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RHEOLOGICAL PROPERTIES OF MILK FAT COMPARED TO OTHER FATS:
1-RHEOLOGICAL MODELING AND FLOW PROPERTIES.

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ABSTRACT

Flow properties of buffaloes' and cows' milk fat and lard fat and palm, coconut and palm kernel oils were studied over a temperature range from 35 to 65°C and a shear rate range of 70 to 196 S^{-1}. The samples consistency index, shear rate – shear stress relationship, plastic viscosity, 10-rpm viscosity and viscosity were significantly different from each other ($P < 0.001$) particularly at 40 and 45°C and at 196 S^{-1} shear rate. The above parameters were found to be constant for buffaloes' milk fat prepared from different herds. The five parameters are constant for each fat or oil when measured under the same conditions and therefore could be used for identification.

Keywords: buffaloes' milk fat, cows' milk fat, identification, rheology, vegetable oils, shear, viscosity, flow behavior index, Bingham plastic.

INTRODUCTION

Fats and oils are indispensable part of the food industry. The understanding of rheology of these products (viscosity and flow behavior) is critical in optimizing product development effort, processing methodology, final products' quality and for pipeline transport (Herrera and Hartel, 2000).

Earlier reports (Rielly, 1997) used to define pure oils as Newtonian fluids and fats as non-Newtonian Bingham plastic fluids. However, the flow behavior of these products depends not only on their composition but also on the measurement temperature, which controls the solid fat content (SFC) of the products (Herrera and Hartel, 2000 and Wright *et al.*, 2001). Fats and oils flow curves could be described by the general power law equation ($\tau = k D^n$) which is also applicable to a great number of non-Newtonian fluids over a wide range of shear rates. The equation is modified for plastic flow to be $\tau - \tau_c = k D^n$.

Pure fats and oils are almost constant in their composition and therefore their viscosity and flow behavior are expected to be of constant values at the exact temperature and measurement conditions. In this regard, Boyaci *et al.* (2002) developed an equation to estimate vegetable oil viscosity based on the oil fatty acids contents. Boyaci *et al.* (2003) found that the oil slip melting point was correlated to five fatty acids (16:0, 18:0, 18:1, 18:2 and 18:3) contents of the oil. Paradaker *et al.* (2001) found that the flow of cows' milk was changed when adulterated with synthetic milk and recommended the use of the change in the flow behavior index and the consistency index for detecting cows' milk adulteration. If the flow properties of pure fats and oils can be used for their identification, it would be advantageous. Currently, fats and oils identification depends on their fatty acids chemical constants (iodine number, Reichert missel value, melting point etc.) which are time consuming, costly and do not give clear cut identification (William, 2003).

There are number of fats and oils widely used in the dairy industry, namely buffaloes' and cows' milk fat and palm, coconut, and palm kernel oils. Usually, a single fat or oil is used in processing a product. However, in case of the expensive butter oil there is a possibility of adulterating it with one of the vegetable oils or in rare occasions with lard. For the importance of butter oil, its rheological properties particularly in products like butter was thoroughly studied to control its spreadability but not for fat identification (Herrera and Hartel, 2000 and Wright *et al.*, 2001).

This work was carried out to study the flow properties of buffaloes and cows' milk fat and number of other fats and oils that are used to adulterate them in order to determine the feasibility of using these properties as physical constants for their identification.

MATERIALS AND METHODS

Materials:

Buffaloes' and cows' milk were obtained from the faculty of Agriculture dairy herd and butter oils were prepared by the boiling off method. Buffaloes' butter oil was prepared from two different herds one of faculty of Agriculture and the second from a private farm. Other fats and oils were obtained from commercial sources.

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 ($\tau = \tau_{\circ} + \eta \times D$, τ = shear stress, $\tau_{\circ}$ = 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

Shear stress of the samples were determined over a shear rate range of 74 to 196 S^{-1} and at a temperature range from 35 to 65°C. Table (1), reports the shear stress of the samples at the lowest and highest shear rate used at different temperatures.

