

Coconut Oil Based Low Temperature Liquid Hair Oil Formulations with Ester Modification

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Abstract

We have reported in this research work for coconut oil based low temperature hair oil formulations using coconut oil's glycerolysis, glycolysis & trans esterification reactions with Glycerol, Glycol, Ethanol & Butanol and methanol and interesterified the coconut oil & its Ethyl alcohol esters also. The Glycerol & Poly Ethylene Glycol (Molecular Weight 180-210) was used to esterify the Coconut Oil in this work using chemical & enzyme catalyst. The ethyl esters & butyl esters gave 0 & -5°C solidification points respectively using *versa transform 2.0* enzyme of *Novozymes* make at 0.4% doses per *Novozymes* protocol. In the Inter-esterification experiments between coconut oil and ethyl esters of coconut oil, the same enzyme was used. The glycerol & coconut oil enzymatically produced have 6° solidification point (S.P.) (table 2). Glycol monoesters of 60°C solidification point (S.P.) was obtained by chemical interesterification using 0.25% *Noah* at 130-140 °C in 2-3 hours (730 mm vacuum) & its product was enzymatically interesterified with ethyl esters of 3°C S.P. to prepare modified esters of 4 °C S.P.. Ethyl esters of 3°C yielded on interesterification with enzymatically produced glycerol esters of 6°C S.P. a 3.5°C S.P. product. Butanol & methanol esters prepared enzymatically were of low S.P. By chemical method for glycerol esters S.P. was high.

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I. INTRODUCTION:

About 66% of the Indian hair oil market is supplying coconut oil as a base oil in hair oil formulations apart from other hair care products and cosmetics and growth shall be 14% per annum proved true [1]. For winter season most of the popular manufacturers are blending cosmetic grade light liquid paraffin, the mineral refined oil from about 70-90% extent [2]. Awareness of the manufacturers led them to supply the people coconut oil and sesame oil blends with some bio active materials obtained from natural essential oils for more benefits [3,4]. Our objective was to make CCNO or its derivative to be in majority in the hair oil formulations, to remain them liquid in winter and using mono unsaturated fatty acid

based oil also if need be by inter esterification without blending the mineral oil [3,4,5]. The need of this research was motivated due to difficulty of coconut vegetable oil application in winter because of its solidification at about 20 degree °C and melting point of about 26 °C (table 1). The coconut oil being nature's gift with low & medium carbon straight chain fatty acids in majority has maximum penetration in hairs and scalp for their protection of hair follicles from some surfactant's damage as used in shampoo (low molecular weight which can penetrate easily in to the hair structure) [4,5]. When compared the coconut oil was found to be the better than sunflower oil & mineral oil in that order for hair nourishment and protection by penetration due to

its chemical structure (4). Recently a prominent Ayurvedic co. [15] marketed 20% coconut oil, 75% sesame oil & essential oil extract in hair oil formulation; some others are also marketing hair oil formulations without mineral oil.

II. Materials & Methods:

The characteristics of the oils used are as per Table 1 of Kamani Oils, Mumbai, chemicals of analytical grade reagents make of E Merck India, Filter paper of Whatmann 42 no., G E healthcare U.K. were purchased from local Kanpur Market, Eversa Transform Lipase liquid enzyme 2.0 of Novozymes was a gift (Table 2) The apparatus of 4 neck round bottom flask with stirrer, temperature Pocket & sample/ stop cock make Borosil India, condenser, lab vacuum pump make S. Lite, Delhi through catch pot connection was assembled.

Coconut oil & Glycerol the monoglycerides and were first prepared as suggested by [10,11] using the chemical catalyst. The reactions were carried out using the chemical catalyst NaOH (quantity being 0.20% plus that required to neutralize free fatty acids present in coconut oil) at the elevated temperature of 160- 180^o C for 3 hours with 100 gram of oil and 50 gram and even more of Glycerol as suggested & under suitable vacuum, so that the glycerine should not distil in place of nitrogen inert atmosphere [12]. And Glycerol and coconut oil was interesterified using 1% Zinc oxide catalyst at 130-140^o C in 2 hour gave 20^o S.P., at 675 mm vacuum, at 160^o C & 500 MM vacuum 18^o C, S.P. while glycerine was more than 50% excess as recommended also [14].

