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Modified Biodiesel for foamless Detergents

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ABSTRACT

Methyl esters of various vegetable oils (Biodiesel) are the future Green-fuels from renewable resources. Several methyl ester plants have been installed in India and abroad. However the production of methyl esters becomes uneconomical due to cost and availability of seed. Competitive Price of crude petroleum and inherent difficulties in processing of methyl esters, the plants of huge capacity have been installed can remain ideal. In some situations it is very necessary to modified methyl ester and uses it in certain alternative products. In the present research work, rice brain oil methyl ester has been prepared by standard technique and then modified by reaction with maleic and phthalic anhydride. The selected modified malenized oil has been used in foamless ecofriendly powder detergent formulations. The samples have low to moderate foam and good stain removing properties for stain of soil, tea, coffee and spinach. The products are containing small amount of sodium tripolyphosphate (5% or less) and hence they labeled as ecofriendly. The results are comparable to commercial products and they can be produced at competitive moderate price.

Keywords: Methyl esters, malenized oil, Sodium tripolyphosphate.

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INTRODUCTION

The world production and consumption of biodiesel (methyl ester of fatty acids) is increasing every year. In India the production and consumption of biodiesel is facing several problems. However, large plantations of zetropa, karanja and other oil seeds have been taken up on massive scale. Several plants producing biodiesel are installed Tamil Nadu, Madhya Pradesh and other states. Sometimes it is not economical and technically viable to use biodiesel as fuel because of availability of seed, comparative cost of crude petroleum products and technically inferior quality of biodiesel. The present work is aimed at modifying biodiesel with maleic and phthalic and produces a malenized methyl ester which can be used in preparation of foamless detergents. We must have a readymade technology available for modification and industrial use of methyl esters in products like foamless detergents. The work has been carried out in following stages.

We have already used malenized oils in paint strainers [1], cream and lotions [2] and liquid soaps [3]. This work encouraged us to use modified biodiesel in powder detergent compositions.

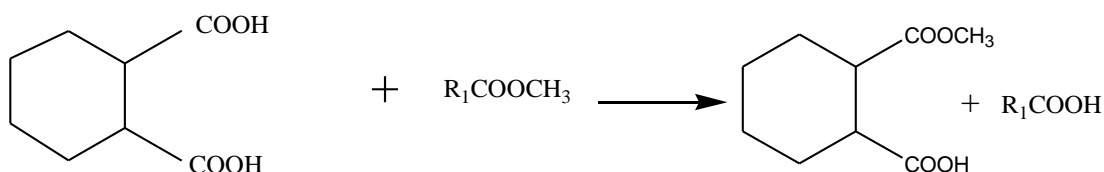
MATERIALS AND METHODS

Rice Bran oil was obtained from market. The constants of this oil are reported in table no. 1. The oil is modified to methyl ester by using standard technique using Rice Bran Oil Sodium methoxide and methanol.

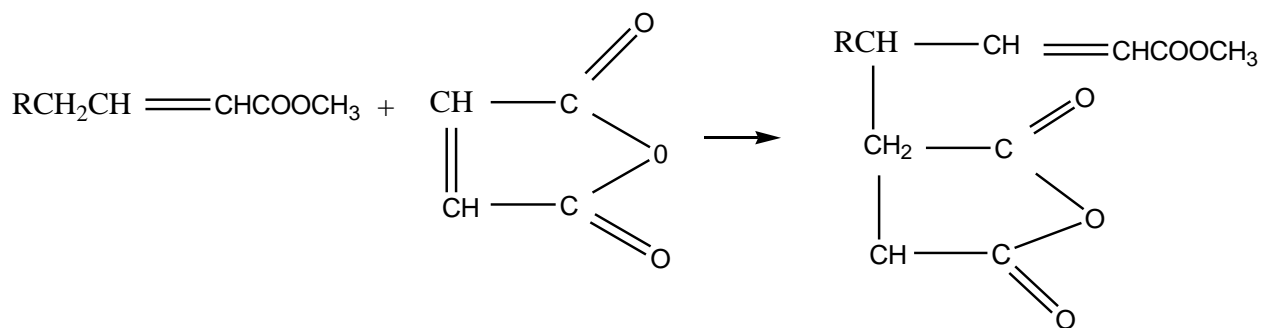
Chemistry of Possible reactions of methyl esters

The following chemical reactions are possible between methyl ester and maleic and phthalic anhydride.