The shear stress of the sample was directly proportional to the shear rate and inversely proportional to temperature (r = -0.98 at $P < 0.01$). This is expected since increasing the temperature reduces SFC of the sample and its viscosity and increases its fluidity (Herrera and Hartel, 2000 and Wright *et al.*, 2001).

Table (1): Shear stress of pure fats and oils at shear rates of 73.4 and 196 S^{-1} at different temperatures.

Samples	Shear rate, S^{-1}: 73.4					196				
	Temperature, °C									
	35[2]	40[3]	45[3]	55[3]	65[3]	35[1,2]	40[3]	45[3]	50[3]	65[3]
	Shear stress, D/Cm^2									
Buffaloes' milk fat	28.9	23.8	20	16.9	10.9	65.1	63.6	52.9	45	29
Cows' milk fat	29.6	24.5	20.7	17.5	11.5	65.9	65.1	54.3	45.9	29.8
Palm oil	34.8	28.6	24.3	20.1	12.9	77.4	76.9	63.7	53.2	34.2
Coconut oil	23	19.1	16	13.7	8.9	51.5	50.8	42.5	36.6	23.6
Palm kernel oil	27	28.6	18.9	15.8	10.2	61.7	61.3	49.7	42.3	25.4
Lard fat	31.9	26.7	22.5	18.9	12.4	71.6	70.9	59.2	50.7	32.8

1- The shear stress values were reported at shear rate of 164.9 S^{-1} since beyond this rate lard and palm oil samples did not show any shear stress at 35°C because this was beyond the measuring range of our viscometer.

2- Compared to buffaloes' milk fat, the shear stress were significantly different at $P < 0.05$ from lard, coconut and palm oils but not significantly different from palm kernel oil and cows' milk fat.

3- The differences between shear stresses were significantly different at the $P < 0.001$ level between all samples at temperatures and shear rates ranges used.

Figure (1) illustrates the shear stress - the shear rate relationship of the samples at 40°C. Shear stress differences between samples were the largest at the highest shear rate of 196 $S^{-1}$and at 40 and 45°C. The differences between all samples were highly significant at $P < 0.001$ at the whole range of temperature and shear rates. Within the sample, the shear stress changed inversely by temperature and the changes were significant at $P < 0.001$. The 35°C temperature was exceptional since at this temperature the differences between buffaloes' and cows' milk fat were insignificant but each of them was significantly different ($P < 0.05$) from lard fat and coconut and palm oils.

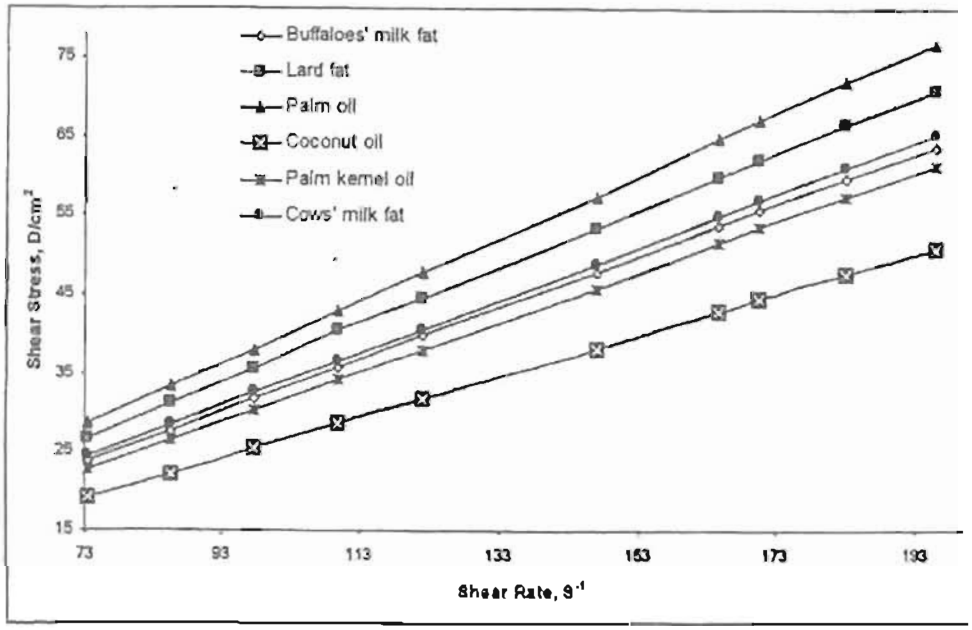

Figure (1): Shear stress of pure fats and oils at different shear rates and at 40°C

