

Evaluation of Physicochemical Properties of Cow Ghee before and after Hydrogenation

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Abstract: Cow ghee was analyzed for physicochemical characteristics before and after hydrogenation for quality comparison, extension of shelf-life and for improving its palatability, acceptability. Concerning the least amount of catalyst used and least iodine value, hydrogenated cow ghee was prepared at 0.075% w/w catalyst, 0.86 MPa of pressure and 408 K of temperature. The Fourier transform infrared spectroscopy spectra showed the characteristic peak at 966/cm corresponding to *trans* compounds for cow ghee (CG) and hydrogenated cow ghee (HCG) examined. The results indicated the presence of *trans* fatty acids (TFA) in CG and HCG. Increase in specific gravity, melting range and decrease in solidification temperature of HCG indicates that an increase in solid fat content as compared to CG. Increase in acid value, decrease in ester value and saponification value indicates that an increase in free fatty acid content in HCG. Decrease in iodine value of HCG indicates that degree of unsaturation was reduced to a minimal level and conversion of unsaturated fatty acids to saturated fatty acids occurred. Hydroxyl value indicated the presence of hydroxyl group in CG and HCG. No significant increase in heavy metal content and nickel has been observed due to good laboratory practices. Improvement of traditional ghee processing parameters and quality properties are necessary, using good manufacturing practices on unit operation. In addition, proper packaging in containers injected with inert gases such as nitrogen and addition of antioxidants for storage and distribution will be an advantage.

Keywords: Cow ghee, Hydrogenated cow ghee, Iodine value.

Introduction

The word ghee is evolved from Sanskrit word ghruta. Ghee is a common Indian name for clarified butter fat. The origin of ghee making probably lies far beyond recorded history. The word itself stems from the old Sanskrit 'ghr' which means bright or to make bright. When sprinkled on fire, butterfat enhanced its brightness merged with cause. Butterfat was later christened ghruta, which evolved into ghee.

Ghee – Nomenclature

Ghee is known by various names in various languages corresponding to products in which it is contained¹(Table 1).

Preparation of Ghee²

In India, considerable amount of ghee is prepared by housewives at home by traditional methods. Ghee is also produced on cottage and commercial scale.

Ghee may be produced through heat clarification of cream or via conversion into butter, followed by heat desiccation. At home housewives prepare ghee using cream obtained by skimming-off the thin semisolid layer formed at the air liquid interface of milk which is heated above 90°C. When cream in sufficient quantity has been collected, it is mixed with equal amount of quantity of cold water and churned. Granules of butter formed during churning are skimmed off and collected in a suitable container and heat-clarified to obtain ghee.

Traditionally, ghee is produced both on the domestic scale by first converting milk into curd by fermentation process (*Lactobacilli*), churning curd to produce butter and subjecting butter to heat clarification to yield the final product.

Clarification by heat is done either on an open fire or in a steam-jacketed hemispherical kettle. During initial heating of butter, extensive frothing takes place, which must be controlled to avoid losses associated with boil-over. As the moisture evaporates and frothing subsides caramelization of curd particles is noticeable. At this stage frothing completely subsides and emission of moisture bubble also ceases. Heating is discontinued as soon as curd particles attains desired golden yellow or brown colour. The residue is allowed to settle and clarified fat is decanted.

Cow ghee is of special medicinal interest.³⁻¹⁸ Cow ghee is used as hot melt coating agent in the design of sustained release pellets.¹⁹ Fats and oils exhibit certain physical and chemical characteristics for differentiation. Exact procedures have been laid down by many statutory bodies world over. In India, the best known methods are those published by Indian Standard Institution,²⁰ The Indian Council of Agricultural Research²¹ and the Ministry of Food and Agriculture.²²

