Detection of Pig and Buffalo Body Fat in Cow and Buffalo Ghees by Differential Scanning Calorimetry

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ABSTRACT

Adding small amounts of pig or buffalo body fat to cow or buffalo ghee results in the appearance of an extra peak located at high temperature in the melting and crystallization curves as determined by the differential scanning calorimetry (DSC) technique. Ghee adulterations with these animal fats at levels down to 5% are clearly seen in the crystallization diagrams. Quantitative measurements can be obtained by this method in the case of adulterations with buffalo body fat. On the other hand, this method does not detect vegetable oils such as coconut oil, and gives similar results for cottonseed-fed buffalo ghee and ghee adulterated with animal body fats.

INTRODUCTION

Ghee (butterfat), one of the most important dairy products in India, is prepared from cream or butter by a heat clarification process (1-4). It is frequently adulterated to meet the demand which exceeds the supply and to increase profit margins. A statistical study of ghee adulteration over a period of 13 years (1960-72) showed that 16% of the samples investigated were adulterated and that the average of adulteration was 12% (5).

Adulterants fall into two main categories: vegetable oils and fats, and animal body fats. Adulteration with vegetable fats and oils can be detected by several thin layer chromatographic techniques (6-10). Animal body fat adulteration is more difficult to detect (11). For this purpose, chromatographic techniques cannot be applied, except in the case of tallow adulterations (10). Furthermore, ghee obtained from the milk of buffaloes fed on cottonseeds has similar properties to ghee adulterated with animal body fats (11).

Recently, encouraging results have been obtained for detecting animal body fats in ghee using differential scanning calorimetry (DSC) (12). By this method, ghee adulterations with goat body fat were detected and estimated from the 10% level (12).

This paper deals with the detection and determination of ghee adulterations with other animal body fats, i.e., with pig and buffalo, using DSC technique. Trials made to detect vegetable oil adulteration, and to distinguish adulterated ghees from the one obtained with cottonseed fed animals using DSC technique are also reported.

MATERIALS AND METHODS

Ghee samples came from cow or buffalo herds kept at the National Dairy Research Institute by a procedure already described (12). Animal body fats were prepared from adipose tissues as previously mentioned (12).

Body fats and ghee samples were individually melted to 50 C. The resulting liquids were then mixed so that the body fat contents were between 5 and 20%. To test the method for adulteration with vegetable oils, coconut oil was added to some samples. Prior to analysis, all samples were stored at 15 C for at least one month.

Analyses were made using a heat flow differential scanning calorimeter (Model TA 2000 B Mettler Instrument Ltd., Zürich, Switzerland) calibrated with 99.9999% Indium (Preussag Metall Ltd., Göslar, Germany).

15-25 mg fat were heated from -30 to 70 C at a heating rate (H_R) of 2 C/min and then cooled to -40 C at a cooling rate (C_R) of -1 C/min. The reference used was air.

For data treatment (mainly curve integration), the calorimeter was connected to a Hewlett-Packard 3354 Laboratory Automation System, according to a scheme already described (13).

RESULTS

DSC melting curves of animal body fats as illustrated in Figure 1 exhibit several endothermic peaks, one of them being located at ca. 50 C. This melting behavior is totally different to that of cow and buffalo ghees which are completely molten at this temperature. Similarly, animal body fat crystallization is almost complete at 15 C, whereas ghees only begin to crystallize at this temperature (see Fig. 2).

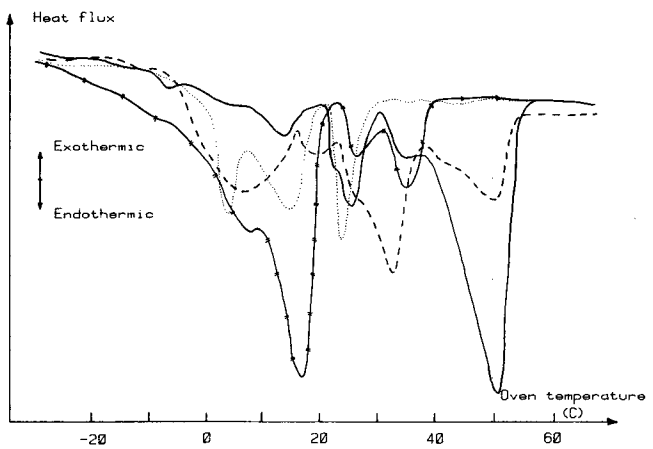

FIG. 1. DSC melting diagrams of ghees and animal body fats. ····· Cow ghee; —//— buffalo ghee; ––––– pig body fat; —— buffalo body fat.