Other than the temperature, the fatty acid contents of the sample controls its flow resistance. At a particular shear stress, the shear rate produced by the samples were in the following descending order coconut oil > palm kernel oil > buffaloes' milk fat > cows' milk fat > lard > palm oil. This order was found to follow the sample contents of fatty acids particularly the two long chain palmitic (16:0) and stearic (18:0) fatty acids as modified by the short (6:0, 8:0 and 10:0) and medium chains (12:0 and 14:0) fatty acids. The long chain fatty acids enhance the oil or fat sample flow resistance while the short and medium chains reduce it. According to Table (2), palm oil contained the highest contents of 16:0 and 18:0 (~47%) accompanied with the lowest contents of the short and medium chain groups; therefore, it showed more resistance to flow than any other samples. On the other hand buffaloes' milk fat while contained the second highest concentration (~45%) of 16:0 and 18:0 showed flow resistance far less than lard which contained less of the above acids (~37%). This was because buffaloes' milk fat contained more of the short and medium chains (~9.2%) than lard (~1.6%). Coconut oil which showed the lowest flow resistance contained the lowest concentration of the long chains and the highest concentration of the short and medium chains. Following the same idea of the effect of fatty acids contents on the flow properties of vegetable oils, fatty acids contents were used to estimate their viscosity and the slip melting points (Boyaci *et al.*, 2002 and Boyaci *et al.*, 2003).

Table (2): Fatty acids composition of number of fats and oils[1].

Fatty acid	Coconut oil	Palm kernel oil	Buffaloes' milk fat	Cows' milk fat	Lard	Palm oil
	Fatty acids, g/10					
Short chain	14	7.2	2	1.8	0.1	0
Medium chain	61.4	63.4	7.24	6.63	1.5	1.1
Palmitic (16:0)	8.2	8.1	18	16	23.8	43.5
Stearic (18:0)	2.8	2.8	27	26	13.5	4.3
Total saturated	86	82	54.26	50.5	39	49
Total monounsaturated	6	11	20	20.4	45	37
Total polyunsaturated	2	2	6	5.57	11	9

1- According to William (2003).

Table (3) presents regression equation (Y= *a* + X *b*) with it's constant (*a*) and regression coefficient (*b*) for predicting (significant at $P < 0.001$) the shear rate at any shear stress for the range of temperature used in this work.

Table (3): Prediction of shear rate at any shear stress (regression of Y on X) for the range of temperature used

fat / oil	Equation Constants[1]	Temperature, °C 40	45	50	55	60	65
Buffaloes' milk fat	a	0.5859	-0.5560	-0.3060	-0.3713	-0.2751	-0.8473
	b	3.0616	3.7122	4.3523	5.0987	5.8965	6.7779
Lard	a	-1.2388	-1.5446	0.0509	-0.5837	-0.4316	-0.6310
	b	7.2843	3.3300	3.9130	4.5287	5.2048	5.9903
Coconut oil	a	-0.1279	-2.1480	1.0393	-0.4297	0.5263	-0.2256
	b	3.8512	4.6508	5.3263	6.2897	7.1823	8.2930
Palm oil	a	1.5191	-2.1857	-0.6389	-0.1814	-0.9551	-0.6372
	b	2.5266	3.1042	3.6852	4.3026	5.0057	5.7422
Palm kernel oil	a	1.5777	-0.4818	0.4287	0.1297	0.6714	0.6714
	b	3.1711	3.9433	4.6246	5.4338	6.2560	6.2560
Cows' milk fat	a	-0.0419	-1.5914	-1.6295	-1.1238	-0.7997	-4.2975
	B	3.0094	3.6297	4.2913	5.0009	5.7932	6.6956

1- Y is the depended variable (shear rate, S^{-1}), X is the independed (predictor) variable (shear stress, D/Cm^2), *a* is the constant (Y- intercept) and *b* is the regression coefficient (slope).