The determined analytical characteristics are of course reflections of the nature of the constituents which make up the fat. Fats are almost entirely triglycerides of fatty acids. Since glycerol only constitutes about 10%, it is the nature of the fatty acids and the manner of distribution of these acids as glycerol tri-esters which determine the various characteristic exhibited by the whole fat. Ghee is unique among natural fats in that it contains a large proportion of fatty acids and as a consequence, many of its characteristic is quiet distinctive. Hydrogenated oils are manufactured by hydrogenation of vegetable oils, during which a reduction in the unsaturation of oils and an increase in the isomerization at the double bonds take place. The *trans* isomers thus formed affect the physical and chemical properties of the final products as they have higher melting points and greater stability.²³

Physicochemical characteristics are of basic importance for cow ghee before and after hydrogenation which has been evaluated. Of these, melting range, Solidification point, Specific gravity determines the physical characteristics. Acid value determines number of mg of potassium hydroxide required to neutralize the free acids in 1.0 g of the substance. The ester value determines the number of mg of potassium hydroxide required to saponify the esters in 1.0 g of the substance. The hydroxyl value is the number of mg of potassium hydroxide equivalent to hydroxyl content of 1.0 g of the substance. Iodine

value is the number of g of iodine absorbed by 100 g of the substance. The peroxide value is the number that expresses, in milliequivalents of active oxygen, the quantity of peroxide contained in 1000 g of the substance. Saponification value determines the number of mg of potassium hydroxide required to neutralize the free acids and saponify the esters contained in 1.0 g of the substance. The term "Unsaponifiable Matter" in oils or fats refers to those substances that are not saponifiable by alkali hydroxides but are soluble in ordinary fat solvents and to products of saponification that are soluble in such solvents. The anisidine value (AV) is defined as the 100 times the optical density measured in a 1-cm cell of a solution containing the 1 g of the substance to be examined in 100 mL of a mixture of solvents and reagents. Total oxidation value (TOV) is defined by the formula:

$2PV + AV$ in which PV is the peroxide value and AV is the anisidine value

Material and Methods:

All chemicals and reagents used were of analytical grade and were procured. The salt-free butter was purchased from Gourakshan centre, Amravati, India. Double distilled water was used throughout the study. Parr hydrogenator was used to carry out hydrogenation using nickel as a catalyst.

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a rapid analytical technique that measures vibrations of bonds within functional groups. *Trans* absorption region was found to be in the range of 995–937/cm with a peak at 966/cm.²⁴ FTIR spectral studies were carried out using an FTIR spectrometer (Perkin Elmer Spectrum 2000, Norwalk, CT). The samples were smeared onto KBr windows and the spectra were recorded from 400 to 4000/cm.

Laboratory Processed Cow Ghee

The salt-free butter was purchased and processed into ghee using industrial creamery butter method.^{25, 26} Butter was melted at 60°C and transferred into a boiling pan at 90°C to drive off moisture. It was finally clarified at 115°C, allowed to sediment, decanted, filtered and packed for analyses.

Preparation of hydrogenated ghee

The hydrogenation process was carried out in a 2-liter batch agitated reactor with a 4-bladed disk turbine. Hydrogenation reaction is carried out at different temperature, pressure and concentration of catalyst so as to get least the iodine value of hydrogenated cow ghee and meet the specifications of USP30-NF25.²⁷ Concerning the least amount of catalyst used and least iodine value, hydrogenated cow ghee was prepared at

0.075% w/w catalyst, 0.86 MPa of pressure and 408 K of temperature.

0.075% w/w of catalyst, nickel on silica/alumina, was transferred into the reactor and subsequently nitrogen was purged to remove the air inside the reactor. For changing the salt and/or oxide forms of the catalyst to the active metallic form, hydrogen was blown on the catalyst at the flow rate of 100 ml/min at 300°C for 4 hours. After cooling to room temperature, a 500-ml cow's ghee was filled and heated to 408 K desired temperature. When achieving a certain temperature, the reactor was pressurized to get 0.86 MPa of pressure with hydrogen and the agitator was operated at the rotational speed of 500 rpm. Hydrogenated cow ghee was cooled to 80°C and the catalyst was removed by vacuum filtration. The products were kept hermetically in the amber glass bottles at room temperature.

