Study of Diethanolamide from Custard AppleSeed Oil (*Annona Squamosa L)*

Lokhande A. R.[1*], Patil V. S.[2], Wani K. S.[3]

[1*&3]*Department of Chemical Engineering, SSBT's College of Engineering and Technology, Bambhori Jalgaon (MS), India*
[2] *University Institute of Chemical Technology, North Maharashtra University, Jalgaon, (MS), India*

Abstract

Diethanolamides are nonionic emulsifiers widely used in industries such as cosmetics and detergent industries as a foam booster. Diethanolamideswere prepared fromcustard apple seed oil (Annona Squamosa L.)and based on the experimental results a fatty acid to diethanolamine ratio of 1:2 (w/w) i.e. 1:5 (5.37) (on molar basis) and a temperature of 150 ^{O}C were found suitable for the synthesis of fatty acid alkanolamides of custard apple seed oil.The diethanolamide have established their places as an important raw materialofproducts ranging from laundry detergent to better quality shampoos because of their various detergent properties.

Keywords: Custard apple seed oil, mixed fatty acids, diethanolamine, alkanolamides.

1. Introduction

Annona is genus of tropical fruit trees belonging to family of *ANNONACEAE*. Custard apple is cultivated in Maharashtra, Andhra Pradesh, Karnataka, Bihar, Orissa and Tamilnadu.According to an estimate made by Indian Council of Agricultural Research (ICAR), custard apple trees are grown in about 40,000 hectares and can yield about 4 lakh tones seeds. This in turn can yields 1.12 lakh tones oil [1].

Alkanolamides are condensation products of the reaction of a primary or a secondary alkanolamine with a fatty acid, methyl ester or a triglyceride. Their chemical properties vary, depending on the length of their hydrocarbon chain and the nature of substituent on nitrogen atom [2]. Fatty alkanolamides are compounds that exhibit low reactivity and high thermal stability. Since the amide linkages are very stable chemically and not easily degraded in alkaline media, they are of great interest for application requiring relatively stable emulsifier [3]. Alkanolamides have a broad spectrum of uses such as in shampoos, detergents, cosmetics, lubricants etc [4].

Thiswork focused on the synthesis and characterization of the diethanolamide from non-traditional oil i.e., custard apple seed oil (*Annona Squamosa L.)* by heating at 100^{O}C, 120^{O}C and 150^{O}C. The physico chemical analysis of the custard apple seed oil is also studied.

2. Materials and methods Materials

Fruits of Custard apple seed (*Annona Squamosa L.*) not damaged when chosen and procured from the local market and stored under cool dry storage conditions.The outer dried surrounding pith of the fruit was removedand the seeds were air-dried in an oven at 40 ^{0}C to reach constant moisture content (6.5%). The dried seeds were cracked manually, the shells carefully removed and the kernels thus obtained were crushed and ground in agrinding mill, theground kernels with particle size of 0.5 mm were used foroil extraction. The kernels obtained were stored until further investigations.
All solvents used were of analytical grade. Petroleum ether, n-heptane, ethanol and diethyl ether, carbon tetrachloride, HCL, NaOH, H2SO4, NaOH, and KOH were obtained from S.D. Fine Company and Qualigen Company, Mumbai.

2.1 Methods

The approximate analysis of seedwere analyzed for moisture content, crude protein, crude fiber, ash content and yield of oil content was

determinedaccording to the AOCS official method [5, 6].The physico chemical analysis of custard apple seed oils were carried out for moisture content, specific gravity, refractive index, acid value, saponification value, iodine value, peroxide value, unsaponifiable matter, flash point, fire point byusing AOCS official methods [7].

2.2 Extraction of oil by Soxhlet apparatus

The oils from the seeds were extracted exhaustively with analytical grade solvent ether (b.pt. 60-80) in soxhlet extractors according to theAOCS official method [8]. The oils obtained by Soxhlet extraction from custard apple seed (Annona Squamosa L.) (CASO) was then kept in dark bottles and stored at cool place forfurther analysis.

