MICROWAVE-ASSISTED POLYMERIZATION OF MALENIZED VEGETABLE OILS

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A B S T R A C T

The present work is aimed at studying the microwave synthesis of malenized oil based on coconut oil, linseed oil, rosin, and maleic anhydride. Various parameters like reaction temperature, microwave power have been studied to get excellent desired properties of the malenized oil. The main advantages of microwave technique are reducing the time of reaction from eight hours to three minutes. The powder detergents by using microwave synthesis malenized oil gives results which are on par or some times better than conventional methods. Microwave reactor can be desired route which is financially and technically viable options for future time. The overall concept is to promote green chemistry by using cooking oil for making environment free from pollution to some extent

Keywords: conventional synthesis, malenized oil, microwave synthesis, green chemistry

1. Introduction

Microwave synthesis [1] represents a major breakthrough in synthetic chemistry and methodology. Conventional heating, long known to be inefficient & time-consuming, has been recognized to be creatively limiting as well. Microwave synthesis gives organic chemists more time to expand their scientific creativity, test new theories & develop new processes. Instead of spending hours or even days synthesizing a single compound, chemist can now perform that same reaction in minutes. In concerned with rapidly expanding application based microwave synthesis can be effectively applied to any reaction scheme, creating faster reaction, improving yield, & cleaner chemistries.

The CEM Focused Microwave™ Synthesis System, Model Discover, is designed to enhance the ability to perform chemical reactions under controlled conditions on a laboratory scale. The System facilitates either homogeneous or heterogeneous solution phase chemistry, solid phase chemistry or chemistry conducted on solid supports. It accommodates vessels ranging in volume from 5ml to 125ml for reactions performed under atmospheric conditions and a 10ml vessel with septa for reactions performed at elevated temperatures and pressures.

Microwave energy is applied to the vessel contents (reactants, catalysts, salts, solvents and/or solid supports) to accelerate the chemical reaction. The microwave absorption properties of some liquid and solid materials, due to their polar and ionic characteristics, have the capability to significantly enhance chemical reactions relative to traditional energy application (heating) techniques. The microwave interaction properties with the reactants, intermediates, catalysts, solid supports and salts provide unique opportunities for the synthetic chemist.

1. 1 malenized oil

A number of methods have been suggested for improving the properties of drying oils which involve the separation of the better-drying from the poorer drying components (segregation), the shifting of non-conjugated double bonds to conjugated form (isomerization) and the removal of water to introduce a new double bond (dehydration). There is another method of adding unsaturated compound to the unsaturated part of the oil molecule, thus increasing its complexity and heat reactivity. The compound referred to as Maleic treated or **Malenized oil**[2]**.** Maleic

anhydride along with phthalic anhydride can be used for modification and the modified oil is known as malenized oil.

Since the maleic is added near the unsaturation section of the fatty acid radical it retards oxidation slightly so that maleic treated oils do not show greatly increased air-drying properties. Maleic anhydride is a dibasic acid which reacts with both conjugated and isolated double bonds in the following manner.

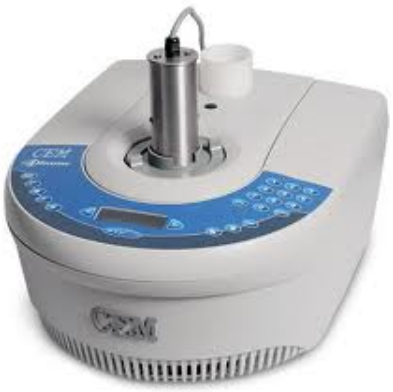
The product obtained from maleic addition is known as adduct which when neutralized with inorganic alkali, ammonia or an amine gives water miscible oils. These "Solubilized" oils may be used for different application like water paints, emulsion, disinfectants etc. based on the amount of maleic allowed to react with oil. Usually 10-15% of maleic anhydride is sufficient to produce the desired increase in net reactivity in the non-conjugated oils.

2. Experimental

2.1 synthesis of malenized oil in microwave reactor

1) Microwave reactor

The preparation of malenized oil was carried out in Bench Mate type microwave reactor. The reactor is operated as closed system.



Bench Mate type microwave reactor

2) Reaction programming

1. Malenized oil from various compositions was prepared by batch process. The reaction temperature and addition of ingredients are given in table no.2.
2. The Vegetable Oil, rosin, Maleic anhydride and Glycerol along with catalyst are well mixed to give a homogeneous mixture in test tube and test tube is packed with scapta cap.
3. 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.
4. After 10 min the reactor stopped automatically.
5. After cooling, reaction mixture was taken out of the reactor.
6. Ten samples were studied at different temperatures and microwave power and setting time of 2 to 7 mintues.

