Methyl Ester Isolation And Its Modification To Increase The Usability As Cleaning Agents

Madhura Bhalerao, Dr. Vijay Y Karadbhajne
Department of Oil, fats and Surfactants Technology, RTM Nagpur University, Laxminarayan Institute of Technology, Nagpur 440033, India.

Abstract

Evolution of Polymeric Surfactants has been started since many years. Application of polymeric surfactants into various fields has increased and mainly used into formulation of paints and cleaning agents which basically replaces the petroleum origin raw materials used in its synthesis. The current research work research work focuses on synthesis of polymeric surfactantusing vegetable oil.Vegetable oil is converted into methyl ester and further copolymerised with Maleic and Pthalic Anhydride to give modified methyl Ester. This polymeric surfactants has further been used for formulation of powder and liquid detergents.

Keywords: *copolymerisation , polymeric surfactants , modification , surfactants.*

INTRODUCTION

Invention of soap, detergents and surfactants has lead to revolutionary changes in need of people in the world. As cleaning is the basic need whether it may be floor cleaning, utensil cleaning , Bath purpose, Clothing all are fulfilled with different range and choices of products.

Different types of surfactants are available with variance in quality with different price values. This lead an increase to huge market of surfactants. Available surfactants in the market has constituents which are obtained from processed fraction of crude oil.

Hence, this research work is aimed at examining the possibility of replacing petroleum based materials, like Linear Alkyl Benzene Sulphonate (LABS) ,Alpha Olefin Sulphonates AOS etc. in detergents, with polymerized material based on methyl esters of vegetable oils. Detergents are formulated based on polymerised material.Viability of the detergents, that are prepared during this work, is examined through comparison of their performance under different scenarios with that of the commercial detergents available in the market.

There have been ongoing efforts in area of development of alternative fuels from various renewable resources like vegetableoils.In India,efforts are already underway to establish Jatropha,Karanja,Neemand other vegetableoilsasa starting material for producing biodiesel.

However,thesealternative fuels haven't yet found the wide usage, even as fuel blenders oradditives,duetoissuesrelatedtotheirlower performanceandoperational difficultiesascomparedtothepetroleumbased traditional products.

Therefore, it is necessary to find an alternate use of methyl esters of vegetable oils that are most likely to be available as biodiesel in a huge amount in near future. This research work examines opportunities for using methyl esters of vegetable oils as surfactants in detergents. Hence replacing petroleum based materials in detergent like LABS with the renewable alternatives based on vegetable oils.

Selection of Vegetable oils

Looking after the vegetable oil scenario in India, it is expected to give priority to those oils, which are not being generally used for human consumption. Among vegetable oils, rice bran oil and linseed oil are used in this work for production of the polymer.Linseed oil is suitable for human consumption. However, because of its strong flavour and odour it is only a minor constituent of human nutrition. It is generally consumed as a nutritional supplement. India is one of the major producers of linseed oil with 7% of the total world's production. Therefore, linseed oil is used for this work.

MATERIALS AND METHODOLOGY

- Syntheses & Analyses of Modified Methyl Esters

Modification of the methyl esters is effected by maleic anhydride, phthalic anhydride etc. through malenisation. The Malenized methyl esters are comparable to polymers in terms of their various

characteristics. Polymers typically possess higher molecular weights.

- Malenized Methyl Ester

The reaction between maleic anhydride and unsaturated systemsis well known and the process, when applied to fatty acids, is referred to by term — Malenisation. The compound referred to is Maleic treated or Malenized methyl ester of vegetable oil. Malenisation is usually performed on oils to improve their properties. Malenized fatty acid methyl esters give better products due to their higherdegree ofunsaturation as compared to the triglycerides present in corresponding vegetable oils.

- Modified Malenized Methyl Esters

Maleic anhydride along with phthalic anhydride and the methyl ester are known as modified Malenized methyl ester. The methyl esters are modified by reacting them with various chemicals like maleic anhydride, phthalic anhydride etc. to get value added polymers.

These modified methyl esters are studied for their physicochemical properties and spectroscopic characteristics. The physicochemical properties studied include acid value, iodine value, viscosity, molecular weight and Hydrophilic Lipophilic Balance (HLB) ratio which relate to the detergent performance, with the spectroscopic data confirming the presence of certain groups in the compounds. The Malenized methyl esters used in this research work have been prepared by using Conventional Heating Method

- Phthalic Anhydride (PA) Based Copolymers

More over PA is not easily homopolymerized. PA co- polymerizations are being explored as a technique to improve the physicochemical properties of polymers by increased polarity, rigidity, glass transition temperature and functionality. The PA residue on the polymer backbone is known to promote hydrophilicity and adhesion, improve dye ability.

EXPERIMENTATION

Synthesis of Methyl Ester

Methyl Esters of the selected vegetable oils are prepared using standard conventional process. The methyl esters are analysed for determining their physicochemical properties.

Ester conversions of 96-98% are obtained by trans esterifying refined oils with methanol, ethanol and butanol at 60°C, 75°C and 114°C for 1 hr with 0.5% sodium methoxide. The best combination of alkali-catalysed esterification condition is as follows

6:1 methanol/oil molar ratio; 0.9% w/w of KOH related to the quantity of starting oil; 60 °C reaction temperature and 60 min reaction time. The maximum conversion efficiency was98.7% under these reaction conditions.

Modification of Methyl Esters

Procedure:

The preparation of the ME was carried out in a four neck glass reactor

↓

Vegetable oil is in the reactor and heated to remove moisture

↓

Add sodium methoxide and heat at 60^0C for two hours

↓

Leave it for 4 hours for settlement of glycerol

↓

Take out Methyl Ester by decantation {glycerol}

↓

Wash ME with water and heat it to remove water

↓

Add maleic anhydride and malenisation is carried out for 150^0C for one hour

↓

Mixture is further heated gradually up to 250^0C for next three hours

↓

Addition of pthalic anhydride and heat it upto 200^0C

↓

Modified Methyl Ester is synthesised

Preparation of soap

Soap (%Solid = 60.58%): Methyl Ester, prepared from rice branoil,heatedto60-70 °C along with addition of 20% NaOH solution with constant steering to form the soap.

Soap (%Solid = 60.05%): Methyl Ester, prepared from rice branoil,heatedto60-70 °C along with

addition of 20% KOH solution with constant stirring to form the soap.

APPLICATIONS OF MODIFIED METHYL ESTERS

- The modified methyl ester after neutralisation by alkali is selected for formulating various powder and liquid detergents by varying the compositions.
- The resultant formulated samples are studied for their physicochemical properties like pH, % Solid, Surface Tension and Foam height.
- Performance of the detergents, on various cloth types, is determined in terms of the detergency values. The performance of the detergents is compared with that of the commercial detergents available in the market.

IDENTIFICATION OF OPTIMAL FORMULATIONS

The best performing detergents are identified on basis of their detergency value. These detergents are analysed for their compositions and physicochemical properties to determine their behaviour.

Formulations of best performing powder detergents

SET 1: Powder Detergents synthesised from MME

Ingredient %Composition byWt.	**PD-1**	**PD-2**	**PD-18**
Acid Slurry	5.76	3.80	3.87
A.O.S.	3.84	3.80	3.87
MME M1	3.20	5.71	9.67
Dolomite	25.62	28.90	29.03
Sodium Carbonate	25.62	28.90	29.03
Sodium Silicate	4.27	4.86	4.83
STPP	4.27	4.75	4.83
Urea	2.56	2.85	2.90
SLS	2.13	5.00*	-
Optical Brightner	2.56	11.43	-
Distilled Water	20.16		-
			11.97

SET 2 : Composition of Powder Detergents Based on MME M2

Ingredient % Composition by Wt.	**PD-B1**	**PD-B2**	**PD-B3**
Acid Slurry	4.41	4.58	4.55
A.O.S.	4.41	4.58	4.55
Neutralized MME M2*	8.82	9.13	11.80
Dolomite	30.89	31.97	30.83
Sodium Carbonate	26.48	27.44	26.29
Sodium Sulphate	4.41	4.58	4.55
STPP	2.64	2.73	2.72
SLS	9.40	9.13	9.10
EDTA	0.17	0.18	0.17
Foam Booster	0.88	0.90	0.90
CMC	0.44	0.41	0.45
Distilled Water	7.04	4.37	4.18

SET 3 : Composition of Liquid Detergents Based on Soap of Rice bran ME (Neutralised by NaOH)

Ingredient % Composition by Wt.	**LD-1**	**LD-2**
A.O.S.	-	7.00
SLES	6.00	6.00
Soap	12.01	6.00
SLS	10.00	-
Tween 20	1.72	0.86
Glycerine	8.44	5.91
Sodium sulphate	5.00	-
Distilled Water	56.83	74.23

Ingredient % Composition by Wt.	**LD-3**	**LD-4**	**LD-5**
A.O.S.	7.00	7.00	-
SLES	6.00	6.00	-
Soap	6.00	6.00	6.00
SLS	10.00	10.00	5.00
Tween-80	0.84	0.84	3.00
Glycerine	4.22	-	2.00
Sodium sulphate	-	-	3.00
Sorbitol	-	-	-
Distilled Water	65.94	70.16	

SET 4 : Composition of Liquid Detergents Based on Soap of Rice bran ME (Neutralised by KOH)

Ingredient % Composition by Wt.	**LD-6**	**LD-7**
A.O.S.	7.00	-
SLES	-	3.00
Soap	6.00	6.00
SLS	-	5.00
Ethyl Cellulose Solution	0.56	0.65
Glycerine	8.44	-
Acid slurry	-	-
Distilled Water	78.00	85.35

RESULTS AND DISCUSSION

Ingredient % Composition by Wt.	LD-8	LD-9
A.O.S.	7.00	3.50
SLES	-	3.00
Soap	6.00	9.00
SLS	-	-
Ethyl Cellulose Solution	0.55	0.46
Glycerine	8.44	4.22
Acid slurry	-	-
PVA (10%)	-	0.90
Sorbitol	-	-
Distilled Water	78.01	78.92

In the present work we have synthesized six different MMEs, four of them based on methyl ester prepared from rice bran oil and two of them based on methyl ester prepared from linseed oil. In these MMEs, proportion of maleic anhydride has been changed from 5 to15 %.

MMEM1,in which15% maleic anhydride has been used, has highest viscosity and acid value. The HLB value of MME M1 is high too, i.e. 11.96, as compared to the MMEs of the other batches.

All samples are insoluble in water but completely soluble in alcohol and acetone. MME M1 andM2 have been chosen for detergent preparation due to their high acid value, viscosity and HLB ratio.

ENVIRONMENTAL IMPACT

Some surfactants are known to be toxic to animals, ecosystems and humans, and can increase the diffusion of other environmental contaminants. Despite this, they are routinely deposited in numerous ways on land and into water systems, whether as part of an intended process or as industrial and household waste. A large fraction of dermatological problems in normal working life can be related to exposure of unprotected skin to surfactant solutions.

