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RHEOLOGICAL PROPERTIES OF MILK FAT COMPARED TO OTHER FATS:
2- THE USE OF THE CHANGES IN MILK FAT RHEOLOGICAL PROPERTIES FOR DETECTING ITS ADULTERATION

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ABSTRACT

A method used the changes in flow characteristics of buffaloes' and cows' milk fat for detecting their adulteration with each of the lard fat, palm, palm kernel and coconut oils was developed. The flow characteristics measured were the shear rate – shear stress relationship, consistency index (k), viscosity, plastic viscosity and 10-rpm viscosity. The changes in the flow characteristics of buffaloes' and cows' milk fat by their mixing with 10, 25 and 50% of each oil over a shear rate range from 73 to 196 S^{-1} and temperature range of 35 - 65°C were determined. However, the measurements at 196 S^{-1} shear rate and 40°C were recommended since at these conditions the changes on mixing were the largest. The changes of the above parameters on mixing 10% or more were significant at $P < 0.001$, were particular for each oil and fat and could be used for their identification. There was linear, inverse or direct relationship with R^2 values of > 0.98 between the adulteration percent and the changes they made. Equations for calculating adulteration percent for any shear stress obtained on mixing were calculated.

Key words: buffaloes' milk fat, cows' milk fat, adulteration, rheology, vegetable oils, shear, viscosity, flow behavior index.

INTRODUCTION

Milk fat is the most desirable and expensive fat in many parts of the world. In some Middle East countries and India, buffaloes' milk fat is preferable and more expensive than cows' milk fat. Consequently, adulteration of milk fat and in particular buffaloes' milk fat with vegetable oils is sometimes practiced. Blending milk fat with vegetable oils also could be used for improving butter spreadability and this raises concerns about the standards of butter identity. Detecting milk fat adulteration is done by tedious and time-consuming methods, which depend on fatty acids contents determination and fat or oil physical constants.

Recently, fats and oils rheology (viscosity and flow behavior) were found to be correlated to their fatty acid composition and these properties could be used as physical constants for their identification. Metwally (2004) found that fats and oils flow properties such as shear rate – shear stress relationship, consistency index (k) calculated from the power law equation, viscosity, 10-rpm viscosity calculated from IPC paste model and plastic viscosity calculated from Bingham Plastic model were physical constants for each fat and oil. The determinations of these five parameters were suggested to be used for oil and fat identification. In agreement of this trend, Boyaci *et* *al.* (2002) developed an equation for simple and rapid viscosity estimation based on the fatty acid composition of number of vegetable oils. Boyaci *et al.* (2003) found a linear relationship ($r = 0.956$) between slip melting point of interestrified vegetable oils and the concentration of 16:0, 18:0, 18:1, 18:2 and 18:3 fatty acids. Paradaker (2001) used the change in flow behavior (flow behavior index and consistency index) of cow milk to detect its adulteration with synthetic milk. Marikkar *et al.* (2002 & 2003) used the cooling and heating thermograms for monitoring of tallow, lard and chicken fat adulteration of canola oil.

Buffaloes' milk fat may be adulterated by cows' milk fat or by any of the vegetable oil such coconut, palm and palm kernel. In some rare occasions, lard is also used for adulteration. It would be advantageous to find a simple and fast method for detecting adulteration. This work was carried out to study the feasibility of using the change in flow properties of buffaloes' or cows' milk fat to detect their adulteration with vegetable oils and lard.

MATERIALS AND METHODS

Materials:

Buffaloes' and cows' milk were obtained from the faculty of Agriculture dairy herd and butter oils were prepared from corresponding milk by the boiling off method. Other fats and oils were obtained from commercial sources.

Sample preparations:

Buffaloes' or cows' milk fat was mixed with 10, 25 and 50% of each of the other fats or oils. The samples were melted at 60°C before mixing and left after mixing for 10 min. for equilibrium before the measurements.

Flow properties measurements:

The flow properties of the samples in triplicates were carried out over a temperature range from 35 to 65°C with a concentric cylinder Brookfield Programmable viscometer (Model DV -II+; Brookfield Engineering Laboratories, USA) with UL adaptor and ULA spindle over a shear rate range of 70 to 193 S^{-1}. The samples were allowed to equilibrate at each temperature for 10 min. prior to measurements.

Model analysis:

The flow behavior index and consistency index were calculated using the simple power law rheological model, $\tau = k\,D^n$ where τ = shear stress, n = flow behavior index, k = consistency index and D = shear rate.