2.2 methods of physicochemical analysis

1. Acid Value[3]: The number of milligrams of KOH required for neutralization of 1gm of material under consideration of test. Acid value of the samples was determined by ASTM standard method, using following formula,

$$\text{Acid Value} = \frac{56.1 \times V \times N}{w}$$

where, V and N are the volume and normality of alcoholic KOH solution and w is the weight in grams of sample taken.

2. Saponification value[4]**:** The Saponification value is the amount of alkali necessary to saponify a definite quality of the sample. It is expressed as the number of milligrams of KOH required to saponify 1 grams of the sample. Saponification value is determined using formula,

$$\text{Saponification Value} = \frac{56.1 \times (B - S) \times N}{w}$$

where, B is the reading of blank test, S is the volume of the sample used, N is the normality of alcoholic KOH solution and w is the weight of the sample.

3. Solid Content[5]:

The percentage solid in the malenized oil sample is calculated as follows:

$$\%\ \text{Solid} = 100 - \%\ \text{Volatile Content}$$

4 pH[6]

The pH of sample was measured by using pH meter. The pH electrode was standardized with buffer solutions having pH of 4 and 9.2. For Acidic Medium pH meter was standardized with the buffer of pH =4 and that for basic medium it was standardized with pH = 9.2. The pH electrode was dip into the liquid detergent solution (1% conc.), or solution of powder detergent to find out pH. The reading was noted at which the meter shows stable value.

5. Viscosity[7]

Viscosity of malenized oil / sample was determined by ford cup method. Ford Cup No. 4 consists of a cylindrical metal cup with parallel

side and a conical base. The time required for the cup to get empty through the orifice was noted and result was expressed in seconds.

6. Determination of Molecular Weight[8]

The method available for determining the Molecular Weight of malenized oil is

Viscosity-Average Method

This method depends upon the principle that the limiting viscosity number is proportional to molecular weight, given by Suhulz equation,

$$\eta = \lim_{C\to 0}\frac{\eta_{sp}}{C} = KM^{\alpha} \quad \Rightarrow \ln\eta = \ln K + \alpha \ln M$$

7. Determination of Hydrophilic Lipophilic Balance[9]

It is defined as the ratio of hydrophilic group to hydrophobic group. HLB of the novel malenized oil is calculated by the saponification method. This method includes finding out the saponification number of a malenized oil and acid number of acid present in the reaction mass. Formula for calculation of HLB ratio is given by Griffin (1954). HLB is very important parameter; depending upon the value of HLB the malenized oils are used in following applications.

The HLB is calculated by formula describe by Griffin (1949), given by,

$$HLB = 20\times\left(1-\frac{S.V.}{A.V.}\right)$$

where, S. V. is the saponification value of the malenized oil and A. V. is the acid value of the raw material.

8. Determination of oxirane oxygen value[10]

Oxirane oxygen value can be determined as follows:

0.1N HBr and 0.1N sodium bicarbonate solutions were prepared in glacial acetic acid. HBr solution was standardized by titrating it with sodium bicarbonate solution by using crystal violet indicator. 0.5-0.8 g of synthesized malenized oil was dissolved in benzene and titrated with 0.1N HBr solution by adding crystal violet indicator. Oxirane oxygen value was calculated by using formula,

$$\text{Oxirane Oxygen Value} = \frac{V\times N\times 1.6}{w}$$

Where, V and N are the volume and the normality of HBr respectively and w is the weight of sample.

9. **Measurement of Stain Removing Capacity (%Detergency) [11]**

The samples, which are washed, dried and ironed, are used to find out stain removing capacity. The % detergency is determined using "lamberts and sanders" formula,

$$\%\,\text{Detergency} = \frac{R_W - R_S}{R_O - R_S}\times 100$$

where Rw, Rs, Ro are the reflectance measured on washed cloth, stained cloth and cleaned cloth respectively.

The reflectance of the cloth samples were measured by using "Reflectance Meter" manufactured by Universal Engineering Corporation, Ambala Road, Saharanpur (U.P). This is a digital instrument. This was first standardized by using the magnesium oxide or tile, which is provided along with the instrument. This tile having brightness of 100% that was adjusted by using the knob provided on instrument. Once this is adjusted then samples are kept on the instrument and note down the digital readings and calculate the percent detergency by using above formula.

10. Foam Volume[12]

The volume of foam produced is still very important property of surface active materials. Ability to foam at extreme dilution or under adverse condition may be an important factor in application. Many methods for measuring, foaming, characteristics of composition have been devised.