2.3 Preparation of fatty acid and methyl ester

The mixed fatty acid was prepared by saponification and breaking the soap with 1: 1 sulphuric acids. The mixed fatty acids were dried and analyzed for acid value, iodine value and saponification value and unsaponifiable matter as per AOCS [9].Fatty acid composition was determined by preparing methyl ester of fatty acid, by using measured amount of boron tri fluoride-methanol solution (BF3-125gms /liter of methanol) which was then subjected to gas chromatography.

2.4 Preparation of methyl ester

The ester sample was injected into Gas Chromatography (Model GC-14 of Shimadzu, Singapore). Packed Column was used, its film thickness was 0.31µm, and Column length was 2 meter. The temperature was from 160O C heated to 250 O C (1.5Oc/min) ; injector 250 O C, detector 270 ^{O} C; carrier gas 4.0ml/min hydrogen; 6ml/min air and 4 ml/min nitrogen; manual injection volume < 1 µl. The peak area was computed by integration software of packed column and percentage of fatty acid methyl esters were obtained as weight percent by direct internal normalization [10].

2.5 Preparation of Diethanolamides

Diethanolamide were prepared by reacting mixed fatty with diethanolamine in the ratio of (1:2 w/w) in a three necked flask equipped with an agitator and thermometer, maintaining temperature at 100 OC, 120 OC and 150 OC for 7 hours. The reduction acid value was considered to be the progress of reaction. The diethanolamide so prepared were tested in standard detergent solution (0.1% w/w) for change in foam height and foam stabilization by Ross miles6 method and yield of amide percentage at different reaction time on the basis of nitrogen content.

3. Result and Discussion

The proximate analysis of custard apple seed, physicochemical analysis of custard apple Seed Oil (CASO) and mixed fatty acids is reported in table no. 1 and 2.

Table No.1 shows that moisture and volatile matter, Crude Protein, and ash content was found to be low and crude fiber.

Table No. 1 Proximate analysis of Custard apple seed

Sr.No.	Particulars	Obtained values[a]	Reported Values	
			Ref no.[11]	Ref no.[12]
1	Moisture and Volatile matter(%)	6.4±0.3	6.7±0.2	7.7
2	Crude Protein (%)	15.9±0.5	17.5±0. 2	8.5
3	Crude Fiber(%)	17.6±0.2	16.8± 0.2	5.2
4	Ash Content (%)	1.77±0.2	2.2±0.2	9.7
5	Oil Content (%)	28.03±0.5	27.8±0.4	40.0*

(17.6%) and oil content (28.03%) was found to be more as compared to A.A. Mariod et.al

[11] in Annona Squamosa but these values were more than, the Annona Muricata reported by A. Kimbonguila, et. al [12]. From the literature survey it was observed that the oil content in custard apple seeds 23 to 28%, this value is nearer to determined value.

* Oil extracted with ether.a Values are mean± S.D of triplicate determinations

a Values are means ±S.D of triplicate determinations

Table No. 2 Physiochemical Characteristics of Custard apple seed oil

Se No.	Particulars	Results Obtained		Reported Values for crude oil	
		Crude oil	Mixed fatty acids	Ref no.[11]	Ref no.[12]
1	Moisture, (Volatile matter) %	0.66	0.90	NR	NR
2	Color	Pale yellow	Dark Reddish	Brown	Brown
3	Acid Value (mg of KOH/gm oil)	2.49	181.93	1.54±0.1	0.326
4	Iodine Value (wiji's)	89.88	90.31	NR	138
5	Saponification Value	193.91	192.7	184.5±0.11	195
6	Unsaponifiable Matter %	1.34	1.08	NR	1.62
7	Peroxide Value (m.eq. O_2/Kg of oil)	0.83	--	0.9±0.1	NR
8	Flash point ^{0}C	>160	--	NR	316
10	Refractive Index at 30 ^{0}C	1.4660	--	1.470±0.005	NR
11	Sp-gravity at 30^0 C	0.8519	--	0.816±0.001	NR
12	Oil content (%) /Yield %	28.03	92.4	27.5 ±0.1	NR

