SYNTHESIS OF FATTY IMIDAZOLINES BASED ON PALM FATTY ACIDS AND DIETHYLENETRIAMINE THROUGH MICROWAVE IRRADIATION AND THEIR CHARACTERIZATION

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Abstract : This paper describes solvent free microwave synthesis of long chain imidazolines based on palm fatty acid and diethylenetriamine (DETA). This is carried out in an open vessel and the products obtained by this method were found to be in good yields and of high purity. This method produced imidazolines in very less time of 5-10 min and gave yield of 89-91% as compared to very high time of 8-10 h and lower yield of 75-80% by conventional thermal condensation method.
Key words : microwave, imidazolines, non solvent synthesis, cyclization

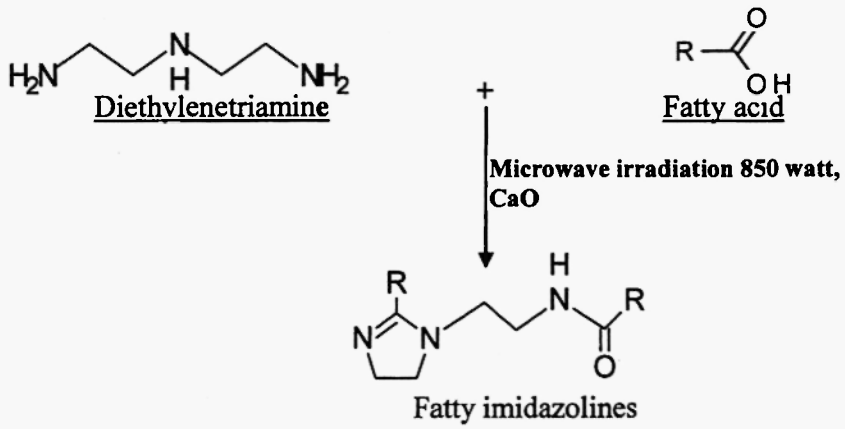
Introduction

Long chain substituted imidazolines are of great importance because of their numerous industrial applications. Fatty imidazolines salts are frequently used as fabric softeners (1), dispersants (2), antistatic agents (3), bleach activators (4), and emulsifiers (5) not only because of their good performance but also for their mild behavior to eyes, skin and clothes (6) and their biodegradability (7). In addition, imidazolines compounds are gaining importance in paint industries and lubricant industries as corrosion inhibitors (8) and.alsobexhibit a wide variety of biological activities (9).

Conventional methods (10) of preparation of imidazolines involve dehydration between fatty acids and polyamines under vacuum. Fatty acids used are generally stearic acid, palmitic acid, lauric acid, oleic acid and some oil like corn oil and rice bran oil. Polyamines used are ethylenediamine (EDA), diethylenetriamine (DETA), ethylene tri amine tetra acetic acid (EDTA), aminoethyl ethanolamine. This conventional thermal method suffer from disadvantages such as long times, low yield of the products and tedious work up (11).

Nowadays, use of microwave irradiation in organic synthesis is gaining special attention due to generally low reaction time, better yield and high purity of products. The world wide increasing trend of production of imidazolines enhance scope of palm oil derivatives for industrial applications as this is readily available in open market @ 20/-kg attracted the attention of authors for synthesis of cheaper product.

This paper describes the microwave synthesis of fatty imidazolines based on palm fatty acid and DETA under non solvent conditions in the presence of CaO as substrate. (Scheme-1)



Scheme-1 : Synthesis of fatty imidazolines through microwave irradiation

Materials

Chemicals used for the synthesis of imidazolines and their quaternized salts were of analytical grade obtained from M/s Qualigens and E. Merck, Mumbai.

Experimental

Characterizarization of raw materials

Acid value (AV) and saponification value (SV) were determined according to BIS method. Acid value and saponificatoion value were found to be 163.8 and 202.8 respoectively. Refractive index of DETA was 1.4826 and purity of DMS was 98%.

Preparation of Imidazolines

In an open Pyrex vessel (500 ml) 20mmol of diethylenetriamine, 40 mmol of the palm fatty acid and 20 gram of calcium oxide were carefully mixed. The reaction mixture was irradiated using power (850 W) of microwave oven for required time (as given in Table 2) and final temperature was noted down. The reaction mixture was allowed to reach at room temperature. Ethyl acetate was added (80 ml) and the mixture was heated until boiling and filtered off while hot, and the filtrate was concentrated under vacuum to dryness, yielding the corresponding product as a white to yellowish brown, solid to semisolid substances (Table-1).

