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POWDER BEHAVIOR OF METHYL ESTER SULFONATES GENERATED BY HIGH SHEAR MIXER

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By

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Methyl ester sulfonates (MES) is an anionic surfactant and can be formulated into powder detergent. However, its hygroscopic behavior and readily soluble in water, limited the powder stability during granulation and storage. The behavior of powder stearin based MES has not been studied thoroughly and it was always facing a problem of caking, lumping and dusty during handling, storage and transportation. Therefore, the main objective of this research is to improve the understanding of powder behavior of MES by high shear mixer or milling with the presence of anti-caking agent and the effect of moisture content towards powder MES. Prior to study the behavior of MES powder, the specification of MES has been determined. Purification of MES through repeated crystallization using ethanol has active content higher than 99% with an increment of 17 to 18%. Moisture content of MES has been dried to 1.7 to 2.2 % while di-salt content was retained less than 5% which is desirable. The composition of MES before and after purification were similar and confirmed by infrared spectrum, ^{1}H and ^{13}C NMR analysis. Evaluation the changes of MES flakes into powder using knife miller with high shear mixer, such as Philip powder blender and laboratory stainless steel grinder, was conducted. The resulted powder MES were evaluated in terms of its particle size, mechanical characteristics and crystalline solid properties using sieve, texture and X-ray diffraction analyzer, respectively. Powdered MES C_{16-18}, ground by knife miller with high shear mixer, is free flowing with less cohesion, little caking and has decreasing compaction coefficient (free flowing with increasing flow speed). Zeolite and soda ash had improved the caking behavior and compaction coefficient of powder MES. The presence of C_{18} in MES C_{16-18} requires a larger amount of anti-caking agent. The cohesiveness of powdered MES C_{16-18} increased with the increase of zeolite addition. While the addition of soda ash in powdered MES C_{16-18} with ratio of 98:2 and 60:40 makes the powder becomes less cohesive. With the increased content of carbon C_{18} in C_{16-18} in ratio 60:40 had retained the moisture content at 3-5%. This mean that MES with higher content of C_{16} had highest moisture content.

The increase moisture content in MES C_{16-18} was exponential with an increase of anti-caking addition. MES C_{16-18} ratio 98:2, 80:20 and 60:40 shows that the increasing of moisture content affected the powder and make it more cohesive and more caking. Cohesion and caking of MES C_{16-18} at ratio 98:2 have higher value compared to other ratios. Therefore, the rheology of MES powdered in term of cohesion and caking can be improved with controlled moisture content with or without anti-caking agent.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
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PERILAKU SERBUK METIL ESTER SULFONAT TERHASIL DARIPADA PENGGILINGAN RICIH TINGGI

Oleh

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Metil ester sulfonat (MES) adalah surfaktan anionik dan boleh diformulasikan menjadi serbuk pencuci. Walau bagaimanapun, tingkah laku MES yang mudah larut dalam air, membatasi kestabilan serbuk semasa granulasi dan penyimpanan. Tingkah laku serbuk stearin MES belum dieksplotasi secara menyeluruh dan selalu menghadapi masalah gumpalan dan berdebu semasa pengendalian, penyimpanan dan pengangkutan. Oleh itu, objektif utama penyelidikan ini adalah untuk meningkatkan pemahaman mengenai tingkah laku serbuk MES semasa dikisar menggunakan pengisar ricih tinggi dengan kehadiran agen anti-pengkekan (zeolit dan soda) dan kesan kandungan kelembapan terhadap MES serbuk. Sebelum mengkaji tingkah laku serbuk MES, spesifikasi MES telah ditentukan. Proses penghabluran MES $C_{16\text{-}18}$ menggunakan etanol mempunyai kandungan aktif lebih tinggi daripada 99% dengan kenaikan kandungan aktif 17 hingga 18%. Kandungan kelembapan MES telah dikeringkan hingga 1.7 hingga 2.2%, sementara kandungan dwi-garam dikekalkan kurang dari 5%. Komposisi MES sebelum dan selepas penghabluran adalah serupa dan disahkan oleh spektrum inframerah, analisis NMR ^{1}H dan ^{13}C. Penilaian perubahan kepingan MES menjadi serbuk menggunakan pengisar pisau dengan pengadun ricih tinggi seperti pengisar serbuk Philip dan penggiling keluli tahan karat makmal telah dilakukan. Serbuk MES yang dihasilkan, dinilai dari segi ukuran zarahnya, ciri mekanik dan sifat pepejal kristal menggunakan penganalisis saiz partikel, tekstur dan difraksi sinar-X. Serbuk MES C16-18 yang dikisar daripada pengisar pisau dengan pengadun ricih tinggi mengalir bebas dengan kohesi yang rendah, sifat pengkekan yang rendah dan mempunyai sifat pemadatan yang menurun (bebas mengalir dengan peningkatan kecepatan aliran). Penambahan agen anti-pengkekan (zeolit dan soda) dalam serbuk MES boleh berlakunya peningkatan kohesi, tetapi dapat memperbaiki keadaan pengkekan serbuk MES. Kehadiran karbon C_{18} dalam MES $C_{16\text{-}18}$ memerlukan jumlah agen anti-pengkekan yang lebih banyak. Nisbah MES $C_{16\text{-}18}$ (98: 2) dengan zeolit 10% dan soda 10%, nisbah MES $C_{16\text{-}18}$ (80:20)