Glycerol, Ethyl esters and butyl esters of Coconut oil were also prepared by enzymatic method as per protocol of Novozymes [10]. The conditions were: Enzyme Eversa transform 2.0 of Novozymes, dose 0.4% at 35-40 ^oC for 24 hours were as per supplier's recommendations. The solidification after removal of catalyst and glycerine by gravity and excess of ethanol and Butanol by distillation and hot water washing and drying and yielded product with 0^o C and 2^o C solidification point respectively. The viscosity, density and colour of the product was also measured and is shown in the table no. 4.

Methods used for chemical inter esterification adopted as per Laning (1985), conditions [8] are given in tables no. [2-5] and slightly modified for Trans esterification experiments the Coconut oil was mixed at 60^o C with 6 moles Methanol and 0.30% sodium methoxide using condenser for 3 hours [6,7,8]. The products was neutralized with 0.30% phosphoric acid/ Citric acid (stoichiometrically) & settled to remove glycerol by draining. Then the product was hot water washed, dried under vacuum to 120^o C & cooled to 60^o C.

After obtaining glycol esters of 6^oC, S.P. by chemical method of esterification and Glycerol esters of 6^oC by enzyme method. They were used to interesterification with ethyl esters using the same condition of enzyme method of esterification and the results noted in (table 2).

Following are the characteristics of the coconut oil used in the study.

Table 1: Physical and chemical Characteristics of feed oils

Oils	Free fatty acid	Iodine value.	Saponificat value	Hydroxy value	Melting Point	Solidification point	Fatty Acid Composition
CCNO	1.0	9.7	263	-	25.6	22.0	C6:0-0.2, C8:0-7.0, C10:0-6.3, C12:0-47.9, C14:0-18.2, C16:0-8, C18:0-2.40, C18:1-7.50, C18:2-2.0

III. RESULTS & DISCUSSION:

There is enzyme interest reification process which is simple and economic, It was decided to go for Enzyme interesterification also.

From Coconut oil & Glycerol the monoglycerides were first prepared as suggested by (11, 12) using the chemical catalyst. The reactions was carried out using the chemical catalyst NaOH (quantity being 0.20% plus that required to neutralize free fatty acids present in coconut oil) at the elevated temperature of 160- 180⁰ C for 3 hours with 100 gram of oil and 50 gram of Glycerol or more under suitable vacuum (so that the glycerine should not distil) (12), 14⁰C S.P. Glycerol ester was obtained.

Glycerol and coconut oil was also interesterified using 1% Zinc oxide catalyst at 130-140⁰ C in 2 hour gave 20⁰ S.P., at 675 mm vacuum, at 160⁰ C & 500 MM vacuum 18⁰ C, S.P. while glycerine was more than 50% excess as recommended (11,12). NaOH catalyst at 160-180⁰C and 500 mm Hg vacuum delivered 14⁰ C, S.P. Thus temperature plays an important role. The vacuum has to use optimally not to let glycerol distill. Higher temperature may be tried under nitrogen atmosphere but conditions are not moderate but desired S.P. is not expected by raising the temperature even to 200⁰ C.

The reaction was also carried out at the elevated temperature of 130-140 for 2 hours with 100 gram of oil and 50 gram of Glycol under optimum vacuum (12) so that glycol should not distil and the product 6⁰C S.P. was reported (table 2). The transesterification of Glycol and Coconut oil which gave 6⁰C solidification point was also interesterified with Interesterified EE CCNO + CCNO (50:50) of 4⁰C S.P. in ratio of (47%:53%) and 3.5⁰ C solidification point was found (table 2).

Thus the CCNO was subjected to Glycerolysis with 10% excess stoichiometric proportion of Glycerol with Coconut oil and 0.40% enzyme catalyst Ever transform 2.0, Novozyme make at 37 to 40⁰C temperature for 24 hours. The product was separated from the catalyst and excess glycerol by gravity settling and draining thereafter. Oil was heated to 60⁰ C, hot water washed & dried under vacuum at 120 C & cooling to 60⁰ C. The products solidification point, % monoglycerides & diglycerides was tested. As evident from the table no. 2 the solidification point was 6⁰C. Mono, di & triglyceries, Free fatty acids were tested by GLC (Table 3)