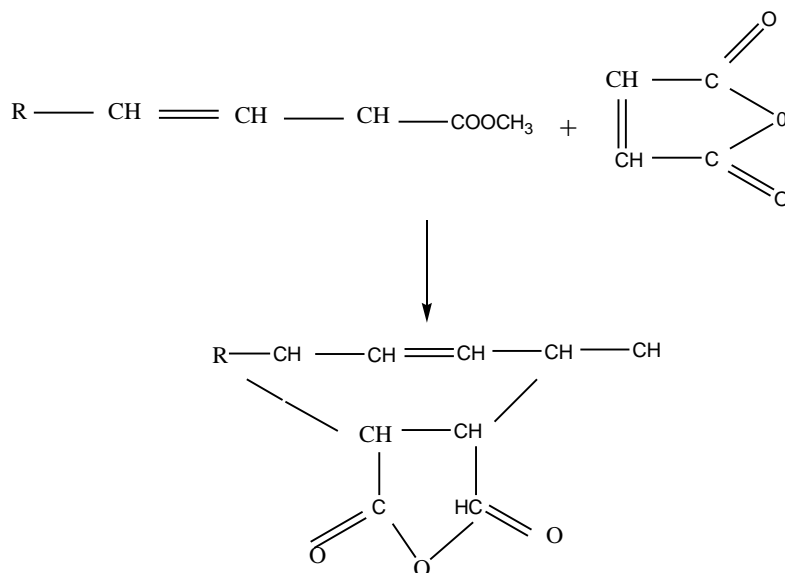
(i) Esters interchange of methyl and Phthalic anhydride.



ii) A path reaction where reaction occurs at allylic position in fatty acid resulting in products with reaction of unstable.



III) Diels alder type addition reaction of addition reaction where non conjugated bonds are first converted to conjugated bonds by heat and then maleic is added.



All these malenized products and ester interchanged product are high molecular weight polymers with free acid groups available for esterification reaction.

Table No:-1 Composition of Malenized Methyl Ester Samples

Sr.No.	INGREDIENTS	M1	M2	M3	M4
1	Methyl ester of rice ban oil	85	83	86	85
2	Maleic anhydride	15	7.5	10	5
3	Phthalic Anhydride	-	7.5		-
4	Oxalic Acid	-	1	2	5
5	Citric Acid	-	-	-	-
6	Benzoic Acid	-	1	2	5

Note: Sodium bisulphate (NaHSO_4) 1.5 % and Sodium bisulphate (NaHSO_3) were used as catalyst on weight basis.

Heating schedule for making malenized methyl ester of rice bran oil

(Total heating Time: - 8hours)

Step 1:- Charge 2 liter glass reactor with methyl ester + maleic anhydride +sodium bisulphite and sodium sulphate as a catalst and other acid.

Step 2:- Heat steadily and slowly to bring the temperatures to 160⁰ c this will take 1 hour. Cook at this temperatures for 1 hour.

Step 3:- Increase the temperature slowly and steadily so that the temperature of 230⁰ c is maintained. Now cook for 1 hour.

Step 4:- Rise the temperature to 240⁰ c and heat for 5 hours.

Step 5:- Cool to 80⁰ c and withdraw the sample in brown colored bottle with cork.

The IR and NMR result shows the presence of ester aromatic acid, hydroxyl and ethoxyl group in polymer.(see table no.). These spectroscopic investigations confirm the possible reactions described above.