Cow Ghee Adulteration

Adulterating cow ghee with either pig or buffalo body fat at the 5% level is detected in the DSC curves by an additional peak at high temperature. In the case of melting curves, this peak appears between 30 and 50 C (see Fig. 3) and for crystallization curves between 12 and 18 C (see Fig. 4). It has to be noted that only pig adulterations above the 10% level are revealed on the DSC melting curves.

The relative area of this additional peak depends on the concentration of animal body fat. As examples, areas of this peak (crystallization DSC curves) are reported in Table IA as a function of animal body fat concentration. Increasing amounts of animal body fat leads to an increase

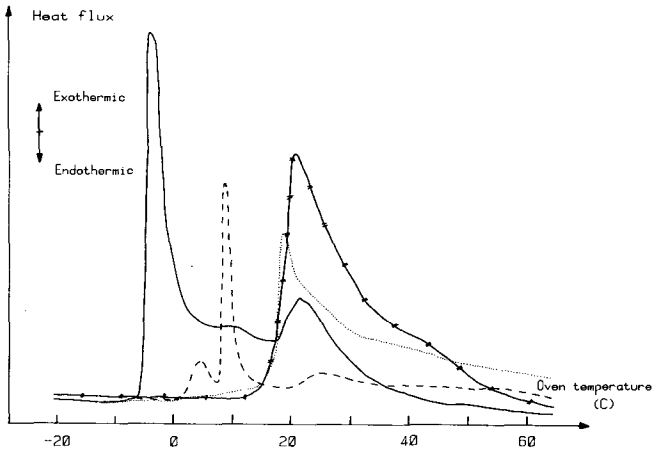

FIG. 2. DSC crystallization diagrams of ghees and animal body fats. ····· Cow ghee; —//— buffalo ghee; ———— pig body fat; —— buffalo body fat.

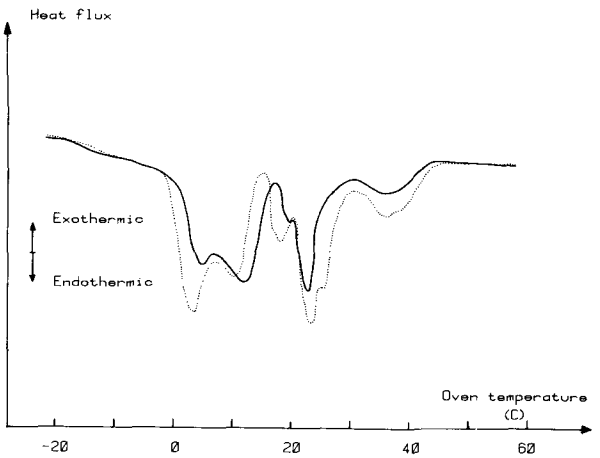

FIG. 3. DSC melting diagrams of cow ghee-animal body fats mixtures. ····· Cow ghee + 10% pig body fat; —— cow ghee + 5% buffalo body fat.

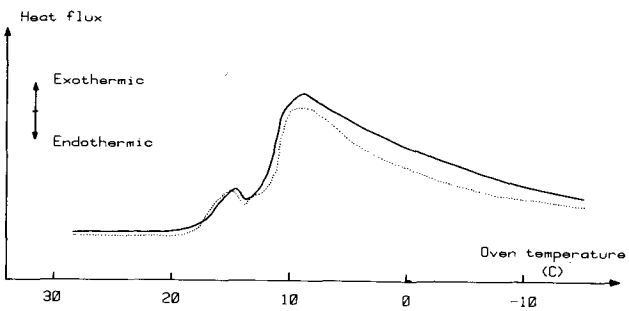

FIG. 4. DSC crystallization diagrams of cow ghee-animal body fats mixtures. ····· Cow ghee + 5% pig body fat; —— cow ghee + 5% buffalo body fat.

in the relative area of this peak. This effect is greater for addition of buffalo body fat than for pig body fat.

Also, the position of this peak changes with the amount of animal body fat in a mixture (see Table IA). When this amount is small, the crystallization of the body fat is strongly influenced by the presence of the ghee and the peak corresponding to the body fat crystallization is located close to the one of the ghee. For higher body fat content, the influence of ghee is smaller and the crystallization peak of the body fat in the mixture draws nearer to the one of pure animal body fat. On the other hand, the change in the crystallization temperature of the additional peak with the animal body fat content is smaller in the case of pig body fat than in the case of buffalo body fat additions (see Table I). This probably results from the crystallization peak of pure buffalo body fat being farther from the one of ghee than the corresponding peak of pure pig body fat.

