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Coconut Oil Based Low Temperature Liquid Hair Oil Formulations with BUTYL Ester and ETHYL Ester Modifications

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Abstract
Coconut oil based low temperature liquid hair oil formulations have been developed with Coconut oil's ethyl ester and butyl ester modifications. Ethyl alcohol and butyl alcohols were used for trans-esterification of the Coconut Oil using sodium methoxide chemical and Eversa Transform 2.0 Lipase enzyme catalysts. The sodium methoxide catalyst used was 0.4% for interesterification of the ethyl and butyl esters with coconut oil at115ºc for 1 hours. The Ethyl Esters (E.E.) obtained had 0°C Solidification Point (S.P.) and butyl Esters (B.E.) (-2ºC) S.P. by using chemical catalyst. The enzymatic Method resulted (-2ºC, S.P.) Ethyl Esters and (-5º C, S.P.) Butyl Esters products. The ester-ester interchange reaction of Coconut Oil with E.E. and B.E. yielded the hair oil formulations of the required S.P. of below 5ºC at optimum ratio. The physical properties of the low temperature hair oil formulations were analysed and compared with the market samples of the leading brands of the coconut oil based hair oils for winter use.

Keywords; *Inter esterification or interesterified (I.E.), Ethyl Esters (E.E.), Butyl Esters (B.E.), Solidification point (S.P.), Eversa Transform 2.0 Lipase Liquid Enzyme (E.T.)*

I. INTRODUCTION

Air pollution cause considerable harm to our hairs and scalp. Regular Hair Oil application can protect health of our hairs and scalp by keeping hairs and scalp moisturized. Hair oils also maintains scalp clean. Certain hair oils and especially addition of suitable essential oils keeps fungus away, help consistent hair growth. Hair oils make the hairs healthy and prevent hair loss along with the lubrication of hairs. Coconut oil helps hair lustre and imparts emollient properties and also the glow to skin. Certain hair oils viz. N. Sativa, Hemp Seed, Rice bran, Sesame, Castor, Coconut etc prevent hair loss also (15-20).

Coconut oil is scientifically highly recommended hair oil due to its fatty acid composition and nutraceuticals present. Its low molecular straight chain fatty acids penetrate in to the hairs and scalp maximum in comparison to other available hair oils (2). Babassu oil and palm kernel oil, cohune and cupea oils belong to the coconut oil family and act almost similarly. Coconut oil is most easily able to fill the gap between hair follicles and stops the entrance inside scalp of the low molecular weight surfactants like Sodium lauryl sulphate (SLS), a major foam booster in shampoo if applied as massage oil prior to washing. SLS can dissolve hair proteins and weaken hairs. As such, repetitions for a long time can result in hair fall (3).

The mono unsaturated fatty acids penetrate inside hairs and scalp slower and poly unsaturated fatty acids still slower and preferably after slight heating as compared to saturated and especially low molecular straight chain fatty acids (3). So, the

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monounsaturated fatty acid predominant oils are the next choice for hair care applications.

Oxidation or rancidity problem in oils depend on their fatty acids and increases as their unsaturation increases. The lower molecular weight fatty acids present in coconut oil have lower solidification point near 21 degree Celsius. During winters it gets solidified hence applying on the head becomes difficult. Most of the Hair Oil manufacturers have resorted to the blending of light liquid paraffin oil of cosmetic grade, a mineral oil in majority proportions to keep the coconut oil liquid in winters (1). This leads to lowering the efficiency of coconut oil benefits. There are oils containing mono and di or poly unsaturated fatty acids as major fatty acids with good amount of natural antioxidants. The latter prevents oxidation to certain extent; acts as free oxygen radical scavenger & so protect from part of harmful ultraviolet radiations of light (6). So they are also used as hair oils accordingly. The market of Coconut oil based Hair oils was 66% approx as per 2009 estimate and increased by 14% per annum as predicted and re-estimated in 2014 (5).