Plastic viscosity of the samples was determined using the Bingham Plastic model ($\tau = \tau_{\cdot} + \eta \times D$, τ = shear stress, $\tau_{\cdot}$ = yield stress, η = plastic viscosity, D = shear rate).

The 10-rpm viscosity of the samples was determined using IPC Paste model ($\eta = k \times R^D$, η = 10 rpm viscosity, k = Consistency multiplier, D = shear Sensitivity, R = rotational speed).

WinGather version 1.1 (Brookfield Engineering Laboratories, Inc., Copyright© 1995) software was used to collect, store and analyze the data on a personal computer connected to the viscometer.

Statistical Analysis:

Numerical results were expressed as the arithmetic mean. Student's *t*-test was used if two samples were compared, while analysis of variance (one or two way ANOVA) was used for multiple comparisons over the temperatures and shear rates used. The statistical significance of the data was determined using Fisher's L.S.D. post hoc test. The statistical significance of correlation and regression coefficients was determined using *t*-test. *P* value was equal to or less than 0.05 was considered sufficient to reject the null hypothesis. Statistical analysis was performed by running the SPSS 12.0 (SPSS Inc., Copyright© 2003, Chicago, IL, USA) package on a personal computer.

RESULTS AND DISCUSSION

The change in shear rate – shear stress relationship, consistency index (*k*), viscosity, plastic viscosity and 10-rpm viscosity of pure buffaloes' or cows' milk fat when mixed with other fats and oils were determined and the information was used to detect their adulteration.

Figure (1) illustrates the shear rate – shear stress relationship of buffaloes' milk fat and its mixtures with 10, 25 and 50% of coconut oil at 40°C. When mixed with other

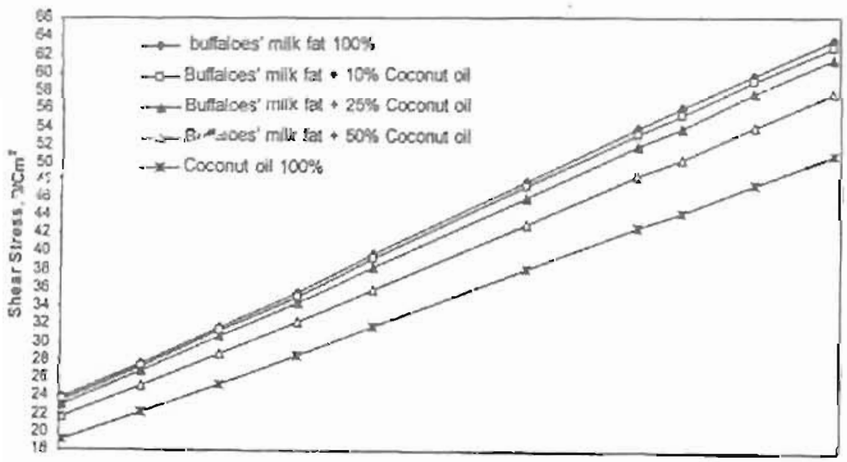

Figure (1): The shear stress of buffaloes' milk fat when mixed with 10, 25 and 50% of coconut oil at

oils, buffaloes' milk fat shear stress increased or decreased according to type of oil all over the shear rate range (73 to 196 S^{-1}). The change was proportional to the mixing ratio and increased with the shear rate. Measurements at 196 S^{-1} shear rate and 40°C were recommended since these resulted in maximum changes.

To investigate the relationship between the mixing ratio and the change in shear rate – shear stress relationship, the adulteration percent was plotted as a function of shear stress at 196 S^{-1} shear rate at 40°C (Figure 2). With coconut and palm kernel oils the shear stress decreased with the adulteration ratio to give a linear inverse relationship with R^2 values of 0.996 and 0.922, respectively. Palm kernel adulteration equation at each shear stress (S) was calculated to be: adulteration, % = - 48.24 S + 3049.4. On the other hand, mixing the buffaloes' milk fat with palm oil (Figure 2) or lard, the shear stress increased with the mixing ratio to give a linear direct relationship with R^2 values of 0.995 and 0.986, respectively. The adulteration equation with lard was: adulteration, % = 20.272 S – 1335.3. The regression coefficients of the linearity of all the values were significant at $P < 0.001$.