Glycerol. Ethyl esters and butyl esters of Coconut oil were also prepared by enzymatic method. The conditions were: Enzyme ever transforms 2.0 of Novozyme, Denmark, dose 0.4% at 35-40 C for 12-18 hours. After removal of catalyst and glycerine by gravity and excess of ethanol and Butanol by distillation and hot water washing and drying and yielded product with 0⁰ C and 2 degree C solidification point respectively as per Novozyme's protocol (10) & their S.P. tested and noted in table 2). Based on their S.P., the Ethyl esters was interesterified with the same enzyme and with (coconut and glycerol), (coconut oil and poly ethylene glycol) blend's esters and result are noted (table 2)

TABLE NO. 2. Solidification points after interestification of CCNO and alcohols at different operating parameters.

S.No	CCNO(gm)	Alcohols (gm)	S.P IE Blends (°C)	Catalyst (wt %)	Temperature (°C)/vacuum	Time (Hrs)
1)	100	Glycerol (50) (3.5 moles)	14	NaOH (0.3%)	160-180, 500 mm Hg	3

					vac.	
2)	100	Glycerol (93) (6.5 moles)	20	zinc oxide (1.0%)	130-140°C (700 mm Hg)	2
3)	100	Glycerol (50),(3.5 moles)	18	zinc oxide (10%)	160(500 mm Hg)	2
4)	100	Glycerol (50)(180% excess)	6	E.T Enzyme (0.5%)	38-40	24
5)	100	PEG (63)	6	NaOH (0.25%)	130-140(730 mm Hg)	2
6)	100	Ethanol (25)	0	E.T Enzyme (0.5%)	38-40	24
7)	100	Ethanol (25)	-5	E.T Enzyme (0.5%)	38-40	24
8)	100	Ethanol (25)	2	E.T Enzyme (0.5%)	38-40	24
9)	100	Butanol (66)	-5	E.T Enzyme (0.5%)	38-40	24
10)	100	Butanol (25)	4.5	E.T Enzyme (0.5%)	38-40	24
11)	50	EECCNO (50)	3	E.T Enzyme (0.5%)	38-40	24
12)	CCNO & Glycerol(1 : 3.5 mole) (80), S.P. 6°C	EECCNO + CCNO, (1:1), (20), S.P. 3°C	4	E.T Enzyme (0.5%)	38-40	24
13)	CCNO+ PEG (1.6 : 1)(47 gm), S.P. 6°C	EE CCNO + CCNO (1:1) 53 gm, S.P. 3°C	3.5	E.T Enzyme (0.5%)	38-40	24
14)	100	29 methanol	2	E.T Enzyme (0.5%)	38-40	24

Table 4 : Coconut based low temperature hair oil formulations physical analysis continued :

S.no	Details of product	Viscosity at 30°C	Density at 30°C	LovibondColor in 1" Cell
1	GLYCEROLYSIS OF GLYCEROL +MECCNO	132.8 at 32°C	0.8788 at 30°C	1.6Y,0.3R
2	MECCNO	3.82 at 34°C	0.8795 at 32°C	1Y,0.3R

3	EE-CCNO	6.1 at 30 ⁰ C	0.8728 at 30 ⁰ C	1.6Y,0.3R
4	CASTOR OIL (CO)	434.2 at 33 ⁰ C	0.965 at 33 ⁰ C	3Y, 0.4R
5	COCONUT OIL (CCNO)	55.1 at 33 ⁰ C	0.9196 at 33 ⁰ C	2Y, 0.3R
6	BE CCNO	9.25 at 32 ^o C	0.88 at 36 ^o C	1.5Y,0.3R
7	50CCNO+50EECCNO	22.2 at 36 ^o C	0.896 at 33 ⁰ C	1Y.0.3R
8	KeshKanti Sesame Oil & CCNO based	47.355 at 32 ⁰ C	0.883 at 32 ⁰ C	Greenish tins
9	64% BECCNO+36%CCNO	16.45 at 20 ^o C	0.912 at 20 ⁰ C	1.2Y, 0.3R

IV. Conclusion :

Alcohol esters gave encouraging results in terms of Solidification Point. Glycerol Chemical esterification requires stringent reaction conditions but captioned enzymatic method is satisfactory. Glycol esterification by chemical and enzymatic both methods are satisfactory. Ethyl esters on above enzyme interesterification also gave desired result.

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