The fatty acid composition of custard apple seeds oil used in the present study and the composition of the custard apple seeds oil (Annona Squamosa L.) reported in the literature are given in Table-3. It also depicts the fatty acid compositions in Annona Squamosa seed oil. Major fatty acid in oil sample were oleic (C18:1) 50.79%, linoleic (C18:2) 25.48%, palmitic (C16) 15.77%, stearic (C18) 7.96%. Oleic/linoleic ratio of Annona Squamosa was 1.99 as compared to 2.2,1.97reported by [11] and [1] respectively and 1.35 was reported by species Annona Muricata[12].

Table No 3 Fatty acid composition of Custard apple seeds oil (*Annona Squamosa L.*)

Se. No.	Name of Fatty acids	Formula	Structure	Weight %	Reported Values		
1	Saturated Fatty acids				Ref[11](a)	Ref[1] (a)	Ref[12](b)
	(a)Lauric acid	$C_{10}H_{32}O_2$	10.0	ND	0.2 ±0.1	0.2533	ND
	(b) Myristic acid	$C_{14}H_{32}O_2$	14.0	ND	0.6 ±0.3	0.0327	ND
	Palmitic acid	$C_{16}H_{32}O_2$	16:0	15.772	15.2 ± 0.5	16.247	20.33±1.34
	Stearic Acid	$C_{18}H_{36}O_2$	18:0	7.964	9.3 ± 0.4	10.306	4.22±0.18
2	Unsaturated Fatty acids						
	Oleic acid	$C_{18}H_{34}O_2$	18:1	50.795	50.5 ± 1.2	47.902	41.41±0.20
	Linoleic acid	$C_{18}H_{32}O_2$	18:2	25.489	22.7 ± 0.6	24.314	30.60±0.18
	Linolenic acid	$C_{18}H_{30}O_2$	18:3	ND	ND	0.826	2.13
	Arachidic acid	$C_{20}H_{40}O_2$	20:0	ND	1.3 ±0.1	ND	ND
	Unsaturated Fatty acids			76.2	73.2	72.216	73.14
	Oleic/Linoleic Ratio			1.99	2.2	1.970	1.35

Table- 4: Analysis of Acid value, Nitrogen content and Amide content.

Se.No.	Time in minutes	Acid value			Nitrogen Content in %			Amide %		
		100 ^{O}C	120^{O}C	150^{O}C	100 ^{O}C	120^{O}C	150^{O}C	100 ^{O}C	120^{O}C	150^{O}C
1	0	63.8	63.8	63.8	1.4	1.4	1.4	9.99	9.99	9.99
2	60	59.2	55.3	50.1	3.2	4.6	6.6	22.85	32.84	47.12
3	180	52.7	43.5	30.7	5.9	7.3	8.5	42.13	52.12	60.70
4	300	46.9	33.2	18.5	7.7	8.8	10.3	54.98	62.83	73,52
5	420	39.8	20.3	10.5	8.9	10.2	12.3	63.55	72.83	87.82

a) Variety Annona Squamosa.
b) Variety Annona Muricata

Table no. 4 shows decrease in acid value and increase in nitrogen content as reaction proceeds at 100 OC, 120 OC, 150 OC, temperature and ultimately yield of amide content. Acid value reduces to 10.5 while nitrogen content and amide content increases to 12.3% and 87.82% at 150 OC at 7th hour's sample.

Table no.5 shows the actual foam height of (Surf Excel) commercial detergent.