Table No-2 Physico-Chemical Analysis of Malenized Methyl Ester Samples

SL.No.	Analysis	Results			
		M1	M2	M3	M4
1	Acid Value[4]	84.37	80.03	69.31	58.98
2	Color	Dark Brown	Dark Brown	Dark Brown	Dark Brown
3	Consistency	Thick	Thick	Thick	Thick
4	%yield	97.71	95.95	94.12	96.18
5	HLB [5]	11.96	11.65	9.94	10.53
6	Refractive Index at 25 ⁰ C	1.4790	1.4730	1.4731	1.4738
7	Solubility (in alcohol)	Insoluble	Insoluble	Insoluble	Insoluble
8	Solubility (in water)	Insoluble	Insoluble	Insoluble	Insoluble
9	Solubility (in acetone)	soluble	soluble	soluble	soluble
9	Average Mol.wt.[6]	1101.91	892.07	932.59	433.59
10	Viscosity By Ford Cup No.4 at 30 ⁰ C [7]	230	215	180	156
11	Sap Value [8]	68.87	62.64	69.18	72.78
12	Iodine Value [9]	60.48	62.41	69.18	72.78

Table No-3 Composition of powder detergent base on Malenized Maleic Ester of Rice ban Oil Sample M2

SL.No.	INGREDIENTS	PDB1	PDB2	PDB3	PDB4	PDB5
1	Acid slurry (70%)	4.6	4.6	4.8	-	-
2	Alpha Olefin Sulphate (70%)	2.6	4.6	6.8	-	-
3	Sodium Carbonate	27.8	27.6	28.8	26.7	36.9
4	Malenized methyl ester naturalized with NaoH(95% solids)	9.3	9.3	9.6	-	-
5	Malenized methyl ester neutralized with triethanol amine (95% solids)	-	-	-	12.8	9.22
6	Sodium Sulphate	4.6	4.6	4.8	---	---
7	Dolomite	32.4	32.2	33.6	37.4	27.7
8	Sodium Tripolyphosphate	2.8	2.8	2.9	5.3	----
9	Sodium Lauryl Sulphate	----	----	-----	8.0	9.2
10	EDTA	0.2	0.2	0.2	0.2	0.2
11	Cocoabetaim foam booster	0.9	0.9	1.0	--	---
12	Carboxyl Methyl Ester	0.5	0.5	0.5	0.2	0.2
13	Distilled Water	14.3	12.7	7.0	9.4	16.5

Table No:-4 Analysis of Powder detergents

SL.No.	Sample	%Solid	PH
1	PDB1	85.64	8.74
2	PDB2	87.14	8.22
3	PDB3	92.90	8.67
4	PDB4	90.59	9.30
5	PDB5	83.44	9.39
6	CD1	93.40	8.53
7	CD2	96.58	8.33

Table No:-5 Physicochemical Properties of Detergent Powders based on Malenized methyl ester 2 (Foam Volume and Surface Tension of Detergents samples)

Property	Conc.	PD-B1	PD-B2	PD-B3	PD-B4	PD-B5	CD1	CD2
Foam Volume in cm3 (cylinder method) [10]	05%	110	120	100	100	100	400	650
	1%	150	200	150	200	150	500	750
Surface Tension in dynes/cm Stalagnometer test [11]	05%	30.32	31.49	31.51	37.51	378.14	30.26	25.11
	1%	29.23	29.58	29.62	33.89	52.38	25.46	23.94

TABLE NO.6- Stain Removing Properties on Cotton, polyester and terricot sample

Note_Stains of soil, tea, coffee and spinach were tested at 1% concentration in distilled water applied as per standards methods.

R0= Reflectance measured on clean cotton cloth =100
 R0 =Reflectance measured on clean polyester cloth =100
 R0=Reflectance measured on clean Teri cot cloth =100
 Rs=Reflectance measured on Soil Stained cotton cloth =29
 Rs=Reflectance measured on Soil Stained polyester cloth =37
 Rs=Reflectance measured on Soil Stained Teri cot cloth =30

Sample	Polyester cloths				Terricot cloths				Cotton cloths			
	Soil	Tea	Coffee	Spinach	Soil	Tea	Coffee	Spinach	Soil	Tea	Coffee	Spinach
PDB1	93.65	95.35	97.73	95.56	95.71	95.92	96.43	95.83	92.96	91.67	93.62	91.81
PDB2	90.48	97.67	97.73	97.78	90.00	93.88	98.21	95.83	97.18	97.92	97.87	97.96
PDB3	80.95	95.35	97.73	97.78	90.00	95.52	98.21	93.75	97.18	95.83	97.87	97.96
PDB4	87.30	97.67	93.18	97.78	90.00	93.88	96.43	95.83	97.18	97.12	97.87	97.96
PDB5	90.48	97.67	93.18	97.78	88.57	95.52	96.43	97.92	97.18	97.12	97.87	97.96
CD1	96.83	97.67	97.73	95.56	98.57	97.96	96.43	97.92	95.77	95.83	97.87	97.96
CD2	98.41	97.67	95.45	97.78	94.29	95.52	98.21	95.83	97.29	97.92	97.87	97.96