The physicochemical properties of Cow Ghee before and after hydrogenation includes melting point, heavy metals, , specific gravity, acid value, ester value, hydroxyl value, iodine value, peroxide value, anisidine value, saponification value, unsaponifiable matter, solidification temperature, TOV were determined by the standard methods described in USP30-NF25.²⁷

Statistical Analysis

The *t*-test was performed on all the collected mean data obtained from physicochemical evaluation.²⁸ Significance was accepted at $p \leq 0.05$.

Results and Discussion:

The FTIR Spectra

The FTIR spectra of the CG and HCG showed a distinct absorption peak at 966/cm (Fig. 1), which is a characteristic of *trans* compounds.²⁹ This indicated the presence of TFA in CG and HCG. Physicochemical Parameters of CG and HCG (Table 2) showed that increase in specific gravity, melting range and decrease in solidification temperature of HCG indicates that an increase in solid fat content as compared to CG. Increase in acid value, decrease in ester value and saponification value indicates that an increase in free fatty acid content in HCG. Decrease in iodine value of HCG indicates that degree of unsaturation was reduced to a minimal level and conversion of unsaturated fatty to saturated fatty acids occurred. Hydroxyl value indicated the presence of hydroxyl group in CG and HCG. No significant increase in heavy metal content and nickel has been observed due to good laboratory practices.

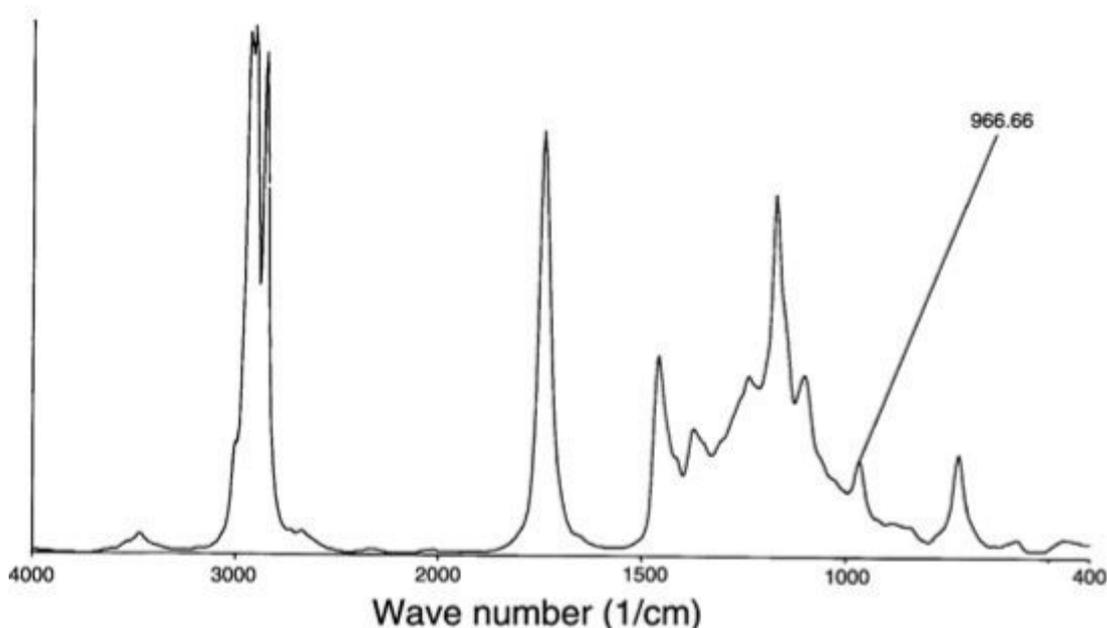


FIG. 1 FTIR SPECTRUM OF HCG INDICATING THE PEAK FOR *TRANS*-FATTY ACIDS

Table 1 Names of Ghee in Various Languages and Societies

Languages	Name
Sanskrit	Ghruta
Hindi and North India	Ghee
South Indian	Neyi, nai
Arabic	Samna, semna, samn
Persian	Roghan
Spanish	Mantequilla fundida
English	Butteroil, butterfat, clarified butter, dehydrated butter, dry butterfat
French	Beurre fondu, graisse de beurre
German	Butteroeel, butterschamelz, floess butter
Italian	Buro fuso, burro cotto, burro colato