Table-1 : Synthesis of imidazolines

S. No.	Palm fatty acid (mmol.)	DETA (mol.)	Molar ratio of fatty acid and polyamine	Power of microwave oven used (watt)	Reaction time (min)	Final temperature (^{0}C) approx.	Amine value (m eq /g)	Yield (%)
1	40	20	2:1	850	10	220	0.8	94.7

Table-2 : Spectral analysis of synthesized fatty imidazolines and their salts

Compound	FT-IR (KBr)	^{1}H-NMR (δ values)	^{1}C-NMR (δ values)
Palm Fatty Imidazoline	CH_3 C-H stretching 2834cm^{-1}, $(CH_2)n$ skeletal 580 cm^{-1}, N-H stretching (secondary amine) 3435 cm^{-1}, -C=O stretching (amide) 1734 cm^{-1}, C=N stretching 1655 cm^{-1} (imidazoline ring)	CH_3 (0.86 ppm, 0.87 ppm, 0.89 ppm), $(CH_2)n$ (1.25 ppm), CH_2 attached to imidazoline ring (2.66 ppm, 2.75 ppm, 2.80 ppm) -CONH- 6.1 ppm equivalent ring methylene group (3.34 ppm, 3.64 ppm.	C2 of imidazoline ring 118.8 ppm, equivalent ring of methylene equivalent methylene carbon 33.1 NHCOR 127.32 ppm, (CH_2) 29.5

Analysis

Procedure for determination total amine value (12)

Melt the sample, if it is not already liquid, in a water bath, mix thoroughly, and accurately weigh 1 to 4g into a 250 ml flask. Add 50 ml of alcohol and boil for 1 min to drive off any free ammonia that may be present. Cool to room temperature. Add 5 drops of bromophenol blue indicator and titrate, while swirling, with 0.2N HCl to the yellow end point.

Calculation Total amine value (m eq /g) = $\frac{V \times N}{S}$

where, V= HCl required for titration of the specimen

N = Normality of the HCl solution

S = Specimen weight of sample

Results and Discussion

Effect of molar ratio of fatty acid and diethylenetriamine on the synthesis of imidazoline

In the present research work, synthesis of imidazolines were carried out at different molar ratios of 2:0.5, 2:0.75, 2:1 and 2:1.5 of fatty acids and amines at constant power (850 watt) for constant reaction time and percentage yield were calculated. In case of palm fatty acid 2:0.5 molar ratio of reactants gave the yield of 46.6% at 850 watt power and 8 min. of reaction time. Increasing the ratio of DETA from 2:0.5 to 2:1 a remarkable increase in the percentage yield from 46.6% to 91.7% was noticed. Further increasing the ratio showed negligible change in the percentage yield of product.

Effect of time on the synthesis of imidazolines at constant molar ratio and power

Effect of time was studied at constant molar ratio (2:1) and constant power (850 watt). Reaction was carried out at constant molar ratio of 2:1 and constant power of 850 for different reaction times. For 9 min. of reaction time, the final temperature recorded was 200^{0}C which resulted in no formation of

imidazolines (supported by spectral results). For 10 min., final temperature was 220^{0}C and percentage yield of imidazolines was 94.7%. Further increase in reaction time from 10 to 11 min. resulted in charring due to very high temperature of 240^{0}C resulted in the charring of reactants.

Spectral analysis

Imidazoline and quaternary imidazoline were characterized by **FT-IR** and **^{1}H-NMR**. The interpretation was confirmed by nuclear magnetic resonance (NMR). The instrumental analysis of imidazoline and quaternary imidazoline confirmed the proposed chemical structure of imidazoline. The formation of imidazoline was confirmed by the FT-IR results indicating CH_3, CH- str. at 2834.35 cm^{-1}; $(CH_2)_n$ skeletal at 719.51 cm^{-1}; NH_2, N-H stretching at 3427 cm^{-1} ; N-H deformation at 1458.32 cm^{-1}; stretching C-N at 1238.41 cm^{-1} (amide group); stretching C=O (amide group) at 1655.07 cm^{-1}.In ^{1}H-NMR spectra of compounds, peaks at 3.0-3.6 ppm showed the formation of imidazoline ring. The presence of amide group was confirmed by the presence of peaks present at 6.0 to 7.0 ppm.

Conclusion

Classical methods of imidazoline synthesis involved long reaction time (8-10 hrs) and comparatively lesser yield (85-87%). Microwave synthesis is an excellent methodology for the synthesis of long chain dialkylamidoethyl imidazolines. The procedure avoids the employment of reduced pressures and long reaction time as it is carried out in an open vessel and takes few minutes for the synthesis of alkyl imidazolines, which on quaternization give quaternary imidazolines.

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