the soap content, and the saponification yield is 88 and 93% respectively. For other SBC:PFAD ratios the soap content shows clearly a maximum at water content 20% w/w (based on total feedstock). From a practical stand point the achieved highest soap content is about ~70% w/w in bars made from SBC:PFAD 1:3; 1:4; 1:5 mixtures. In order to limit the residual amount of unreacted NaOH, we have selected the ratio of 1:3, corresponding to (i) the highest soap yield (93.2%) and (ii) a proportion of 20% of incorporated water, for preparing soap bars and checking the cleaning efficiency. In fact the chosen SBC:PFAD ratio in the selected mixture is the closest to the real production in a CPO refining plant, producing in average 1.5% and 5%, respectively.

3.4. Cleaning efficiency of obtained soaps.

Soap efficiency can be determined through its detergent power or its microbial removal. This last was used here. Based on the above results regarding the soap content, the best compounds were prepared, and total microbial counts were made before and after hand washing with the following products: SBC-soap (water content 30%), waste oil soap (water content 30%), PFAD-soap (water content 35%) and SBC-PFAD soap (SBC:PFAD ratio 1:3, and water content 20%) [17]. Average total viable microbial count (TVC) before hand washing with SBC-soap of 1.4±0.3 log cfu/cm^2 is reduced significantly after hand washing to 0.7±0.2 log cfu/cm^2 (Table 1), achieving a cleaning efficiency of 49±4%. The cleaning efficiency is lower with waste oil-soap and with PFAD-soap (30±6 and 37±8%, respectively), but the maximum (74±10%) is noted in the case of the SBC-PFAD mixture. This is to be compared to the efficiency of only 60±13% measured when using a commercial soap bar taken as reference, and to data reported in the literature [10]. Thus it can be concluded from above results that the soap prepared from the mixture of the two by-products, is by far more efficient (about the double) than the soap from the same by-products used separately. This may come from a contribution of (i) a mechanical effect of the clay, and (ii) non-soap components from SBC (carotenes, tocols) [2] which may combine with the relatively high soap content from PFAD, for forming a more active formulation. This found synergistic effect is a key advantage, to our knowledge never described in the case of CPO refining by-products.

Table 1. Total microbial count and cleaning efficiency before and after hand washing with SBC-soap, Waste oil-soap, PFAD-soap and SBC+PFAD-soap.

		SBC-soap	SBC waste oil-soap	PFAD-soap	SBC-PFAD -soap	Commercial Reference
Total microbial count (log cfu/cm^2)	**Before washing**	1.4±0.3^a	1.8±0.3^a	1.7±0.4^a	1.2±0.3^a	1.8±0.2^a
	After washing	0.7±0.2^b	1.3±0.3^b	1.1±0.3^b	0.3±0.2^b	0.7±0.3^b
Cleaning efficiency (%)		49±17	30±16	37±6	74±13	60±15

Values within the same column having the same or without superscript are not significantly different ($p > 0.05$); Data are written as mean value and standard deviation.

Table 2. Sensory evaluation and overall acceptability of SBC-soap, Waste oil-soap, PFAD-soap, SBC+PFAD-soap.

		SBC-soap	Waste oil-soap	PFAD-soap	SBC+PFAD-soap
Sensory Evaluation*	**Color**	4.5±1.8	4.3±1.9	5.1±1.7	4.5±1.8
	Lathering ability	3.5±2.0	4.7±2.0	5.5±2.0	5.8±2.0
	Odor	3.5±2.2	3.6±2.1	5.2±1.7	4.5±2.2
	Consistency	4.5±2.0	5.9±2.0	6.0±2.0	5.5±2.0
	Overall acceptability	4.5±1.8	4.5±1.8	4.5±1.8	4.5±1.6

*Using a nine-points hedonic scale (1, dislike extremely; 5, neither like nor dislike; 9, like extremely).

Table 3. Effect of added citrus oil on odor test and on overall acceptability of SBC-soap, Waste oil-soap, PFAD-soap, SBC+PFAD-soap.

		Odor test*		**Overall acceptability***	
Added citrus oil (%)		0.0	**1.25**	**0.0**	**1.25**
Soap sample	SBC-soap	3.5±2.2	5.1±2.0	4.5±1.8	5.6±1.7^b
	Waste oil-soap	3.6±2.1	5.5±2.1	4.5±1.8	6.2±2.0^b
	PFAD-soap	5.2±1.7	6.6±1.9	4.5±1.8	6.2±1.4^b
	SBC+PFAD-soap	4.5±2.2	5.5±1.5	4.5±1.6	6.0±1.4^b

*Using a nine-points hedonic scale (1, dislike extremely; 5, neither like nor dislike; 9, like extremely).

3.5. Sensory quality and consumer acceptability.

In order to complement the above chemical and physicochemical results, a range of sensory properties was evaluated by a panel of 30 people for soap samples above used for measuring the cleaning efficiency. The rating covers a nine-point scale, 9 correspondings to the best score; 5 to the middle of the scale, panel members neither liking nor disliking. Let us first consider the soaps without added citrus oil in Table 2. PFAD-soap shows the highest score regarding the colour test (5.0-5.7), but the mixture with SBC (1:3 SBC-PFAD), leads to losing this potential improvement. However, the above mixture shows the highest rating for the leathering property (5.6-6.6), especially when compared to SBC (3.5-4.8). As a matter of fact SBC gives the lowest score for the five investigated quality parameters. However, among tested properties, the odour shows the lowest rating for the four tested soaps, as low as 3.5 in the case of SBC-soap. In an attempt for masking the smell of these by-products, citrus essential oil was added during the manufacture of soap bars, 1.25% w/w, based on the range advised by the supplier (0.5-2% as flavoring agent in detergents). Table 3 shows that the odour perception was clearly improved for all products, providing a rating above 5 (up to 6.6 for SBC-PFAD-soap). Citrus oil does not clearly improve other properties, but the overall acceptability climbs from 4.5 up to 6.0-6.2 for PFAD-soap and for the mixture, thus resulting in a real improvement.

Thus, it can be concluded that adding citrus oil has a positive effect, especially improving the odour rating compared to the corresponding starting soap. Worth noting that the best score for all tested properties and formulated soaps is about 6, lower than the value found for a reference commercial soap bar (8.2). However, the improved properties brought by simply adding citrus oil shows that these soaps could be improved by optimizing the formulation for a selected market target.

4. CONCLUSIONS

One of the most interesting results from this work is the manufacture of the soap derived from SBC:PFAD mixtures. In spite of noted low saponification yield for SBC alone, the soap yield was strongly improved in the case of SBC:PFAD mixtures (92% instead of 56%), close to the one found for PFAD alone. Given the complexity of this triphasic reaction medium, this could come from interfacial and other physicochemical effects, allowing a more complete reaction. Regarding the cleaning efficiency, the innovative idea to investigate mixtures of SBC and PFAD proved to be highly beneficial, doubling the reduction of the microbial count, in comparison to PFAD–soap or SBC-soap alone. The encouraging rating of the acceptability from the sensory panel test could be increased by adapting the formulation, as demonstrated by adding citrus essential oil. This study shows an innovative way for co-valorising two important by-products of palm oil processing, with a synergistic effect when mixing them. A combined chemical and physicochemical investigation is now necessary for explaining the complex phenomena responsible of the peculiar behaviour of the SBC when used alone or mixed to PFAD, in order to better take advantage of it when optimizing the saponification reaction and the cleaning efficiency, towards a better valorisation of these by-products amounting ~6% of refined palm oil or 3-4 million tons per year worldwide.

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