Table 2 Physicochemical Parameters of CG and HCG

Sr.No.	Physicochemical Parameters	CG (Mean \pm S.D.)	HCG (Mean \pm S.D.)
1	Specific gravity* (g/cc)	0.9390 \pm 0.0007	1.1230 \pm 0.0005
2	Melting range ($^{\circ}$ C)	37.2-37.4	41.8-44.2
3	Acid value*	0.374 \pm 0.02	0.482 \pm 0.02
4	Ester value*	224.126 \pm 0.03	223.918 \pm 0.03
5	Hydroxyl value	16.436 \pm 0.16	16.430 \pm 0.13
6	Iodine value*	36.72 \pm 0.217	3.46 \pm 0.114
7	Peroxide value*	8.1 \pm 0.245	10.22 \pm 0.286
8	Saponification value	224.5 \pm 0.14	224.4 \pm 0.14
9	Unsaponifiable Matter* (%)	0.9232 \pm 0.0037	0.9872 \pm 0.0070
10	Solidification temperature ($^{\circ}$ C)	21.0-22.2	16.2-18.4
11	Anisidine value*	10.14 \pm 0.167	17.24 \pm 0.261
12	Heavy metals* (%)	0.0006 \pm 0.0001	0.0008 \pm 0.0001
13	Limit of nickel(μ g/g)	>0.1	>0.1
14	TOV*	26.34 \pm 0.59	37.68 \pm 0.81

All the determinations are carried out five times. *Indicates the significance ($p \leq 0.05$)

Conclusion

According to this study, the use of good manufacturing practices on unit operations is important.

Processing of good quality industrial Cow ghee requires facilities such as a separator, pasteurizer, butter churn, a ghee pot and efficient filters.^{25,26} Proper packaging material is another very important item required for storage and distribution and to prevent tempering and contamination.^{25,26} Usually lacquered tins or cans and Polyvinyl Chloride (PVC) containers are ideal to prevent permeability, oxidation, rancidity and tempering.³⁰⁻³² Introduction of anti-oxidants and inert gases such as nitrogen injected into the container before packaging to create an air-tight lid may prevent air induced oxidation and may therefore improve the products quality. Concerning the least amount of catalyst used and least iodine value, hydrogenated cow

ghee was prepared at 0.075% w/w catalyst, 0.86 MPa of pressure and 408 K of temperature. From the safety point of view, it is necessary to evaluate the physicochemical parameters of cow ghee before and after hydrogenation. From observed evaluation of physicochemical parameters, CG and HCG could be safely and routinely used for nutritional and medicinal formulations