Buffalo Ghee Adulteration

The addition of pig or buffalo body fat up to 15% to buffalo ghee gives little change in its DSC melting pattern: the highest peak of the pure buffalo DSC melting diagram slightly shifts to a higher temperature in the presence of the animal body fat.

However, from a 5% level of incorporation, animal body fats are revealed in the DSC crystallization curves by an additional peak at high temperature (see Fig. 5).

As in the case of cow ghee adulterations, the greater the level of animal body fat in buffalo ghee, the greater the relative surface of the additional peak and the higher its location on the DSC diagram (see Table IB). For the same reasons as above (buffalo and cow ghees crystallizations are very similar), the peak displacement is greater for buffalo than for pig body fat additions.

DISCUSSION

Determination of the Experimental Conditions

Detecting adulteration of ghees by animal body fats using the DSC technique is more sensitive with crystallization curves than with the melting curves.

The presence of the additional peak at high temperature on the DSC crystallization curves reveals adulteration by pig or buffalo body fat, and the relative area of this peak or its location on the DSC curve measures the degree of adulteration.

However, DSC crystallization digrams of cottonseed-fed buffalo ghee also exhibit this additional peak located at high temperature. Therefore, differentiation of ghee adulterated with animal body fat from cottonseed-fed buffalo ghee is not possible, using the DSC technique. Cottonseed-fed buffalo ghee is readily detected by other simple tests such as "methylene blue" (14) or "Halphen" tests (11), which can be used to screen samples prior to DSC analysis.

Measurements based on crystallization diagrams have the further advantage of avoiding problems linked to polymorphism of fats, so that the results are independent of the thermal treatment of the samples prior to analysis. Therefore, all the results discussed below refer only to DSC crystallization curves.

However, the scan rate of the furnace affects the DSC pattern of a given sample, particularly in peak width and shape (15). With all other parameters kept constant, an increase in the cooling rate leads to the coalescence of the two exothermic peaks corresponding to the crystallization of the ghee and the animal body fat.

Thus, the crystallization curves of cow ghee containing 5% animal body fat recorded at -2 C/min show one exothermic peak with only a shoulder at high temperature. Decreasing the cooling rate to -1 C/min gives DSC curves exhibiting two well resolved exothermic peaks for all the

TABLE I

Influence of the Animal Body Fat Concentration on the DSC Crystallization Curves of Cow and Buffalo Ghees

(A) Cow Ghee Adulterations

Pig body fat (%)	Buffalo body fat (%)	Adulterant peak area (%)	Adulterant peak temperature (C)
5	–	6.3	15.6
10	–	7.4	15.8
20	–	8.0	16.6
–	5	6.5	15.5
–	10	15.4	19.2
–	20	32.9	24.7

(B) Buffalo Ghee Adulterations

Pig body fat (%)	Buffalo body fat (%)	Coconut oil (%)	Adulterant peak area (%)	Adulterant peak temperature (C)
5	–	–	5.9	16.3
10	–	–	6.5	16.8
15	–	–	8.8	16.8
–	5	–	7.5	16.8
–	10	–	18.5	21.9
–	15	–	26.9	23.9
–	–	10	0.0	–
–	5	5	9.5	16.8
–	10	5	18.0	21.3
–	5	10	7.2	16.8
–	10	10	8.4	17.8
10	–	10	6.4	15.8

adulterated ghees investigated. Therefore this cooling rate was used.

Detection of Pig and Buffalo Body Fats

The influence of pig body fat on the DSC crystallization pattern of both cow and buffalo ghees is smaller than that of buffalo body fat. Both fats can, however, be detected in ghees from the 5% level or even lower and thus lower than the detection limits for goat body fat (12).

Pig body fat addition is harder to quantify than buffalo body fat. In fact, the relationship between the relative areas of the additional peak and pig body fat concentrations is not linear (see Table I): although this area increases markedly up to 5% pig body fat, the subsequent increase between 5 and 20% animal body fat is small. Because of this, quantitative determination of pig body fat based on the relative area of the additional peak does not seem to be accurate. The same is observed with the extra peak position, which varies little as a function of the pig body fat level, and is therefore of doubtful value for the quantitative determination of pig body fat addition in ghees.

In the case of buffalo body fat adulteration, the relationship between the relative area of this additional peak and animal body fat concentration is linear, allowing quantitative determinations of this fat in cow or buffalo ghees (see Fig. 6). The slopes of those lines are less than 1. This comes from the difference between ghee and animal body fat enthalpies, those of animal body fats being approximately twice those of ghees. Consequently, before quantitative analysis, proper calibration is required.

The relationship linking the position of the additional peak to buffalo body fat concentration is not linear (see Table I). The location of this peak may, however, also serve to estimate the amount of buffalo body fat in ghees, provided a previous calibration has been achieved.