dengan zeolit 15% dan soda 20% dan nisbah MES C_{16-18} (60:40) dengan zeolit 20% dan 15 % soda adalah peratus agen ati-pengkekan yang optimum bagi mendapatkan ciri-ciri serbuk yang sangat baik dari segi kohesi, pengkekan dan kestabilan aliran. MES dengan kandungan karbon C_{16} yang lebih tinggi mempunyai kandungan kelembapan yang lebih tinggi. Peningkatan kandungan kelembapan pada MES C_{16-18} sangat pesat dengan peningkatan penambahan anti-pengkekan. Kandungan kelembapan yang tinggi telah mempengaruhi serbuk MES dan menjadikannya lebih padu dan berlakunya pengkekan. Reologi serbuk MES dari segi kohesi dan pengkekan dapat dibaiki dengan mengawal kandungan kelembapan dengan atau tanpa agen anti-pengkekan.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CH3COOK	Potassium acetate
CMC	Critical micelle concentration
CI	Carr compressibility index
CrI	Crystallinity Index
FAES	Fatty alcohol ether sulfates
FAS	Fatty alcohol sulfates
FT-IR	Fourier transform-infrared spectroscopy
HR	Hausner ratio
IPA	Isopropyl alcohol
KI	Potassium iodide
KCl	Potassium chloride
K2CO3	Potassium carbonate
LAB	Linear alkyl benzene
LAS	Linear alkyl benzene sulfonates
LiCl	Lithium chloride
MES	Methyl ester sulfonates
MgCl2	Magnesium chloride
MgNO3	Magnesium nitrate
NaCl	Sodium chloride
NMR	Nuclear magnetic resonance
PFAD	Palm fatty acid distillates
PKFAD	Palm kernel fatty acid distillates
PSD	Particle size distribution
PSFD	Powder flow speed dependency
RH	Relative humidity
SEM	Scanning electron microscopy
XRD	X-ray diffractometer

CHAPTER 1

INTRODUCTION AND OVERVIEW

1.1 Introduction

Asia Pacific in general and Malaysia, are blessed by the abundance availability of palm oil and palm kernel oil. Ratio of hectarage versus oil extraction rate (OER) was very much higher for palm oil as compared to other seed oils (Basiron, 2007). Natural feedstock such as palm oil and palm kernel oil derivatives offer interesting possibilities as natural and green surfactants (Knaut and Richtler, 1985). Malaysian Palm Oil Board (MPOB), through its research activities had produced an anionic surfactant from palm-based methyl ester. This surfactant is known as alpha sulfonated methyl esters or methyl ester sulfonates (MES). In early 2000, MPOB had purchased a 20 kg per hour sulfonation pilot plant from Chemithon, USA to produce palm-based MES and evaluate the technical and commercial viability of the project. The pilot plant was commissioned in late 2001 and several hundreds of kilograms of MES were produced since then.

MESs were shown to be scum dispersant in the 1960s, and thus, their sulfonation mechanism (Stirton, 1968; Weil et al., 1953), characteristics, application, and manufacturing process (Stein and Baumann, 1975; Kapur et al., 1978) have been extensively studied. They have only recently been found to be applicable as a main component of laundry detergent products, and their manufacture on a commercial basis is now possible. Methyl ester sulfonate is used for partial substitution of many non-biodegradable surfactants for the manufacturing of detergents and dishwash formulations. Methyl ester sulfonate is better tolerant to hard water, better detergency in low temperature, and is biodegradable. For the formulation of the dish wash, methyl ester sulfonate is employed in the form of the flakes that can be used as active ingredient.

MES can also be formulated in laundry detergent formulation especially powder detergent. MES is environmentally friendly and can be produced at lower cost compared to petroleum-based surfactant, linear alkyl benzene sulfonates (LAS). Furthermore, with the inconsistency price of petroleum-based feedstocks, renewable resources feedstock such as palm oil would create interest among the detergent manufacturers due to its price competitiveness. The product compositions for the six methyl ester sulfonate examples are presented in Table1.1.