Thus the modification of the coconut oil is required if we want to use it purely or in combination with other good hair oils. The oil modification can be in the form of fractionation and re-fractionations, fractional distillation of fatty acids and low molecular weight fatty acid's re-esterification with glycerol, dehydrogenation of fatty acids or inter-esterification which includes acidolysis, glycerolysis and ester-ester interchange or trans-esterification(7,8).

II. MATERIALS AND METHODS

Coconut Oil, Chemicals of LR grade, Whatman Filter used were purchased from the market. The Eversa Transform 2.0 Lipase enzyme was provided by Novozymes. The characterization methods of B.I.S. were adopted (9-10).

The trans-esterification reaction was carried out in the 4 neck round bottom flask (Figure no. 1) fitted with stuffing box and stirrer. The other necks have been fitted with thermometer pocket, condenser and plug cork. The Condenser was replaced by the vacuum connection through catch oil to lab vacuum pump. Thermostatically controlled suitable capacity Mantle Heater and RPM regulator, Hot Plate, Air oven, Refrigerator, 3 digit accuracy weighing scale, Titre Test Apparatus as per IUPAC method along with other characterization apparatus, suitable G.L.C. model of make Varian was also used .

Butyl and Ethyl esters were prepared by chemical process using industrial practice and as suggested by D. Rousseu and slightly modified (12) from mixing coconut oil & 85-100% excess methanol (by weight) using alkali 0.50% NaOH or 0.4% sodium methoxide as catalyst at 60°C at 90 RPM for 3 h in 4 neck flask.

The product after reaction is neutralized with phosphoric acid, settled to drain glycerine, methanol is recovered by distillation. Product at 600 C was washed with hot distilled water and vacuum dried.

Enzymatic process of Trans-esterification using oil and alcohol was done as per protocol of Novozymes using Eversa Transform 2.0 Lipase Liquid Enzyme of Novozymes. Temperature condition of 35-400C at 0.30-0.40% dose at 90 RPM were used (13). The Butyl & Ethyl esters of Coconut (EECCNO & BECCNO) were prepared by Chemical and Enzyme interesterification method as per reactions conditions and analysis mentioned in Table no. 2. The BECCNO & EECCNO were ester ester interchanged with Coconut oil in optimum ratio using Sodium Methoxide Catalyst at 115°C under Vacuum and 1.0 hour reaction time. The reaction conditions and results of analysis are shown in the table no. 3 and table no. 4.

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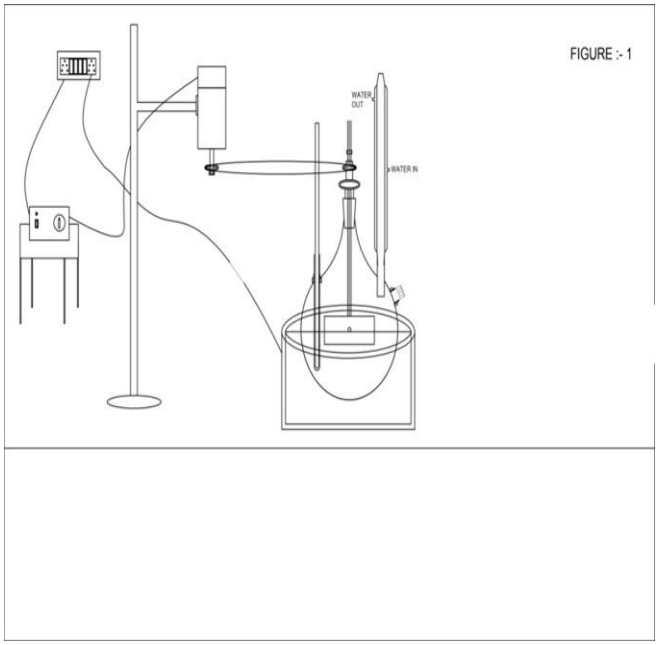

Experimental setup for interesterification

The oils used had physico-chemical analysis as per standard analysis methods as per (Table 1)