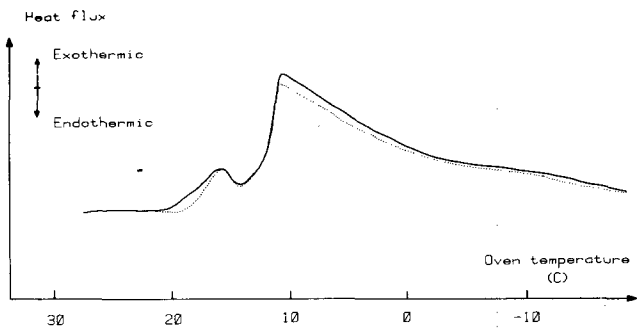

FIG. 5. DSC crystallization digrams of buffalo ghee-animal body fats mixtures. ····· Buffalo ghee + 5% pig body fat; —— buffalo ghee + 5% buffalo body fat.

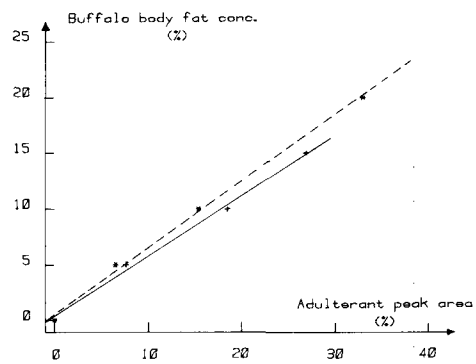

FIG. 6. Quantitative determination of ghees adulteration with buffalo body fat. ——— Cow ghee; —— buffalo ghee.

Influence of Coconut Oil

Detecting ghee adulteration with coconut oil up to the 10% level using the DSC technique is not possible, since the DSC pattern of ghees shows no change with the addition of the vegetable fat.

In presence of both buffalo body fat and coconut oil, the DSC crystallization of ghee exhibits the characteristic peak located at high temperature, provided that the animal body fat concentration is equal or superior to 5%. Buffalo body fat can therefore be detected as from the 5% level, whether the ghee contains vegetable fat or not.

Quantitative determination of buffalo body fat in ghee is, however, not possible in the presence of vegetable fat. For samples containing only 5% coconut oil, the relative area of the additional peak corresponds to the buffalo body fat concentration; adding more coconut oil reduces this area (see Table I).

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Continuous Acidulation of Soapstock and Recovery of Acid Oil[1]

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ABSTRACT

Requirements for water pollution abatement have created a need for much better recovery of fatty material from soapstock acidulation processes. The present methods of recovery lack reliability, or are relatively capital intensive, or both. A new, continuous system consisting of equipment for acidulating the soapstock, decanting the bulk of acid oil from acid water, and treating the acid water in a coalescer for further separation of emulsified acid oil is described. The emphasis is on operating results from a pilot process using a variety of soapstocks. Fat concentrations below 150 ppm in acid water can be achieved reliably. The process is relatively compact, and simple to operate.

INTRODUCTION

In alkali-refining of triglyceride oils, soapstock is produced as a byproduct. It consists of ca. 70-95% water and 5-30% of fatty material, depending on refining practice and the equipment used. Most of the fatty material, 60-70%, is in the form of sodium soaps of fatty acids with the remainder made up of triglycerides, phosphatidic material, and minor amounts of other, oil-derived compounds.

To recover the fatty material (acid oil), the soapstock is acidulated with sulfuric acid to liberate the fatty acids. This acidulation must be carried out to a relatively low pH of 2-3 to ensure that no soaps remain, which would tend to interfere with the separation of the acid oil phase from the acid water phase. Batch as well as continuous acidulation is being practiced.

The problems associated with the acidulation of soapstock are well known. They are, mainly, the corrosive nature of the process, and the fact that the separation of the acid oil phase from the acid water phase is often relatively poor, which leads to high fat losses and waste-water highly contaminated with fatty material.

The difficulties with corrosion of equipment and buildings are of course solved by using corrosion-resistant materials, but it must be admitted that the costs are considerable. It is therefore of interest to have a relatively compact process arrangement which requires less outlay in building space and equipment. This means that the separation of acid oil from acid water after the acidulation should not require a long time or very elaborate equipment.

Doing the acidulation reaction in a continuous process mode is of course not very difficult to accomplish. Achieving adequate phase separation in a relatively short time with a variety of soapstocks can be very difficult. The problem of oil/water separation has assumed even greater importance in recent years because of much more stringent requirements on the fat content of waste-waters. Regulations now specify that only up to 150 ppm of fatty mate-

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