

Comparative Study of Rheological Characterization and Classification of Honeys with Their Physicochemical Properties

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Abstract—This study explores the application of rheology as a tool for assessing “honey” samples for authenticity and quality. Honey was serially diluted to different percentages of sucrose and each was analysed rheologically at different temperatures to obtain calibration curves for subsequent evaluation of different “honey” samples. Levels of adulterations were determined for honey samples in Nigeria. Pure honey exhibits shear thinning rheological behaviour while the behaviour of sucrose melt tends towards Newtonian. The rheological profiles of samples were determined using RV DV-III Ultra Programmable Rheometer at low shear rate (0.1 - to 2.45S^{-1}). The Power law and Carreau Yasuda models provided good correlations of the data. The Carreau Yasuda model gave a better fit with pure honey while Power law model correlates better with sucrose melt. Proximate and Chromatographic characterizations of honey which provide acceptable measures of honey quality corroborated the conclusions derived from the rheological characterization of this study.

Index Terms—Honey, Rheology, Power law model, Carreau-Yasuda model, sucrose adulteration

I. INTRODUCTION

Honey is a sweet fluid produced by bees from the nectar of flowers. Fluids like honey flow when subjected to shear. How they respond to input stress is at the heart of rheological testing and may be a complex issue. The composition of a material is the determining factor of its rheology. When this composition is altered, either by changing the proportion of the component substances, or by the addition of other materials, a change in its rheological properties is quite likely to occur [1].

There are many types of fluids which may be pure substances, mixtures, dispersions and/or solutions. They fall into categories of either simple or structured fluids [2]. Each has its own unique behaviour when subjected to shear. Materials which are made up of more than one phase, such as solid particles dispersed in a

liquid, oligomers in solutions, and gas particles in a foam or emulsion of immiscible liquids are considered structured fluids. Honey and most food materials belong to the category of structured fluids [3].

Structured fluids do not obey simple linear relationship between applied shear stress and shear rate. Nearly all these materials have their viscosities decreasing with increasing shear. This phenomenon of shear thinning becomes progressively larger as the volume concentration of particles increases. The measured rheological responses reflect the macroscopic state of the fluid. There are however, affected by changes and properties at the molecular and microscopic level. A major challenge is to establish links between macroscopic rheological properties with changes at the molecular and microscopic levels [4]. Rheological data on honey together with data on its composition and structure should lead to understanding the relationship between them. In turn such knowledge should lead to the improvement in the assessment of the integrity of honey presented for consumption through the development of cheap rheological methods. The quality of the samples using already established physicochemical and chromatographic analyses shall be determined. The results of the analyses shall be compared with that obtained using rheological characterization. Adebisi *and coworkers* [5] and Ayansola and Banjo, [6] characterized Nigerian honey using their physicochemical properties. