Microwave Assisted Synthesis Of Modified Methyl Esters And Its Application Into Formulation Of Detergents

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

Abstract
Microwave energy is a unique source because it creates heat deep within the material being processed. This property results in much shorter process time, higher yield of finished product and better quality than conventional processing.Microwave interacts with dielectric material to generate heat by the agitation of molecule in a alternating electromagnetic field.The unique property of microwave to penetrate deeply into material of interest reduces the process time, often by much as 10 to 1 and it reduces the cost of processing. Space saving is other reason for choosing microwave. Long stretched processing line can be compressed into a fraction of space. Thus it reduces the cost of construction & substantial economic saving. Modified Methyl Ester(MME) was synthesised at optimum temperature and input power of microwave which has the acid value and HLB ratio of the sample MME as 67.11 and 12.24 and is hence best suitable as an active ingredient for powder detergent.

Keywords: *microwave heating , yield , modified methyl ester ,powder detergent ,process time*

INTRODUCTION

The first successful microwave process on industrial scale was introduced in early 1960.Microwaves cover a broad spectrum & frequencies range from 300 MHz to300GHz.The term microwave denotes technique & concept used as well as range of frequency. Microwave travels in free space at the speed of light & they are reflected by metallic objects, absorbed by some dielectric material & transmitted without significant absorption through other dielectric material for e.g. water, carbon, & food with high water content are good microwave absorbs, glass, ceramic & most thermoplastic material allow microwave to pass with little or no absorption.

Factors which are considered while using microwave processing are as follows:

- Geometry: Materials that are thick & therefore difficult & time consuming to process by conventional heating means.
- Temperature sensitivity: Material adversely affected by using usual processing temperature.
- Cost : costly material generally can tolerate the higher cost of microwave processing.
- Uniqueness, a unique product or attribute of a product is obtained by the use of microwave heating.
- Batch to continuous processing, where batch process can be converted to a continuous process because of a substantial reduction in a process time.

How Microwave Heating Differs from Conventional Means

Conventional Heating Methods

In all conventional means for heating reaction mixtures, heatingproceedsfroma surface, usually the inside surface ofthereactionvessel.Whetheroneusesa heating mantle, oil bath, steam bath, or even an immersion heater,themixturemust be in physical contact with a surface that is at a higher temperature than the rest of the mixture.
In conventional heating, energy is transferred from a surface, to the bulk mixture, and eventually to the reacting species. The energy can either make the reaction thermodynamically as applied or it can increase the reaction kinetics. In conventional heating, spontaneous mixing of the reaction mixture may occur through convection, or mechanical means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel. Equilibrium temperature conditions can be established and maintained.

Although it is an obvious point, it should be noted here that in all conventional heating of open reaction vessels, the highest temperature that can be achieved is limited by the boiling point of the particular mixture. In order to reach a higher temperature in the open vessel, a higher-boiling solvent must be used.

Methods of Microwave Heating

Microwave heating occurs somewhat differently from conventionalheating.First,the reaction vessel must be substantially transparent to the passage ofmicrowaves.The selection of vessel materials is limited to fluoropolymers andonlyafewother engineering plastics such as polypropylene, or glass fibre filled PEEK (poly ether-ether-ketone). Heating of the reaction mixture does not proceed from the surface of the vessel; the vessel wall is almost always at a lower temperature than the reaction mixture. In fact, the vessel wall can be an effective route for heat loss from the reaction mixture.

Second, for microwave heating to occur, there must be some componentofthe reaction mixture that absorbs the penetrating microwaves.Microwaves will penetrate the reaction mixture, and if they are absorbed, the energy will be convertedintoheat. Just as with conventional heating, mixing of the reaction mixturemayoccurthrough convection, or mechanical means (stirring) can be employed to homogeneouslydistribute the reactants and temperature throughout the reaction vessel.

Microwave heating mechanism

Microwave energy is a unique source because it creates heat deep within the material being processed. This property results in much shorter process time, higher yield of finished product and better quality than conventional processing.

When microwave are intercepted by dielectric material such asfood,theyinteract with dielectric material, giving of energy which result in a increase in temperature of material. There are two mechanisms by which microwaves produceheatinthe dielectric material.

- Ionic polarization

  Ions gets kinetic energy in presence of electric field which are accelerates the ions. This Kinetic energy results in heat generation gained by the collisions of ions.
- Dipole rotation

  In presence of electric field , heat is generated on rotation of molecule which can be varied by the change in polarity of electric field.
- Penetration Depth

  It is the depth from the surface of the material at which the power has been reduced to one half of the total incident power.

MATERIALS AND METHODOLOGY

The present work is aimed at studying the microwave synthesis of MMEs based on methyl ester prepared from rice bran oil and maleic anhydride. Various mole ratios, reaction temperatures, microwave power and time of reaction will be studied. The idea is to develop a MME with higher acid value and with good surfactant characteristics.

Various MMEs prepared under different parameter will be thoroughly analyzed for Acid Value, Viscosity, HLB Ratio, Density, pH, IR Spectroscopy, NMRandColourcharacteristics. The sample with desired HLB ratio viscosity and color will be selected and its properties will be compared with the conventionally synthesized MME. The MME by conventional method will also be prepared using conventional modes.

This experiment will help us to identify the formulations whicharecomparableand better than the MMEs prepared byconventionalmethod Theroleofvarious vegetable source raw materials can also be successfully studied as the process requires less time and less amount of raw material one can studyvariousbatchesof varying parameters to yield a product best in all concern. The special focus of this method is to promote conventional raw materials of vegetableorigintoreplace partially, if not completely, the part of petroleum based raw materials currently in use. This will help us to reduce dependence on the non-renewable resources like petroleum. The overall concept is to promote green chemistry for synthesis and utilization of MME thus reducing the sources of pollution from the environment.

EXPERIMENTAL WORK

Various batches were synthesised and were analysed for various parameters.

Reaction programming

i) Malenized Methyl Ester from various compositions was prepared by batch process. The reaction temperature and addition of ingredients are detailed below.

ii) Methyl ester prepared from rice bran oil and maleic anhydride along with catalyst are well mixed to give a homogeneous mixture in vials and vials is packed with cap.

iii) The test tube is introduced into the microwave reactor and then temperature, microwave power and time are adjusted. The mixture was kept for 10 min in microwave reactor by setting the time and temperature of reactor.

iv) After 10 min the reactor stopped automatically.

v) After cooling, reaction mixture was taken out of the reactor.

The MME is prepared in the microwave synthesis reactor by using following parameters:

Table 1: Process Parameters for microwave heating method

MME	Reaction temperature in ^{0}C	Microwave power in watt	Reaction time minutes
MM4	240	140	10

Table 2:Analysisof MME and its Physio-chemical Properties of Malenized Methyl Ester by Microwave Reactor

Name of MME	Acid Value	Colour	Consistency	% solid	HLB Value
MM4	67.11	Dark Brown	Thick	95.85	12.24

This composition corresponds to the composition of conventionally synthesized Malenized methyl ester. Hence it can be concluded here that the modified methyl ester obtained by microwave heating method shows the same properties which are obtained by conventional methods. Hence microwave heating in shorter process time yields a better product than opting the conventional method. The reactor is operated as closed system.

Table 3 : Comparison Between Conventional and Microwave Results

Sr.No.	Analysis	Result	
		Microwave Batch	Conventional Batch
1	Acid Value	67.11	84.37
2	Colour	Dark Brown	Dark Brown
3	Consistency	Thick	Thick
4	%Solid	95.85	97.71
5	HLB Value	12.24	11.96
6	Avg. Mol. Wt.	1313.02	1101.91

After studying the data, the MME batch is selected for preparation of the powder detergent due to its colour, viscosity and desired HLB ratio. The MME is used in powder detergent in varying proportion as an active ingredient. All the ingredients of the powder detergents are mixed thoroughly to prepare the powder detergent.

TheacidvalueandHLBratioofthesampleMME is 67.11 and 12.24 is the best suitable as an activeingredientforpowderdetergent.

POWDER DETEGENT FORMULATIONS

Following compositions are ideal foamless detergents and stain removers.

Table 4 : Compositions of Powder Detergents Based on Selected MME batch

Ingredient % Composition by Wt.	MPD-1	MPD-2
Acid Slurry	4.19	1.05
A.O.S.	4.19	1.05
Neutralized MME	4.17	10.60
Dolomite	31.51	31.77
Sodium Carbonate	31.51	31.77
Sodium Sulphate	5.24	5.29
STPP	5.24	5.29
Urea	3.19	3.19
SLS	5.24	5.29
EDTA	0.21	0.21
Distilled Water	5.31	4.49

Table 5 : Compositions of Powder Detergents Based on Selected MME batch

Sr. No.	Sample	% Solid	P^H
1	MPD-1	94.69	8.37
2	MPD-2	95.51	8.36
3	MPD-3	97.27	8.30
4	MPD-4	95.47	8.37

ANALYSIS OF POWDER DETERGENTS

Table 6: Analysis of powder detergent for % solid and pH

Sample	Foam in cm^3, Foam Stability after (Minutes)			
	0	**5**	**10**	**15**
MPD-1	150	100	80	20
MPD-2	80	50	10	-
MPD-3	160	100	70	30
MPD-4	100	60	30	10

Table 7: Analysis of various physical parameters of powder detergents at 1% concentration

Sample	Density g/cc	Surface tension Dynes/cm	% Reduction in surface tension
MPD-1	0.9982	28.70	59.68
MPD-2	0.9982	31.38	55.91
MPD-3	0.9996	32.30	54.62
MPD-4	0.9986	33.16	53.41

In case of cotton cloth, MPD-1 and MPD-2 detergency are better than those of commercial samples.MPD-4 show detergency better than those of commercial samples in case of at all concentrations on all cloths.

ENVIRONMENTAL ASPECTS

The modified methyl ester synthesisedhas same properties as the same as conventional method. The properties are novel and are not harmful to the environment as it is synthesised from vegetable oil which is a renewable and sustainable resource as compared to petroleum origin. Formulated detergents has a negligible use of Acid slurry which is obtain from petroleum fraction. This ingredients are known to be toxic to animals ,ecosystem and humans and increases unnecessary diffusion into the environment.

Ingredient % Composition byWt.	MPD-3	MPD-4
A.O.S.	4.31	2.11
Neutralized Maleinized Methyl Ester	8.62	10.58
Dolomite	32.36	31.76
Sodium Carbonate	32.36	31.76
Sodium Sulphate	5.39	5.29
STPP	5.39	5.29
Urea	3.24	3.18
SLS	5.39	5.29
EDTA	0.21	0.21
Distilled Water	2.73	4.53

CONCLUSIONS

- 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.
- There is tremendous time saving in microwave synthesis, normally 5 to 6 hours are required for malenisation. At 240^0C. The time of reaction is reduced just to 10 minutes. Thus the same reaction can be carried out in a small reactor with little manpower and risk.
- The space required for microwave reactor is very small and man power required can be reduced considerably.
- The initial investment is higher but the recurring expenses, energy expenses are lower in microwave reactor.
- Microwave reactor can be the desired route which is financially and technically viable option of futuretime.
- The reaction time can be reduced from hours to few minutes.
- Microwave synthesised product gives detergents of good quality and performance characteristics.

In future, when microwave heating becomes cheaper, it can be used with advantages.

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