Table (4) reports the flow behavior index (*n*) and consistency index (*k*) of the samples at different temperatures as calculated from the power law equation. The samples showed almost similar flow index with a range from 1.01 to 0.97, which is a slight departure into a non-Newtonian behavior particularly at 45°C. The samples differed in their consistency index without overlapping and the differences between the samples were significant at $P < 0.001$ over the temperature range used. However, the largest differences between the samples were at 45°C, which could be used for samples identification. The consistency index significantly decreased by temperature (r = -0.906 at $P < 0.01$).

Table (4): Flow behavior index and consistency index of pure fats and oils.

Samples	Flow behavior index (*n*)			Consistency index (*k*), cp		
	Temperature, °C					
	40	45	50	40	45	50
Buffaloes' milk fat	1.01	0.99	1	31.7	27.9	23.4
Cows' milk fat	1	0.99	0.99	33.7	30	25.2
Palm oil	1.01	0.98	0.99	37.2	35.5	23.6
Coconut oil	1	0.97	1.01	26.6	25	18.1
Palm kernel oil	1.01	0.99	1	29.6	26.3	21.3
Lard fat	1.01	0.99	1	37.1	32.3	25.6

The sample plastic viscosity, viscosity at 10-rpm and viscosity were determined and the results are illustrated in Figure (2), (3) and (4) respectively. The three measurements decreased by temperature with significantly negative correlation of -0.92, -0.914 and -912 ($P < 0.01$) for viscosity, plastic viscosity and 10-rpm viscosity, respectively. Significant differences at $P < 0.001$ existed between the samples for the three parameters over the temperature range used but the highest differences were at 40°C and 45°C temperatures and the values do not overlap.

To determine the feasibility of using these flow properties as constant standards, two buffaloes' milk fat samples, obtained from two different herds, were analyzed and the results are in Table (5). The differences between the two Buffalo samples were insignificant at $P > 0.05$ with the five parameters leading to the conclusion that the two samples were identical. This proved that the five rheological parameters determined were almost constant for the particular fat or oil regardless of sample source and therefore could be used for their identification.

The differences between the values of these five parameters for different fats and oils were the largest when measured at 40 - 45°C and at 196 S^{-1} shear rate therefore these conditions are preferable during identification.

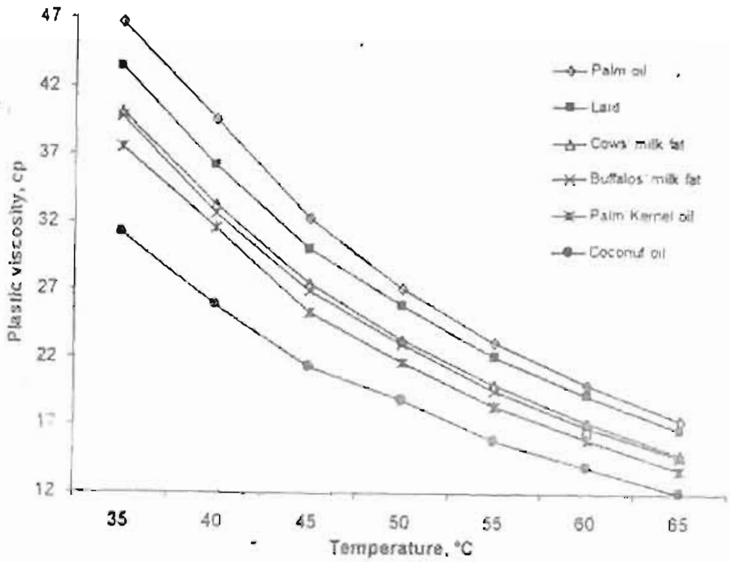

Figure (2): Pure fats and oils plastic viscosity at various temperatures.