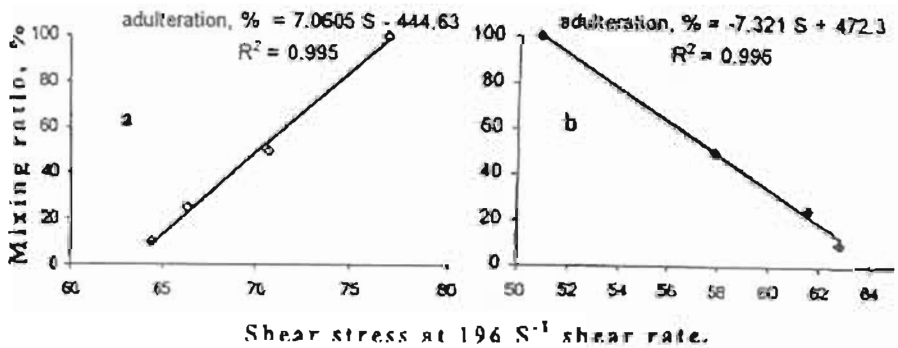

Figure (2): Plot of the relationship between the mixing percent (10, 25 and 50%) of buffaloes' milk fat with (a) palm oil (b) coconut oil and their shear stress at shear rat of 196 S^{-1} at 40°C.

Figure (3) illustrates the changes in the flow characteristics of buffaloes' milk fat when mixed with palm, palm kernel and coconut oils and lard fat over a shear rate range of 73 to 196 S^{-1} and at 40°C. The buffaloes' shear stress at 196 S^{-1} shear rate, consistency index (k), viscosity, plastic viscosity and 10-rpm viscosity increased when mixed with lard and palm oil, while these parameters decreased when mixed with coconut and palm kernel oils. These changes were significant at $P < 0.001$ with all mixing ratios and at all the shearing rate and temperature ranges. The differences from the buffaloes' milk fat increased by the mixing ratio but decreased with the temperature. Highest differences were at 40°C. Again, the change in the above parameters with the mixing ratios showed either linear, direct or inverse relationship with $R^2 \geq 0.9$.

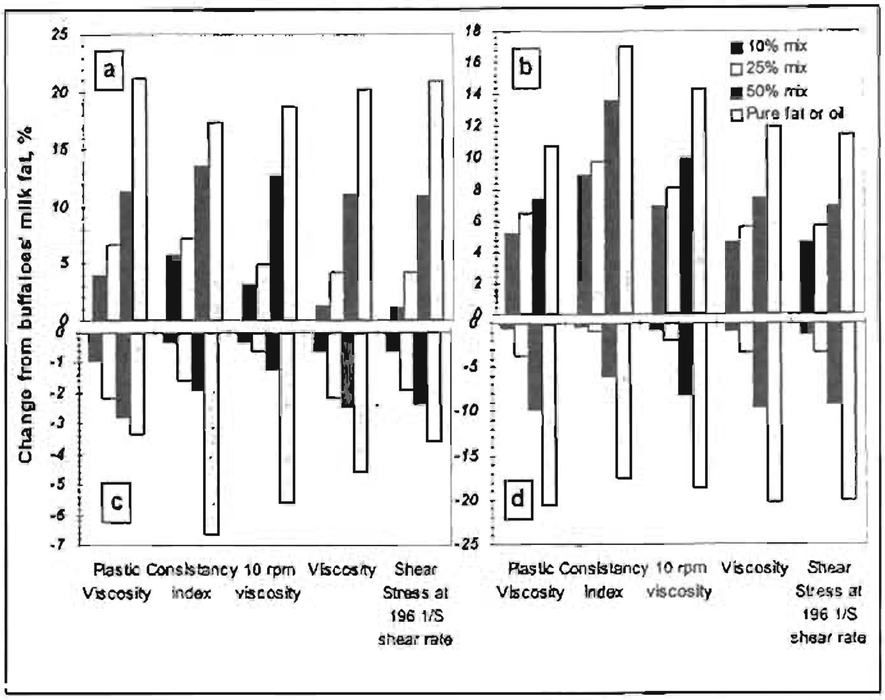

Figure (3): The change in the flow characteristics of buffaloes' milk fat when mixed with different ratio of (a) palm oil, (b) palm kernel oil, (c) lard and (d) coconut oil at 40°C.

As with buffaloes' milk fat, mixing cows' milk fat with coconut and palm kernel oils shifted the shear stress to lower values depending on the mixing ratio. The change showed a linear inverse relationship with R^2 values of 0.995 and 0.973, respectively. Coconut oil adulteration equation at each shear stress (S) was found to be: adulteration, % = - 6.6524 S + 436.74. Figure (4) reports the plot of the relationship between the mixing ratio of cows' milk fat with palm kernel and palm oils and their shear stress at shear rate of 196 S^{-1}. Mixing cows' milk fat with palm oil (Figure 4) and lard increased the shear stress to higher values corresponding to the mixing ratio to give a linear relationship with R^2 values of 0.996 and 0.986, respectively. The equation with lard was: adulteration, % = 193972 S - 1315.3. Again, the regression coefficients of the linearity of all the values were significant at $P < 0.001$. Therefore, at any shear stress the use of the above equations would give adulteration percent of buffaloes' or cows' milk fat with one of the above oils and fat.