CONCLUSIONS

- MME M1 is based mainly on ME of Rice Bran Oil and 15% maleic anhydride. In MME M2, 7.5% phthalic anhydride and 7.5% maleic anhydride has been used.
- NMR and IR data for MME M1 and M2 confirms the presence of ester and -COOH group.
- Informulationsconventionalactive materials like acid slurry andA.O.S.whicharepetroleumbased are successfully replaced,withsoap based on Methyl Esters of vegetable oils.
- Also,theliquiddetergentsarefree from sodium carbonate, dolomite and other salts.
- In conventional liquid detergents we used very high proportion of SLES 10-12% which has been reduced to 3-6% in this work. This helps lower the cost of the liquid detergents prepared.
- The best performing detergents mentioned above have demonstrated the ability of the MMEs to entirely replace petroleum based active materials in detergents at a cost as low as Rs. 25 per Kg (approx.). The cost of the MME is as low as Rs. 55 per Kg (approx.).
- In India there is a need to promote liquid detergents in varioussectors.The liquid detergents prepared are of moderate cost and many of themhave shown better results.
- The best performing detergents mentioned abovehavedemonstratedthe ability of the soaps, prepared from methyl esters of vegetableoils,toentirely replace petroleum based active materials in detergents at a cost as low as Rs.40 per Kg (approx.).
- Thedetergentsmentioned above have the following features that will help open avenues in reducingthe dependency on petroleum:
    - Excellent detergency and stain removing capacity
    - Free from phosphate, A.O.S. and Acid slurry hence eco-friendly
    - Effective at lower concentrations and lower cost of preparation hence highly economical and performance-wise.

The rapid increase of free fatty acids (FFA) in bran after milling has been recognized as a serious problem for rice bran industries. The principalcause of oil deterioration in the bran during storage is the activity of the lipase enzyme in the presence of moisture. For this reason only 6.5% of world rice bran oil potential is evaluated as edible and the rest for industrial product purposes. This makes the inedible rice bran oil suitable for this work.

Some surfactants have proposed or voluntary restrictions on their use. For example, PFOS is slated for persistent organic pollutant (POP) status by the Stockholm Convention. Additionally, PFOA has been subject to a voluntary agreement by the

U.S. Environmental Protection Agency and eight chemical companies to reduce and eliminate emissions of the chemical and its precursors.

REFERENCES

[1] Schwab, A.W., Bagby, M. andFreedman, B., ―Preparation andProperties of Diesel Fuels from Vegetable Oils, Fuel 66:1372-1378 (1987).

[2] Demirbas, A., ―Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions, Biomass And Bioenergy 33 (2009), Page No. 113-118.

[3] Lin, L., Ying, D., Chaitep, S., Vittayapadung, S., ―Biodiesel production fromcrude rice bran oil and properties as fuel, Applied Energy 86 (2009), Page no. 681-688.

[4] India's Paper:The Need For Inclusion Of RiceBran Oil In The Standards For Named Vegetable Oils, Codex Committee on Fats and Oils, Joint FAO/WHO Food Standards Programme, Eighteenth Session, 3-7th February, 2003.

[5] Govt. Of India - Economic Survey 2007-2008

[6] Holmberg, K. and Johnsson, J., ―Addition of Maleic Anhydride to Esters of Mono-unsaturated fatty acids, Acta Chemica Scandinavia B 36, Page No. 481-485.

[7] Sultan Chand and Sons, Page No. 3, 132-3, 135 (1999).

[8] Chattopadhyay, P.K.,Modern Technology of soaps., detergents andToiletries, 2nd edition, Page No. 8-10.

[9] Fisher, L.A., Hayward, G.R., The Basics of Resin Technology, OCCA Student Monograph No. 10, Oil & Colour Chemists' Association, Page No. 12-13.

[10] Bartlett and Nozaki, JAOCS, 78 (3), 1998, Page No. 15 - 26.

[11] Hoi Y.H., ―Baily's Industrial oil and fats products, 5, Fifth edition, John Wiley and Son's, Inc, New York, Page No. 78-80, 1996

[12] P.L. Soni and H.M. Chawla a Textbook of Organic Chemistry, 28th Edn. Schwartz, A.M. & Perry, J.W., ―Surface active agents. Their Chemistry and Technology. Interscience Publishers, Inc. New York,1949, Page No. 51

[13] BhaleraoM and Dr. Karadbhajne V Y,'AKinetic Study On Malenisation of Soybean Oil' ,International Journal of Innovations In Engg Research and Technology(IJERT) in Vol 5 ,Issue – 2 , Feb 2018.

[14] Bhalerao M, Ansari N F and Dr. Karadbhajne V Y,'A kinetic Study on Malenised Castor Oil',International Research Journal of Management Science and Technology in Vol 9 , Issue 4 ,2018.