Table 1: Physical and chemical Characteristics of feed oils -

Oil	Free fatty	Ioc val	Sapon n value	Hydr valu	Mel Poi	Solid n point	Fatty Acid Compositi
CC	1.0	9.7	263	-	25.6	22.0	C6:0-0.2, C8:0-7.0, 6.3, C12:0-47.9, C14 C16:0- 8.4, C18:0-2.40, C18:1-7. C18:2-2.0
CO	0.20	87.	174	164	2.0	(-2)	C16:0-1.02, C18 C18:1-3.42, C18:1&12-0H--88.26 4.33, C18:3- 0.53, C20:1-0.40, C22:6- 0

III. RESULTS & DISCUSSIONS

BECCNO were prepared using 6 moles of butyl alcohol with 1 mole of CCNO prepared 0° C and (-5° C) S.P. by Chemical and Enzymatic procedures respectively. The EECCNO by chemical and enzymatic methods were of 1 and (-1°C) respectively.:

Experimental Results Table no. 2: Trans-Esterification of CCNO, Alcohols

CC NO, (g)	Alco hols, (g)	**%Cat alyst**	**Tem p-eratu re**	**Atmosp here** to condense r	RP M	Ti me, h	S.P ., °C
CC NO	BtO H6 mol e	0.5% NaOC H3	60°C	To condense r	90	3	(-1)
100	BtO H, 66	E.T. 2.0 Enz., 0.4%	DO	do	90	24	(-5)
CC NO 1m ole	EE 6 mol e	0.5% NaOC H3	60°C	do	90	3	1
CC NO 1m ole	EE 6 mol e	E.T. 2.0 Enz., 0.4%	60°C	do	90	24	(-1)
100	Et OH, 25g	E.T. 2.0 Enz., 0.4%	DO	do	90	24	0

Experimental Results Table No. 3- Interesterification CCNO and BECCNO:

CCNO (g)%, S.P. 22°C	Butyl Ester%, S.P.(-2°C)	%Cat alyst NaOC H3,	Tem pe-raptu re, °C	Vacu um, mm Hg	RP M	Ti me, h	S.P. ,°C
50	50	0.40	115	755	90	1	4.5
45	55	0.40	115	755	90	1	3.0
40	60	0.40	115	755	90	1	2.0
36	64	0.40	115	755	90	1	1.7

Experimental Results Table No. 4: Ester-Ester Interchange (CCNO and EE)

% CCNO (g), S.P., 22°C	%Ethyl Ester, S.P., (-2°C)	%Cat alyst, NaOC H3	Tem pera-ture °C	Vacuum , mm	Time, h	S. P. °C
50	50	0.40	115	755	1	5. 5
45	55	0.40	115	755	1	4.

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						0
40	60	0.40	115	755	1	3.0

As illustrated in table no. 3, the experiments were processed by varying the ratio of CCNO from 50 to 36% in the intervals of 5%. Accordingly the ratio of BECCNO was increased from 50 to 64% at the 5% intervals. At 45 to 36% CCNO and 55 to 64% proportions of BECCNO, the results of S.P. of hair oil formulation are as desired.

As illustrated in table no. 4, the experiments were processed by varying the ratio of CCNO from 50 to 40% in 5% intervals. So, the ratio of EECCNO were increased from 50 to 60% in the interval of 5%. At 45 to 40% CCNO and 55 to 60% ratio of EECCNO, the results of S.P. of hair oil formulation are as desired.

The butyl ester's and CCNO, ester-ester interchange results is slightly better in regard to S.P. than ethyl ester and CCNO.

The CCNO+EECCNO(50:50), I.E., S.P. 3°C (from 46 to 55%) was ester-ester interchanged with coconut oil (54 to 45%) to increase the coconut oil content and viscosity in the hair oil formulations to obtain 3.7 to 3°C preparation. The ester-ester interchange reaction of the BECCNO and EECCNO products too with (50CCNO+50CO, IE S.P. 11.20 C) was done to get desired S.P. and higher coconut fatty acids in the product and lower the viscosity due to more castor oil. Ethylene glycol ester from enzymatic trans-esterification of coconut oil and ethylene glycol (molecular weight 62) using 1:3.2 mole ratio in 50% weight were ester-ester interchanged with [IE – CCNO+EECCNO(50:50)], S.P.5.5°C- 50% weight to get the desired formulation of low S.P. of 3°C. The viscosities of trans-esterified products were seen and found to be lower. These were also ester-ester interchanged with the coconut and viscosities seen, compared with the market samples of the premium brands for winter use and found as desired. The colours were also seen and are very light. All the results are given in Table no. 6.