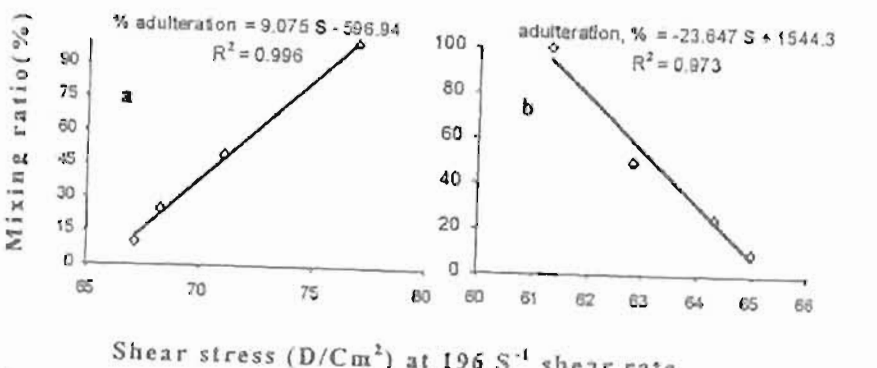

Figure (4): Plot of the relationship between the mixing percent (10, 25 and 50%) of cows' milk fat with (a) palm oil (b) palm kernel oil and their shear stress at shear rat of 196 S^{-1} at 40°C.

Figure (5) shows the change In the flow characteristics of cows' milk fat when mixed with palm, palm kernel and coconut oils and lard over a shear rate range of 73 to 196 S^{-1} and at 40°C. The changes trend in cows' milk fats' five parameters were similar to the changes with the buffaloes' milk fat and the deviations were also significant at $P < 0.001$. The relationships between the changes of the above parameters with the mixing ratios were found to be linear, direct or inverse relationship with $R^2 \geq 0.9$.

Table (1) shows the effect of mixing buffaloes' with cows' milk fat. The behavior was somewhat different from mixing with other oils and lard since both fats are very close in their fatty acids contents. Buffaloes' milk fat contained slightly more of 16:0 and 18:0 fatty acids (45 vs. 42%) and of the short and medium chains fatty acids (9.2 vs. 8.4%) (William, 2003). The buffaloes' milk fat contents of the later groups caused it to be more fluid showing more shear rate at the same shear stress than cows' milk fat. These differences In the flow behavior, though small, were significant and could be used for detecting the mixing (Table 1).

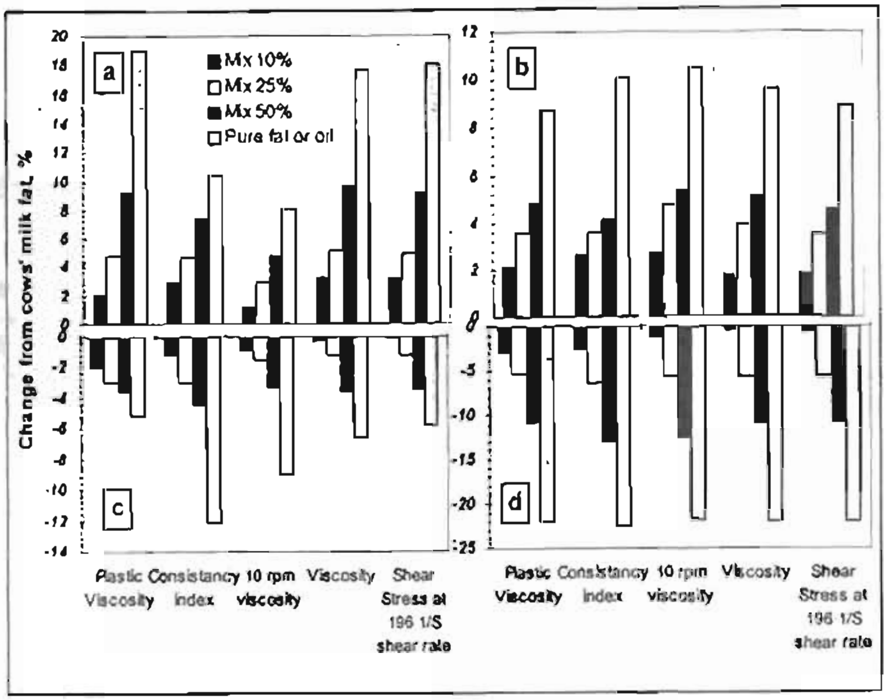

Figure (5): The change in the flow characteristics of cows' milk fat when mixed with different ratio of (a) palm oil, (b) palm kernel oil, (c) lard and (d) coconut oil at 40°C.