Table No. 5 Foam height of Commercial detergents powder used

Se. No.	Name of commercial Powder	Colour	Foam Height in (mm)	
			Initial	After5 Minutes
1	Surf Excel	White	118	111
2			120	111
Average			119	111

- Name of commercial Powder : Surf Excel
- Percentage of Diethanolamide added : 0.1%
- Reaction Time : 7 Hours

Table No. 6 Foam boosting and stabilizing properties of diethanolamides

Se. No.	Reaction Temperature in ^{O}C	Foam Height of Standard detergent solution + 0.1% Diethanolamide in (mm.)		Foam height of standard detergent solution in (mm)		Percentage increase in foam height	
		Initial	After 5 Minutes	Initial	After 5 Minutes	Initial	After 5 Minutes
1	100	121	113	119	111	1.68	1.80
2	120	127	116	119	111	6.72	4.50
3	150	129	123	119	111	8.40	7.20

Table no. 6 depicts the foam heights of the diethanolamides with standard detergent solution only immediately and after 5 minutes is reported. The maximum foam height (129mm) is obtained for the prepared diethanolamide at 150 OC and 7th hours sample; it shows an increase of 8.40%in immediate foam and 7.20% after 5 minutes in comparison with foam height (119mm) obtained from standard detergent solution.

4. Conclusion

Custard apple seeds oil (Annona Squamosa L.), non-traditional oil contains Oleic acid and Linoleic acid as the principle fatty acids and the proportion of unsaturated fatty acids is greater than the saturated fatty acids. The amide content of alkanolamide synthesized increases with time and temperature during reactions. The diethanolamide were synthesized at moderate conditions with high percentage of conversion of amide content. These amides are found to be nonirritant to the skin, and can be used in various detergent formulations. Surfactants have good commercial potential because they are obtained from cheap raw materials and do not required costly fats or pure fatty acids for their manufacture and in demand for other value added applications.

5. References

[1] D. C. Sikdar. “Physico-Chemical Properties of Oil Extracted from Custard Apple Seeds”. Chemical Engineering World, Biocides, November [2010] pp. 89 -91.

[2] Bilyk A, Bestine R.G, Piazz G.J, Feairheller, S.H. and Hass, M.J “A novel technique for the preparation of secondary fatty amide”. J. of Amer. Oil Chem. Soc; Vol. 69, pp. 488-491 (1992),

[3] Muargord, T, Remaud- Simeon, M, Petre, D and Monsan,P “Enzymatic synthesis of glycamide, surfactant by amidation reaction”, Tetrahedron Elsevier volume 53, (14), pp.5184-5194 (1997).

[4] KuanJu Liu, Ahindra Nag, and Jei- Fu Shaw, “Lipase- catalyzed synthesis of fatty acid diethanolamide”,J. Agric. Food Chem. 49(12), pp. 5761-5764(2001).

[5] Association of Official Analytical Chemists-AOACOfficial Methods of Analysis, 15th edn. Washington, DC, USA, (1990).

[6] Official methods &recommended practices of the American Oil Chemists Society, AOCS, 4th edn, IL Official Method Ba 84, reapproved (2006).

[7] Official methods and recommended practice of the American oil chemists society, AOCS In (ed), 4th edition, Champaign, IL Official Method To la-64, reapproved (2006).

[8] Official methods & recommended practices of the American Oil Chemists Society, AOCS, 4th edn. Champaign, IL Official Method Ai 3 75, reapproved (2006).

[9] Indian Standard Methods of supply and Test for Oils and Fats..ISI: 548(Part-I)(1964)

[10] Christie, W.W., “Preparation of ester derivatives of fatty acids for chromatographic Analysis”.Advance in Lipid Methodology –Two pp 69-111 (1993)

[11] Abdalbasit Adam Mariod, Yousif Mohamed Ahmed, “Annona squamosa and Catunaregam nilotica Seeds, the Effect of the Extraction Method on the Oil Composition”, J Am Oil Chem. Soc.Vol.87.pp. 763–769 (2010)

[12] A. Kimbonguila, J.M. Nzikou, L. Matos, B. Loumouamou, C.B. Ndangui, N.P.G. Pambou-Tobi, A.A. Abena, Th. Silou, J. Scher and 4S. Desobry,“Proximate Composition and Physico chemical properties on the Seeds and Oil ofAnnona Muricata grown in Congo- Brazza ville”, Research Journal of Environmental and Earth Sciences, Vol. 2(1) pp.13-18 (2010).

.