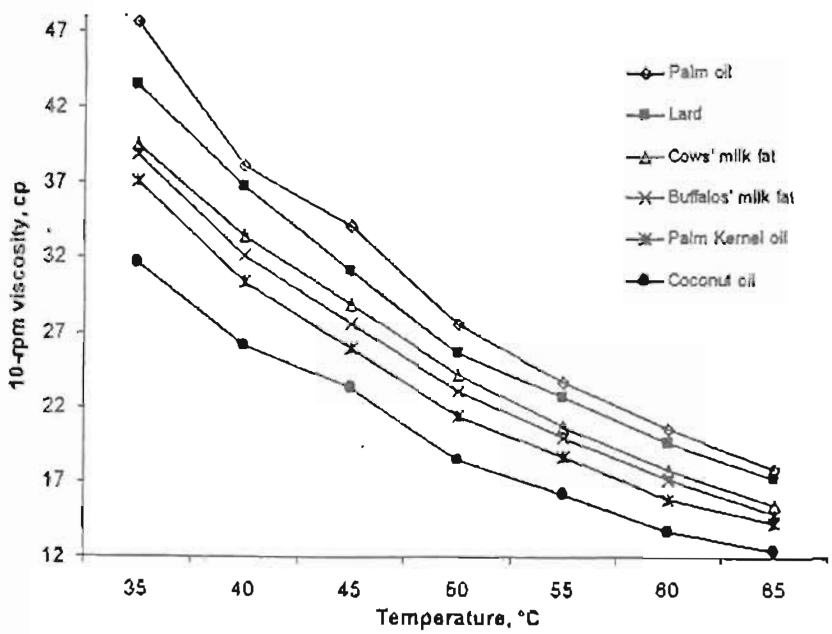

Figure (3): Pure fats and oils 10-rpm viscosity at various temperatures.

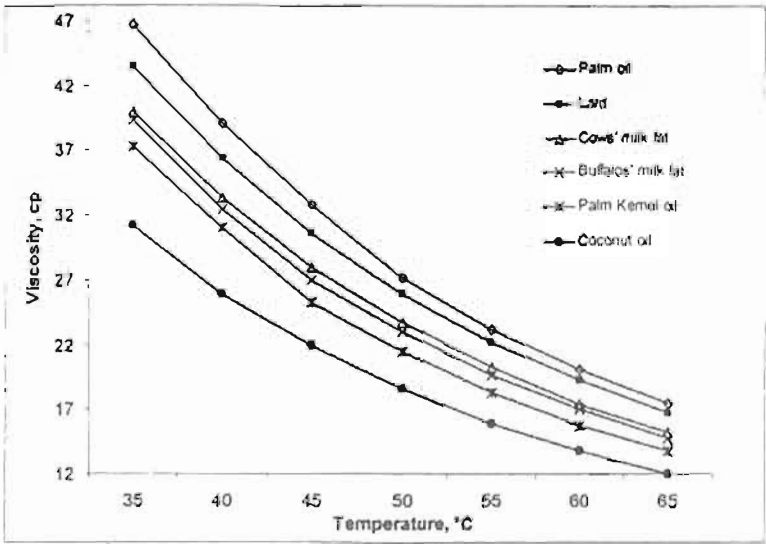

Figure (4): Pure fats and oils viscosity at various temperatures.

Table (5): Flow properties of two different samples of buffaloes' milk fat at various temperatures.

Parameter	Temperature, °C	Sample	
		A	B
Consistency index, cp	40	31.6	31.7
	45	27.8	27.9
	50	17.3	17.3
Shear stress at shear rate 196 S^{-1}	40	62.9	63.6
	45	52.7	52.9
	50	44.7	45
Plastic viscosity, cp	40	32.4	32.6
	45	26.5	26.9
	50	22.8	23
10-rpm viscosity, cp	40	31.8	32.1
	45	27.3	27.6
	50	22.7	23.1
Viscosity, cp	40	32.2	32.4
	45	26.9	27
	50	22.9	23

REFERENCES

Boyaci, I. H.; Karabulut, I. and Turan, S. (2003). Slip Melting Point Estimation of Fat Blends Before and After Interesterification Based on Their Fatty Acid Compositions. J. Food Lipids 10 (3): 193-202.