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References

- International Dairy Federation, International Standard 1958.
- Aneja, R.P., Mathur, B.N., Chandan, R.C., Baneya, A.K., Technology of Indian Milk Products, A Dairy India Publication Sachi, p.184 (2004).
- The Ayurvedic Encyclopedia, Natural Secrets to Healing, Prevention and Longevity, Swami Sada Shiva Tirtha, Ayurveda Holistic Center Press, NY, USA, p. 145 (2005).
- Sabine, D. Nature, 199, p. 811 (1963).
- Mishra, L.C., Scientific Basis for Ayurvedic Therapies, CRC Press, Boca Raton, p. 45 (2004).
- Singh, K.P., Singh, R.H., J. Res. Ayurveda Siddha, 6, p. 132 (1985).
- Serhan, C.N., Chiang, N. Rheum. Dis. Clin. North Am., 30, p. 69 (2004).
- Kyriakis, J.M., Avruch, J. Physiol. Rev., 81, p.807 (2001).
- Fulzele, S.V., Satturwar, P.M., Joshi, S.B., Dorle, A.K., Indian Drugs, 39(1), p. 42 (2002).
- Achliya, G.S., Wadodkar, S.G., Dorle, A.K., Indian J. Pharmacol., 37(1), p. 33 (2005).
- Achliya, G.S., Wadodkar, S.G., Dorle, A.K., J. Ethnopharmacol., 94 (1), p. 77 (2004).
- Achliya, G.S., Wadodkar, S.G., Dorle, A.K., Indian J. Exp. Biol., p. 499 (2004).
- Achliya, G.S., Barabde, U., Wadodkar, S.G., Dorle, A.K., Indian J. Pharmacol., 36(3), p. 159 (2004).
- Shahani S., Indian Drugs, 36, p. 628 (1999).
- Achliya, G.S., Wadodkar, S.G., Dorle, A.K., J. Ethnopharmacol., 90, p. 229 (2004).
- Achliya, G.S., Kotgale, N.R., Wadodkar, S.G., Dorle, A.K., Indian J. Pharmacol., 35, p. 308 (2003).
- Achliya, G.S., Wadodkar, S.G., Dorle, A.K., Indian J. Pharm. Sci., p. 252, March-April (2004).
- Satturwar, P.M., Fulzele, S.V., Joshi, S.B., Dorle, A.K., Indian Journal of Experimental Biology, 41, p. 1447-1451, (2003).
- Sakarkar D. M., Jaiswal S.B., Dorle A. K., Deshmukh V.N., International Journal of PharmTech Research, Vol.1, No.4, p. 1167-1172, (2009)
- Indian standard methods of samples and terttor oils and fats: IS 548: Indian Standard Institution New Delhi, (1963).
- Indian Council Agricultural Research. Methods for the analysis of ghee, Manager of publications. Delhi Misc. Bull No 64 (1946).
- Marketing sever No. 81, Methods of sampling and testing butterfat (ghee and butter) under Agmark, Directorate of Marketing and Institution, Ministry of Food and Agriculture, Government of India (1953).
- Lo, Y.C., Handel, A.P., J. Am. Oil Chem. Soc. 60, 815-818, (1983)
- Sedman, J., Vande voort, F.R., Ismail, A.A. J. Am. Oil Chem. Soc., 74, 907-913, (1997)
- Ganguli, N.C., Jain M.K., Ghee: Its Chemistry, Processing and Technology. Journal of Dairy Science, 56; P.19-25, (1973)
- Macrae R., Robinson R.K., Sadler M.J., Ghee. In: Encyclopedia Food Science, Food Technology Nutrition; San Diego Academic Press, 4: 2186-2192, (1993)
- United States Pharmacopoeia, 30th ed., National Formulary, 25th ed., The United States Pharmacopeial Convention, Rockville, p.158, (May 2007)
- Townend J., Practical Statistics for Environmental and Biological Scientists, England: John Wiley and Sons Ltd; 270-276, (2002)
- Alonso, L., Fraga, M.J., Juarez, M., Carmona, P., J. Am. Oil Chem. Soc. 79, 1-6, (2002)
- AOAC. Association of Official Analytical Chemists. Official Methods of Analysis, 6th Edn. Washington D.C., 1995; 41: 1-43.
- James C.S., Analytical Chemistry of Foods. UK Blackie Academic and Professional, Bishobriggs, Glasgow, UK, 1979; 152-154.
- Kirk R.S., Sawyer R., Pearson's composition and analysis of foods. 9th Edn. Longman Scientific & Technical, USA, 1991; 98-102.
- Mehlenbacher V.C., The analysis of Fats and Oils. The Garrard Press, Champagne Illinois, USA, 1960; 188-235.
