IMPROVED TECHNOLOGY FOR THE PRODUCTION OF PALM-BASED DIHYDROXYSTEARIC ACID (DHSA)

by: PARTHIBAN SIWAYANAN; NORIN ZAMIAH KASSIM SHAARI; ZULINA ABD MAURAD; HALIZA ABD AZIZ and SALMIAH AHMAD

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Hydroxy fatty acids have great interest to the industry because of their different behaviour compared with ordinary fatty acids. Currently, the main source of hydroxy acids provide by nature is castor oil. This oil is not available in Malaysia and because of that, studies were initiated to produce the compound by other means. C18:1 fraction of palm kernel oil-based crude oleic acid, a low value co-product produced during the production of C12 -14 acids is an important raw material for preparing hydroxy acids. The C18:1 fraction in the commercial palm-based crude oleic acid in Malaysia is between 70% – 78%. *Table 1* shows the fatty acid composition (FAC) of commercial crude oleic acid. This fraction contains a degree of unsaturation and therefore a site for further chemical modifications. One possible chemical modification is by converting the unsaturation to an epoxide followed by hydrolysis to yield dihydroxystearic acid (DHSA).

TABLE 1. FATTY ACID COMPOSITION (FAC) OF COMMERCIAL CRUDE OLEIC ACID

Fatty acids	% Range
C8:0	0.1 - 0.8
C10:0	Trace - 1.2
C12:0	0.9 - 2.4
C14:0	0.3 - 1.5
C16:0	3.1 - 5.5
C16:1	0.1 - 0.3
C18:0	1.2 - 7.6
C18:1	71.4 - 78.0
C18:2	11.8 - 17.3
C18:3	Trace - 0.6
C20:0	0.1 - 0.5
C others	To 100
Iodine Value, g I_2/100 g	87 - 95
Acid Value, mg KOH g^{-1}	180 - 204

DHSA derived from crude oleic acid is a specialty chemical, which is formed by reacting crude oleic acid and peracetic acid in the presence of hydrogen donor such as water. The process involved in the conversion of crude oleic acid into DHSA via peracetic acid has been patented in Malaysia (PI 9 804 456). The DHSA molecule bears three functional groups, one carboxyl and two hydroxyl groups at 9 and 10 position of C18 chain. This structure, as shown in *Figure 1*, offers interesting possibilities for various applications. Laboratory findings at MPOB have confirmed the technical viability of palm-based DHSA as ingredient in cosmetic formulations.

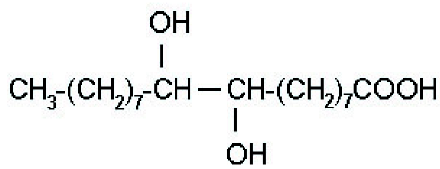

Figure 1. 9, 10 dihydroxystearic acid structure.

In view of these findings and the commercial potential of the DHSA, the laboratory process of DHSA has been scaled-up into a pilot plant production with the aim to evaluate the economic feasibility of the production process and also to carry out large-scale performance evaluation of the palm-based DHSA. *Figure 2* illustrates the pilot plant facilities at MPOB, which is capable of producing 500 kg of crude DHSA per batch operation. The DHSA produced from the pilot plant is termed as crude DHSA since the purity of the product is within 55% - 58%.

Figure 2. Pilot plant facilities at MPOB.

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Malaysian Palm Oil Board, Ministry of Plantation Industries and Commodities, Malaysia
P. O. Box 10620, 50720 Kuala Lumpur, Malaysia. Tel: 03-89259155, 89259775, Website: http://mpob.gov.my Telefax: 03-89259446

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One of the properties required for DHSA in order to be used as cosmetic ingredient is minimal skin irritation. The crude oleic acid normally contain a substantial amount of C8 – C10 acids, which makes the crude DHSA to be irritant to the skin. Therefore, the crude DHSA has to be purified via crystallization process using selected solvent and then will be subjected to drying process. The purity of final DHSA obtained is within the range of 70% to 80%. The dermal irritancy of purified DHSA is found to be not irritating.

CRUDE DHSA PRODUCTION VIA PERACETIC (PAA) ROUTE

The peracetic acid (PAA) route was employed in the early operation of the pilot plant. In this process route, as shown in *Figure 3*, the PAA is preformed *in situ* by reacting the glacial acetic acid (>99%) and hydrogen peroxide (50%) in the presence of sulphuric acid. This PAA, which acts as an oxidizing agent, spontaneously converts the unsaturation present in the crude oleic acid to form the epoxides. These

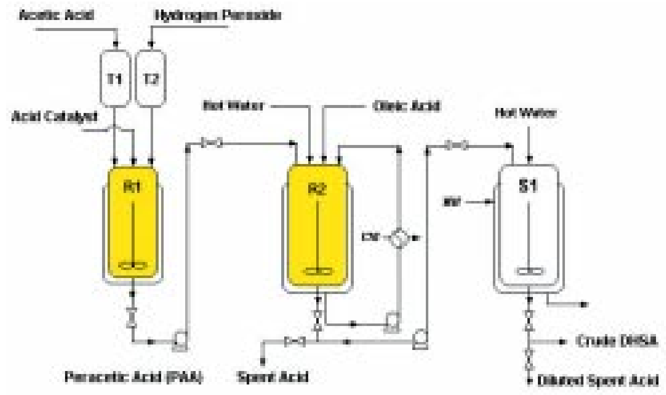

Figure 3. Process flow diagram of PAA route.

epoxides will be hydrolyzed to produce the crude DHSA. Both the epoxidation and hydrolysis processes are carried out in R2 reactor. The unreacted acid or spent acids will be removed while the crude DHSA will be washed five to six times with hot water in S1 settler to remove the remaining acid present in the crude DHSA. The washed crude DHSA contains 55% – 58% of DHSA.