Bubble Cylinder Method: Foam characteristics are measured in terms of volume. The following steps were carried out for it. 100 ml solution of particular concentration, whose foam characteristics is to be measured, was taken in 1000 ml capacity cylinder. 30 up-down rotations within time period of 30 seconds were given.

1. The cylinder then kept on table and observed the foam above liquid level and reading was recorded.
2. The readings were measured for 0, 5, 10, 15 min. respectively.
3. Same procedure was carried out for the solution of different concentration like 0.1%, 0.25%, 0.5% and 1.0%

11. Surface Tension [13]

Surface tension may be defined as the force in dynes acting at right angle to the surface of a liquid along one-centimeter length of the surface. It is generally represented by the symbol γ and expressed in dynes/cm. The effect of surface tension is to reduce the area of the surface to a

minimum. Hence drop of a liquid has minimum surface area for a given volume. The rise of liquid in a capillary tube is well known phenomenon. This can be explained in terms of surface tension. We have used stalgmometer method to measure the surface tension of liquid.

3. Result & Discussion

1. Malenized oil has been prepared by conventional and microwave technique. A combination of linseed oil and coconut oil has been used. Linseed oil having very high iodine value (175-190) can find enough sites for Malenized reaction Coconut oil has a specialty of low molecular weight fatty acids with low percentage of unsaturated fatty acids. A small quantity of oxalic acid and citric acid has included with the hope that they will give good cleansing stain removing and other desirable characteristics of detergents. Benzoic acid has been included in the formulations to work as a chain stopper as vigorous reaction of maleic anhydride can give high molecular weight which are not desirable. A proportion of linseed oil is essentials to have more sites for interactions with maleic anhydride.
2. Various parameters of microwave synthesis like reaction temperatures, microwave power (in watts) and reaction time have been studied. The temperature of 60 to 225° has been tried; the wattage was changed from 50 to 200 watts while a variation of time from 2 to 7 minutes has been experimented. After the desired time the samples were cooled and transferred to stoppered bottles.
3. The physicochemical properties of malenized oil synthesized in microwave reactor and samples prepared in conventional heating are given in table no.4. All the samples are thick with % solids of 85 to 88% showing 84 to 86% yield in reaction. The acid value and HLB ratio indicates that sample M-6(7) with an acid value of 37.56 having HLB ratio of 13.2 is best suitable as an active ingredient of detergent.
4. The comparative results of conventional batch (M-6) and microwave synthesis batch M-6(7) are given in table no.5. The reaction time has been reduced from 5 - 6 hours to 3 minutes. The heating is quicker and easier, and it gives product of good homogeneity, transparency and rheology. The acid value, average molecular weight and HLB value of conventional batch are comparable to microwave synthesized malenized oil. The HLB value and molecular weight of microwave synthesized malenized oil is slightly higher than conventionally synthesized malenized oil. The foaming property and foam stability is moderate. These compositions have less foaming compared to commercial samples Thus; from the study of various parameters we can recommend the standard conditions for getting a good product with homogeneity, transparency and viscosity.
5. Various stains like soil, tea, coffee and spinach can be successfully removed by using malenized oil in powder detergent. In some formulations the stain removing is better or superior than the commercial samples which were tested simultaneously.
6. All samples have excellent foaming properties and foam stability (1% concentration) than commercial samples. There is a better surface tension reduction at 1% concentration and comparable to commercial products tested simultaneously. The samples PD-4(C) and PD-5(M) are the best from stain removing point of view.

4. conclusion

1. The Following standard conditions can be recommended for novel malenized oil i.e. Time 3 minutes, Temperature 150°C and Wattage 140watts.

2. A comparison of conventional methods of cooking with microwave synthesis has been undertaken. The microwave synthesis gives results which are on par or some times better than conventional methods.

3. There is tremendous time saving in microwave synthesis, normally 3 to 4 hours are required for novel malenized oil. The time of reaction is reduced just to 3 minutes. Thus, the same reaction can be carried out in a small reactor with little manpower.

4. 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. The reaction time can be reduced from hours to few minutes.

5. There is a global trend of using foamless detergents throughout the world; our samples are giving moderate foam so there will be certainly saving of water to some extent which is required from water consumption view point.

Table 1: Experimental formulations of Malenized Oil (M-6) Synthesized by Microwave Method

S.N.	Ingredients	M-6
1	Coconut Oil	40.00
2	Linseed Oil	45.00
3	Maleic Anhydride	10.00
4	Citric Acid	02.00
5	Benzoic Acid	01.00
6	Oxalic Acid	02.00

Sodium bisulphite ($NaHSO_3$) 0.5%, Sodium bisulphate ($NaHSO_4$) 1.5% and Conc.HCl has been used as catalyst.