Boyaci, I. H.; Tekin, A.; Cizmeci, M. and Javidipour, I. (2002). Viscosity estimation of vegetable oils based on their fatty acid composition. J. Food Lipids 9 (3): 175-184.

Herrera, M. L. and Hartel, R. W. (2000). Effect of processing conditions on physical properties of a milk fat model: Rheology. JAOCS 77 (11): 1189-1195.

Paradaker, M. M.; Singhal, R. S. and Kulkarni, P. R. (2001). An approach to the detection of synthetic milk in dairy milk: 4- Effect of the addition of synthetic milk on the flow behavior of pure cow milk. International J. of Dairy Technology 54 (1): 36-37.

Rielly, C. D. (1997). Food rheology. In chemical engineering for the food industry (P. J. Frger, D. L. Plpyle and C. D. Rielly. Ed). Blackie Academic and professional London, UK, first Edition.

William, W. W. (2003). Lipid Analysis. ISBN 0-9531949-5-7. Vol. 15 (William W. Christie, Ed.) The Oily Press Lipid Library. Bridgwater, UK, third Edition.

Wright, A. J.; Scnlon, M. G.; Hartel, R. W. and Marangoni, A. G. (2001). Rheological properties of milk fat and butter. J. Food Sci. 66 (8): 1056-1069.

الخواص الريولوجية لدهن اللبن مقارنة بالدهون الأخرى:
١- النمذجة الريولوجية و خواص التدفق

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من المعروف أن دهن اللبن النقي و كذلك الزيوت و الدهون الأخرى لها تركيب ثابت تقريبا و بالتالي المفروض أن تكون الخواص الريولوجية لها (اللزوجة و خواص التدفق) ثابتة أيضا لذلك كان الهدف من هذة الدراسة هو معرفة مدى ثبات هذة الخواص لكل نوع من هذة الزيوت أو الدهن و بالتالي إمكانية إستخدامها كثوابت طبيعية تستخدم للتعرف عليها و مقارنة هذة الخواص لدهن اللبن بنوعية مع الدهون أو الزيوت الأخرى و التي ينتشر إستخدامها في مصانع الألبان و الأغذية بدرجة كبيرة .

و لمعرفة ذلك تم دراسة خواص التدفق (الإنسياب) لكل من دهن اللبن البقري و الجاموسي النقي و كذلك دهن الخنزير و زيت كل من النخيل و نوى النخيل و جوز الهند و ذلك على درجات حرارة تتراوح مابين ٣٥ – ٦٥ ْم و على معدل قص (قطع) shear rate من ٧٠ إلى ١٩٦ ١/ ث ثم رسمت منحنيات التدفق برسم العلاقة مابين معدل القص و قوة القص shear stress لكل العينات و حسبت بعض المقاييس الريولوجية مثل معامل اللزوجة consistency index (*k*) و كذلك الـ flow behavior index (*n*) واللزوجة البلاستيكية Plastic viscosity و اللزوجة عند سرعة دوران مقدارها 10-rpm و ذلك من المعادلات الرياضية الخاصة بكل نموذج.

أثبت النتائج أن هذة المقايس كانت مختلفة لكل زيت أو دهن إختلافا معنويا كبيرا ($P < 0.001$) على كل درجات الحرارة و لكن كان أكبر فرق على درجات حرارة ٤٠ – ٤٥ ْم.

كما تم تقدير وحساب هذة المقاييس لعينتين من دهن اللبن الجاموسي من مصدرين مختلفين لمعرفة مدى ثبات هذة المقاييس لنوع الزيت أو الدهن الواحد و اثبتت النتائج عدم وجود إختلافات معنوية بينهما. مما يدل على ان هذة المقاييس يمكن إعتبارها من الثوابت الطبيعية للدهون أو الزيوت و بالتالي يمكن إستخدامها في التعرف Identification على نوعية هذة الزيوت أو الدهون.