RESULT AND DISCUSSION

Table 1 shows the composition of malenized methyl ester prepared in the laboratory. Maleic anhydride is used in the entire sample from 5 to 15%. In one sample M2, 7.5% phthalic anhydride has been used. A small proportion of oxalic acid 1 to 5% has been used so that the polymer may have been the cleansing property. The combination of phthalic and maleic anhydride has been used as a normally combination of aromatic and aliphatic ester sometimes gives better detergency. Benzoic acid has been taken in small proportion 1 to 5% to control the polymerization reaction and as a chain stopper. Sodium bisulphate and sodium bisulphite have been used as catalyst.

The heating and order of addition of various ingredients. It shown in table no. 2. Initially slow and steady heating is necessary as maleic anhydride has tendency of subliming at higher temperature. Then in third and forth step the temperature is taken to 230⁰ c to 240⁰ c so that sublimation is reducing to minimum. The sample so prepared is neutralized with NaOH or triethanol amine to get the desired pH.

The composition of foamless detergent is shown in table no. 3. In various compositions small amount of soft acid slurry and alpha olefin sulphonate has been used in formulation PDB1 and PD2 acid slurry and alpha olefin sulphonate have been totally eliminated and triethanol amine neutralized sample has because from 9 to 12% along with sodium lauryl sulphate. The sample PDB4 and PDB5 can be called ecofriendly and free from petroleum product. Sodium carbonate has been used from 27.8 to 36.9%. The other ingredients are common ingredients of detergent composition.



Table no. 4 gives % solid and pH of various formulation prepared. The moisture contain of various sample is similar to commercial sample CD1 and CD2. The pH is also in same range of 8.2 to 9.3.

Table no. 5 gives foaming property and surface tension of various sample. The foam volume is low to moderate in all the samples from PDB1 to PDB2 compare to commercial sample CD1 and CD2. This malenized methyl ester can be recommended for low foaming and washing machine detergent. The lowering of surface tension will certainly help in better contact and removal of dirt and stain.

Table no. 6 gives stain removing properties on various cloths. Thus all samples have well to excellent soil, tea, coffee and spinach stain removing characteristics and they are comparable commercial samples. Thus malenized methyl esters have dual function of foam control as well as stain removing.

CONCLUSION

The following conclusions stand confirm in the light of above experimental work

Methyl ester of rice bran oil can be modified in a simple batch reactor to prepare malenized methyl ester. In biodiesel plant if a small batch reactor of 50 to 100 kg is installed it can be used as alternative raw material useful in foamless detergents.

The reaction condition and catalyst have been standardized to prepare modified methyl ester for use in foamless detergent. The recipe for M2 (Formulation) should be tried on pilot plant scale.

The sample base on methyl ester, maleic anhydride and phthalic anhydride has been selected for preparing foamless powder detergent. It can be used after neutralization with NaOH or triethanol amine. The triethanol amine neutralized sample gives better results.

The foamless detergent base M2 has following special features. The active materials used are small proportion of soft acid slurry, alpha olefin sulphonate, and sodium lauryl sulphate and malenized methyl ester. Sample PDB1 and PDB2 are using only malenized methyl ester and sodium lauryl sulphate so that they can be call as ecofriendly detergent free from petroleum base and containing very small proportion of sodium tripolyphosphate which is major source of river and lake pollution.

All samples have low to moderate foam yet they have excellent detergency for stains of soil tea, coffee and spinach. This is a unique combination of low foam and high detergency, they can be recommended for foamless cleanser and washing machine detergents. The cost is moderate and therefore pilot plant studied should be carried out for this product.



If we use low foaming and foamless detergents we save about two bucket of water from every house. In remote areas and draft like situation this product will serve the national purpose of saving water.

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