METHYL ESTER SULFONATES (MES) – AN ALTERNATE SURFACTANT FROM RENEWABLE NATURAL RESOURCES

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Methyl Ester Sulfonates (MES) from palm and coconut derivatives have been in the limelight with the increase in the crude oil prices and the resultant increase in the prices of the petrochemicals. MES offers an environmentally friendly and viable alternative to the currently used workhorse surfactant alkyl benzene derived from linear alkyl benzene (LAB).

MES has been manufactured in Japan by Lion Corporation and in USA by Stepan and Huish Detergents. Huish produces commercial quantities of MES in a free flowing powder form while both Lion and Stepan have their products in liquid forms.

Several technologies for manufacturing MES have been patented. Huish, which has a plant capacity of 80,000 TPA, uses the Chemithon technology for the MES and the Lurgi technology for the methyl esters (ME). Chemithon has also supplied a pilot plant to the Malaysian Palm Oil Board (MPOB) in Malaysia, a customer in Honduras and a couple of customers in China. The appeal of MES is based on its origin from a renewable oleo-based raw material, its excellent biodegradability, improved calcium hardness tolerance and a good detergency. MES also offers a viable cost alternative to the LAS currently used by detergent producers. The challenges for MES in detergent use include the low foam characteristics and the formulation constraints when using MES in a liquid form in a high pH environment. The availability of MES in a dry free flowing powder or flaked form in recent years has overcome part of the manufacturing issues as the
The viability of MES is dependent on the availability of the ME at a reasonable price. The detergent grade ME can be made in several ways. A simpler option is to transesterify the oil or fat (palm, palmolein or palm stearin with methanol and use a fractionated C16 or C1618 fraction after removal of the unsaturated components. An innovative process followed by Huish fractionates the C16 stream, minimizing the need to hydrogenate the resultant product prior to making the MES. The isolated C18 ME can be used to blend with diesel and add to the biodiesel pool. ME can also be made by transesterifying a palm oil stream after the extraction of minor components (Vitamin E, beta carotene, etc.), separating the glycerine and fractionating the stream to isolate the C16 ME. The transesterification step is a low pressure low temperature process which has been used by the oleochemical industry. An alternate source of ME can also be by esterification of fatty acids, PFAD and acid oils derived from processing of palm oil. However, the esterification process requires a catalyst and higher pressure and temperature resulting in a more expensive processing step.

RBD (refined – bleached – deodorized) palm stearin (RBDPS) is used as a raw material by Huish Detergents. Typically, a 200 TPD facility processing RBDPS and producing a detergent grade C16 ME will require a capital expenditure of around US$ 15 million. The technology producers include Lurgi, Crown Iron Works, Archer Daniel Midlands, DeSmet and a number of smaller players. A table with the manufacturing costs for producing ME is enclosed in annexure 1.

The process of converting ME to MES needs to produce a finished product with acceptable colours and with a control on the di-salt formation during the process. The chemistry for producing MES is enumerated in the chemical equation listed below:
The process for manufacturing MES requires the product to be bleached to get acceptable colours. The Huish plant uses Chemithon’s acid bleach technology using hydrogen peroxide as the bleaching agent. The process uses excess...
quantities of methanol to minimize the di-salt formation and provide the rheology for flow of the actives for producing the MES in a dry form. Lion Corporation, Stepan and Chemithon have patents on their MES processes. A study by Lion Corporation on the C1618 MES showed a superior performance of the surfactant as compared to LAS or AS under low temperature wash conditions and at water hardness of levels of around 100 ppm (SC CO3). The use of the C14 improves the cold water performance. The C16 MES produced by Huish is used in premium detergent powders (Safe ways) and in popular detergent packs (Wal-Mart, COSCO). Lion uses a C1618 MES in a mixed active surfactant system in their compact detergent formulations. Whilst the process challenges for making good quality MES have been addressed, there is room for technology upgradation to minimize the consumption of bleach and solvents used in the process. There is also a need to produce the MES as a granule or bead in order to facilitate its addition in the post-hour process. This will provide the detergent formulators with the flexibility for producing mixed active detergent surfactants and optimizing their formulations based on the market dynamics of the inputs.

The capital costs for an 80,000 TPA MES facility is estimated at around US$ 20 million and the typical manufacturing cost is listed in annexure 2 for reference.

As compared to LAB which is the workhorse of the detergent industry today, the cost of producing a ME and a MES is significantly lower. On equal capacity basis, the cost of a ME plant would be around a fifth of that required for producing LAB. Though the cost of producing MES is higher than the cost of producing LAS, today’s market dynamics offer a cost differential of over US$ 200 to the end users. This provides the economic driver for using a raw material based on renewable resources.

MES is also environmentally friendly and reduces the CO2 emissions when compared with using fossil fuels as the raw material sources.
There is an increased focus by the global detergent producers for formulating MES based products. The formulation challenges in USA include producing stable MES based liquid laundry detergents and detergent bars in Latin America. European detergents will find a synergy when using MES for their low temperature wash cycles. In the emerging markets in India and China, the formulation challenges will include formulating the products with foaming properties.

The Asia Pacific region, where Malaysia and Indonesia lead the world’s palm oil production, offers a stable source for the palm oils or derivatives for producing ME. The interest in biodiesel from palm oil and the need to have a low cold flow plug point (CFPP) will provide the options for producing a C16 ME which can subsequently be converted to a surfactant.

With the support of the palm oil producers, detergent manufacturers, processors and the end consumers, the efforts to make environmentally friendly detergents using MES will come to fruition as the economic drivers support the need to change from a petrochemical based detergent alkylate.

The success of MES will rest on a structured and committed approach by all the players. The crude oil prices have peaked in recent times and are expected to remain high due to the market volatility. Availability of ME in adequate quantities and at prices of around US$ 550 PMT will provide the drivers for producing MES which can be used as a stand alone or co-active surfactant in detergent formulations.

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