Table (1): Flow characteristics of buffaloes' and cows' milk fat and their mixture at 40°C.

Parameter	Sample		
	Buffaloes' milk fat	10% cows' milk fat mixture[2]	Cows' milk fat
Consistency index, cp	31.7	33.1	33.7
Shear stress[1], D/Cm^2	63.6	64.5	56.1
Plastic viscosity, cp	32.6	32.9	33.2
10-rpm viscosity, cp	32.1	33.1	33.4
Viscosity, cp	32.5	23.1	33.4

1- At shear rate of 196 S^{-1}.
2- Buffaloes' milk fat mixed with 10% of cows' milk fat.

The data pointed out that mixing buffaloes' milk fat with 10% of cows' milk fat altered the earlier flow properties significantly at $P < 0.001$. However, at higher mixing ratios (25 and 50%) the five flow parameters changed towards the values of cows' milk fat to give insignificant differences at $P > 0.05$. This means that the flow values of buffaloes' milk fat mixed with more than 10% gave values similar to that of cows' milk fat and this would lead to the conclusion that the mix is purely cows' milk fat. This would protect the consumer and penalize the adulterant.

In conclusion, the change in flow characteristics of buffaloes' and cows' milk fat measured as shear rate – shear stress relationship, consistency index, viscosity, plastic viscosity and 10-rpm viscosity could be used for detecting their adulteration with other oils at level as low as 10%. This method of detection can be applicable to detect adulteration of other oils and fats. The method depends on determining the flow characteristics of pure oils and fats and their mixture at a particular temperature and shear rate. By comparing the flow values of the unknown sample with these piled data and using the adulteration equations, the type and percent of adulteration are identified. For example in this work, the shear stress (at 196 S^{-1} shear rate) of adulterating cows' milk fat (65.1 D/Cm^2) with 10% of lard and palm, palm kernel and coconut oils were 66.3, 67.2, 64.8 and 64.6 D/Cm^2, respectively. If the adulterated cows' milk fat showed lower shear stress than 65.1 D/Cm^2 then the add oil would be palm kernel or coconut and by comparing the exact shear stress values of the mixture with the above data the exact oil is pointed out. It showed be noted that if oil or fat contains any additive, i.e. phospholipids the flow values change from the pure values.

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الخواص الريولوجية لدهن اللبن مقارنة بالدهون الأخرى
٢- استخدام الخواص الريولوجية في الكشف عن غش دهن اللبن النقي

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تهدف هذة الدراسة إلى محاولة استخدام الخواص الريولوجية و خواص التدفق لدهن اللبن البقري أو الجاموسي في تطوير طريقة جديدة للكشف عن غش اي منهما ببعض الزيوت أو الدهن الشائع استخدامها في مصانع الألبان و هي زيت كل من النخيل و زيت نوى النخيل و زيت جوز الهند و دهن الخنزير فتم ذلك عن طريق عمل مخاليط من كل من هذة الزيوت او دهن الخنزير بنسب ١٠ ، ٢٥ ، ٥٠% حجم/حجم مرة مع دهن اللبن الجاموسي النقي و مرة أخرى مع دهن البن البقري النقي ثم قيست الخواص الريولوجية المختلفة لهذة المخاليط و المتمثلة في معامل اللزوجة consistency index ، اللزوجة البلاستيكية plastic viscosity ، الزوجة ، اللزوجة عند سرعة دوران ١٠ دورات/ ق 10-rpm viscosity و ذلك مابين درجات معدل قص shear rate من ٧٣ إلى ١٩٦ ث$^{-1}$ و على مدى من درجات الحرارة مابين ٣٥- ٦٥°م و كذلك قياس قوة القص shear stress عند معدل قص يساوي ١٩٦ ث$^{-1}$.

و كان من أهم النتائج أنة كان هناك فروق معنوية على مستوى $P < 0.001$ بين كل المخاليط و كذلك كانت العلاقة بين نسبة الخلط و قيم هذه المقاييس علاقة خطية عكسية او طردية بدرجة مرتفعة ($R^2 > 0.98$) كما تم حساب معادلات رياضية لحساب نسب الغش في كل حالة مما يشير على أن هذه الطريقة يمكن استخدامها في كشف الغش لدهن اللبن .