Table 2: Conventional Cooking Schedule of Malenized Oil synthesis

S. N.	Temp (^{0}C)	Time (Hr.)
1	200	2.00
2	230	3.00
3	150	0.5

Table 3: Microwave Synthesis of Malenized Oil

Name of Malenized Oil	Reaction temperature in^{0}C	Microwave power in watt	Reaction time in minutes
M-6-1	60	50	2
M-6-2	80	70	3
M-6-3	100	80	4
M-6-4	120	100	5
M-6-5	140	125	6
M-6-6	160	140	7
M-6-7	180	140	3
M-6-8	200	150	4
M-6-9	200	180	3
M-6-10	215	195	3

Table 4: Physico-Chemical Analysis of Malenized Oil M-6 (1) to M-6 (10)

Malenized oil	Acid Value	Color	Consistency	HLB	Viscosity	Foam Height
M-6(1)	43.58	Brown	Thin	13.25	285	350
M-6(2)	42.21	Brown	Thin	14.65	278	400
M-6(3)	41.87	Brown	Thin	13.25	271	350
M-6(4)	40.98	Brown	Thin	13.54	265	450
M-6(5)	39.65	Brown	Thin	13.2	260	500
M-6(6)	38.65	Brown	Thin	12.58	255	550
M-6(7)	37.54	Brown	Thin	13.2	250	700
M-6(8)	36.2	Brown	Thin	12.84	248	450
M-6(9)	35.98	Brown	Thin	13.69	245	500
M-6(10)	34.28	Brown	Thin	12.5	240	600

Note: Malenized oil is soluble in alcohol, NaOH and xylene: butanol

Table 5: Comparison Between Conventional and Microwave Results

S.N.	Analysis	Results	
		M-6 Conventional Method	M-6(7) Microwave Method
1	Acid Value	36	37.54
2	Color	brown	brown
3	Consistency	thin	thin
4	%yield	93.65	88.87
5	HLB	13.8	13.2
6	pH	2.71	2.26
7	%solid	90.25	83.96
9	Viscosity	240	250
10	Oxirane-oxygen	1.6	1.62
11	Avg. Mol. Wt.	3360	3458
12	Time of Reaction	5.30 Hours	3.0 min.
13	Temperature in ^{0}C	230^{0}C	180^{0}C

Table 7: Composition of Powder Detergent Based on Microwave Synthesised Malenized Oil M-6(7)

S. N.	Ingredients	% Composition By Weight					
		PD1	PD2	PD3	PD4	PD5	PD56
1	Linear Alkyl Benzene Sulphonate (75% solid)	7.5	6	4.5	3	1.5	0
2	Sodium Lauryl Sulphate	5	5	5	5	5	5
3	Sodium Carbonate	12	12	12	12	12	12
4	Sodium Sulphate	22	22	22	22	22	22
5	Urea	3.5	3.5	3.5	3.5	3.5	3.5
6	Salt	25	25	25	25	25	25
7	Dolomite	15	15	15	15	15	15
8	Zeolite powder	3	3	3	3	3	3
9	Whither Brightner	3	3	3	3	3	3
10	Neutralized Malenized Oil M-6 (7)	---	1.8	3.6	5.4	7.2	9
11	Distilled water	4	3.7	3.4	3.1	2.8	2.5

Table 9: Comparative Performance of Powder Detergent Based on Conventional and Microwave Synthesized Malenized oils

S. N.	Powder detergent	Physiochemical properties & Effect of Powder detergents on % detergency of 1% conc. on cotton cloths					
		Surface Tension	Foam Volume (cm^3)	Soil Stain	Tea stain	Coffee stain	Spinach Stain
1	PD 1(C)	25.14	500	91.53	85.93	92.75	95.16
2	PD 1(M)	20.13	500	94.56	87.5	94.2	95.16
3	PD 2 (C)	24.17	400	88.05	76.56	82.6	85.48
4	PD 2(M)	19.45	400	94.02	78.12	82.6	91.93
5	PD3 (C)	23.14	400	86.56	81.25	73.91	75.8
6	PD 3 (M)	18.56	350	88.05	84.37	79.1	77.41

7	PD 4(C)	22.15	350	96.24	87.5	94.2	96.77
8	PD 4 (M)	17.58	300	88.05	90.34	94.2	96.77
9	PD 5(C)	21.58	350	80.59	79.68	86.95	90.32
10	PD 5(M)	16.54	300	96.54	81.25	88.4	91.43
11	CD 1	22.1	700	85.09	89.06	92.75	95.16
12	CD 2	23.56	650	89.55	78.12	84.05	80.7

Note: Sample PD (C) represents conventional synthesis sample; Sample PD (M) represent microwave synthesis sample and CD1 & CD2 represents commercial samples.

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