Experimental Results Table No. 5: Ester-Ester Interchange (Glycol esters and Ethtyl esters), (CCNO and Ethtyl esters) and (CCNO+CO), Butyl Esters

Composition A	Composition B	%CCNO/ CCNO+ CCNO esters	NaOCH3 Catalyst	Temp. °C	Time, h	S.P., ^{0}C
CCNO-54%	[EECCNO+CCNO (50:50), S.P.3]-46%	100	0.40	115	1	3.7
CCNO-50%	[EECCNO+CCNO (50:50), S.P.3]-50%	100	0.40	115	1	3.3
CCNO-45%	[EECCNO+CCNO (50:50), S.P.3]-55%	100	0.40	115	1	3.0
(50%CCNO+50% CO –IE), 50%, S.P.11.2	(50%CCNO+50% BECCNO –IE), 50%, S.P.5°C	50/75	0.40	115	1	4.0
(50%CCNO+50% CO –IE), 50%, S.P.11.2	(40%CCNO+60% BECCNO –IE), 50%, S.P.2°C	45/75	0.40	115	1	3.1
(50%CCNO+50% CO –IE), 45%, S.P.11.2	(40%CCNO+60% BECCNO –IE), 55%, S.P. 2.0°C	47.5/ 77.5	0.40	115	1	2.7
(Ethylene Glycol+CCNO-3.2:1 mole) IE, S.P.6.0, 50%, enzymatic trans-esterification by eversa transform 2.0 lipase	[IE – CCNO+EECCNO(50:50)], S.P.5.5°C-50%	25/100	0.40	115	1	3.0

Experimental Results Table No. 6:

1	EE-CCNO	6.1 at 30^{0}C	0.8728 at 30^{0}C	1.6Y,0.3R
2	CASTOR OIL (CO)	434.2 at 33^{0}C	0.965 at 33^0 C	2Y,0.34
3	COCONUT OIL (CCNO)	55.1 at 33^0 C	0.9196 at 33^{0}C	1Y,0.3R
4	BE CCNO	9.25 at 32° C	0.88 at 36° C	1.5Y,0.3R
5	60 BECCNO+40CCN0	16.5 at 35° C	0.906 at 33C	1.2,0.3R
6	64% BECCNO+36%CCNO	16.45 at 20°C	0.912 at 20^{0}C	1.2y, 0.3R

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7	50CCNO+50EECCNO	22.2 at 36° C	0.917 at 36°C	1Y.0.3R
8	40CCNO+60EECCNO	16.24 at 36° C	0.892 at 35°C	1Y,0.3R
9	Garnier Ultra Doux; extract of almomd oil, CCNO & Mineral Oil based	38.488 at 32^0C	0.819 at 32^0C	Slightly greenish
10	Kesh Kanti Sesame Oil & CCNO based	47.355 at 32^0C	0.883 at 32^0C	Slightly greenish

The viscosity results show that IE CCNO+(MECCNO or EECCNO, BECCNO) is better product than MECCNO or EECCNO or BECCNO. The viscosity values of the market leader's products were determined and compared.

IV. CONCLUSION

The Interesterification of Coconut and Ethyl and Butyl esters have found satisfactory for lowering the solidification point of coconut oil for winter

use. The inter esterified coconut oil and castor oil blend was also modified by interesterification with interesterified blend of coconut oil and butyl esters of suitable proportions resulted in increase in coconut fatty acid proportion as desired in regards to more penetration and decrease in viscosity as desired. Care was taken to use maximum ratio of coconut oil.

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