However, the process of converting crude oleic acid into DHSA was reinvestigated with a new process route using performic acid (PFA).

CRUDE DHSA PRODUCTION VIA NEW PERFORMIC (PFA) ROUTE

There are three main reactions involved in this PFA route: (i) reaction between formic acid (94%) and hydrogen peroxide (50%) in the presence of sulphuric acid (catalyst) (98%) to form performic acid, (ii) reaction between *in situ* formed performic acid with the unsaturation present in the oleic acid (70% - 78%) to form the epoxides and (iii) hydrolysis of epoxides to form DHSA. These reactions are carried out in reactor R2. The processing stages and its respective unit operations for PFA route are shown in *Figure 4*.

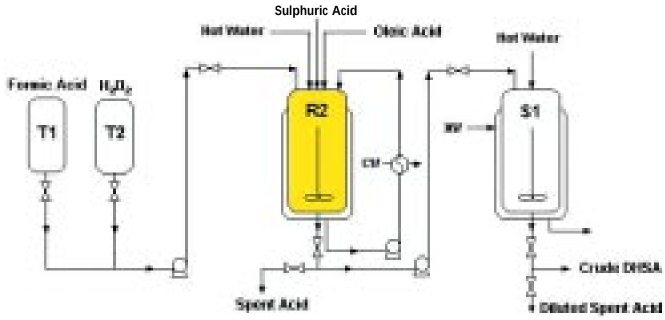

Figure 4. Simplified process flow diagram of PFA route.

ADVANTAGES OF PFA ROUTE OVER PAA ROUTE

The production cost and the yield of crude DHSA based on the PFA route were compared with the previous PAA route. The PFA route has improved the process efficiency from 72.5% to 96% (yield), reduced the production cost by 30% and also reduced the batch processing time from 12 to 10 hr. Moreover, the production of crude DHSA can be carried out in a single reactor (R2 reactor) instead of two reactors as for PAA route.

PURIFIED DHSA PRODUCTION

The washed crude DHSA will be subjected to purification in which it undergoes three processes: (i) crystallization with solvent, (ii) solvent removal and (iii) drying process. Some of the unwanted C8 - C10 acids present in the crude oleic acid, which can cause irritation to the skin, will be removed during the purification process. Various solvents were studied as such or as admixtures with water (in various ratios) for the crystallization or washing purposes. However, after taking into consideration the aspects of safety and cost, isopropanol admixture with water (80:20) was found to be suitable. The crude DHSA (at 60°C), while in liquid form is mixed with isopropanol/water (80:20) at 1:1 w/v ratio. The mixture of crude DHSA and isopropanol/water is cooled at 5°C in order for the crystallization to occur. The DHSA crystals in wetted cake form were separated from the isopropanol using a mechanical vibrating screen (*Figure 5*).

Figure 5. Solvent removal using vibrating screen.

The purity of DHSA after the first crystallization process is about 70%. It is necessary to carry out the second crystallization to the crude DHSA in order to achieve purity up to 80%. After removal of isopropanol through the vibrating screen, the purified DHSA is washed with water. The washed purified DHSA will then be dried. The typical specification of crude and purified DHSA is shown in *Table 2*. The purified DHSA is in powder form, off-white in colour and tasteless with a mild acid odour.

APPLICATION OF DHSA

Purified DHSA is compatible with the ingredient used in make-up and its hydrophobicity accompanied by the good polarity allowed its use as ingredient in coloured cosmetic formulations and as coating agent for pigments. DHSA had been successfully used to produce cosmetic products. DHSA can also be used to produce esters or estolides. These derivatives can be used as cosmetic ingredients in particular the octyl DHSA ester, which was found to produce good liquid crystalline structure and product from it exhibits excellent spreading properties.

CONCLUSION

The laboratory process of crude DHSA had been successfully scaled-up into pilot plant production. A new process route (using performic acid) was employed to replace the peracetic acid route in order to improve the process efficiency, to reduce the production cost and the batch processing time. Several batches of pilot plant production were carried out using new route. The properties of crude DHSA produced from the pilot plant were found to be consistent and reproducible. Scale-up studies on the purification of crude DHSA via crystallization and drying processes were conducted. The purified DHSA was found to be non-irritant and had been used to formulate various cosmetic products.

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TABLE 2. SPECIFICATIONS OF CRUDE AND PURIFIED DHSA

Properties	Crude DHSA	Purified DHSA
DHSA purity (%)	56.6 - 58.0	70.9 - 79.9
Water content (%)	5.2	1.1 - 1.3
OHV (mg KOH g^{-1})	220.7	291.5 - 357.6
Iodine value (g I_2/100 g)	7.3 - 9.1	2.9 - 4.0
Acid value (mg KOH g^{-1})	160.4	172.7
Melting point (°C)	79.4 - 79.8	89.8 - 90.3
Irritancy	irritant	non-irritant
Form/Particle size (micron)	semi-solid	40 - 120

For more information kindly contact:

Director-General
MPOB
P. O. Box 10620
50720 Kuala Lumpur, Malaysia.
Tel: 03-89259155, 89259775
Website: http://mpob.gov.my
Telefax: 03-89259446