Table 1.1: Product compositions for the commercial methyl ester sulfonate (Sheats and Mc Arthur, 2002)

Wt%	Coconut C_{12-14}	Palm Kernel C_{8-18}	Palm C_{16}	Palm Stearin C_{16-18}	Tallow C_{16-18}	Soya C_{18}
Sodium methyl ester sulfonate (α-MES)	71.5	69.4	83.6	83.0	77.5	75.7
Disodium carboxy sulfonate (di-salt)	2.1	1.8	5.4	3.5	5.2	6.3
Methanol (CH_3OH)	0.48	0.60	0.02	0.07	0.00	0.03
Hydrogen peroxide (H_2O_2)	0.10	0.04	0.10	0.13	0.15	0.05
Water (H_2O)	14.0	15.2	1.3	2.3	2.9	1.4
Petroleum ether extractable (PEX)	2.6	2.7	2.1	2.4	4.8	7.2
Sodium carboxylate (RCOONa)	0.2	0.2	0.28	0.3	0.3	0.5
Sodium sulfate (Na_2SO_4)	1.2	1.8	1.6	1.5	2.3	2.4
Sodium methyl sulfate (CH_3OSO_3Na)	8.0	8.4	5.6	7.2	7.7	2.5
10% pH	5.0	5.3	5.3	5.3	5.4	5.8
Klett color, 5% active (α-MES + di-salt)	30	310	18	45	180	410

The primary production methods for powder detergents are spray-drying, agglomeration, and dry mixing using high shear mixer. Spray-drying involves spraying a mixture of liquid and dry ingredients through nozzles to form small droplets, which then fall through a current of hot air and form hollow granules as they dry (Johnson et al., 1996). In agglomeration, dry raw materials are blended with liquid materials by rolling or mixing. While dry mixing using high shear mixer is used to blend primarily dry raw materials, although small quantities of liquids may be added (Palzer, 2011). The anionic surfactant used in detergent and cleaning product formulation is usually in the form of a highly viscous paste, which acts as a binder for the powder particles. Much work has been reported on the agglomeration mechanism and rheology involving LAS (Rough et al., 2003; Rough et al., 2005) but relatively little has been reported on the powder behavior of MES. MES is generally produced in flakes form. Therefore, formulating MES as starting raw material for detergent will need to use dry mixing with high shear method. MES need to be ground before mixing with other materials in detergent formulation.

1.2 Problem statement

In various industries, fine powders are produced in agglomerated form and prone to caking, lumping and dusty, thus, affecting packaging properties. Most agglomerated powders are composed of polar molecules and are water-soluble. Some of these water-soluble substances become increasingly sticky when exposed to an increasing relative humidity (Palzer, 2011). MES is an anionic surfactant and can be formulated into powder detergent. However, its hygroscopic behavior and readily soluble in water, limited the powder stability during granulation and storage (Weil et al., 1953). Therefore, it is critical to study the powder behavior of MES generated by the high shear mixer before mixing with other detergents ingredients. The behavior of powder stearin based MES has not been studied thoroughly and it was always facing a problem of caking, lumping and dusty during handling, storage and transportation. Few studies have been carried out on the solid or crystalline state of anionic surfactants apart from the monocrystalline X-ray diffraction analysis of the hydrated solid of sodium dodecyl sulfate (Kekicheff et al., 1989). To extend this to detergent powders, the crystalline state must be understood since features such as powder caking and the quick dissolving rate of a powder particle in water are closely related to the surfactant solid properties.

A high shear mixing is used in this study as oppose to other mixing processes because this process possesses the advantages of shorter and more efficient run times; and the flexibility to clean components quickly and effectively. A high shear mixer is significantly more capable than a traditional rotor stator mixer. These are the machines that provide more bang for the buck when a traditional rotor stator is not quite up to the task. For instance, an inline high shear mixer allows for the continuous input of raw materials, with a steady output of finished product. Perfect homogenization, emulsification or deagglomeration can typically be achieved with a single, time-saving, highly efficient pass. In contrast, less-powerful rotor stator mixers usually take longer to process ingredients. Similar results may eventually be achieved, but at a greater cost, due to additional processing times and energy expenditures. These machines may also suffer from persistent problems such as forming “fish eyes” or failing to achieve true homogenization of all ingredients.

1.3 Objectives

The overall objective of the research is to improve the understanding of powder behavior of MES by high shear mixer or grinder and during storage and transportation. Specific objectives contributing to the overall objective are address:

(i) To evaluate the changes of MES flakes into powder after grinding in terms of its particle size, mechanical characteristics and crystalline solid properties.

(ii) To evaluate the effect of moisture content of the powder MES with and without anti-caking agent.

1.4. General overview of the chapters

This thesis presents the investigation on powder behavior of MES generated by high shear mixer.

Chapter 1 addresses the background of the research on palm-based surfactant and problem statement when using powder MES in powder detergent manufacturing.

Chapter 2 describes a literature on the properties of powder MES generated by high shear mixer for applying MES to granular detergents. The physicochemical properties, mechanical properties and crystalline solid properties of powder MES are important in relation to the control towards caking due to moisture content. It is also important to improve their flowability and to evade lumping or caking.

Chapter 3 describes the methods on the preparation of MES at different purities, moisture contents analysis, particle sizes analysis and agglomeration with anti-caking agent. The standard procedures to carry out the wet chemical analysis and sample characterization are illustrated.

Chapter 4 elaborates a comprehensive study of the purification process of MES and powder behavior of MES generated by high shear mixer. Powder MES being examined in terms of its particle size and shape, bulk density, the porosity, flowability, crystalline and effect of moisture content toward the powder MES with and without anti-caking agent.

Chapter 5 concludes the overall findings of this work with some recommendations to enhance the powder behavior of MES for future investigation and the impact of the research in powder technology.

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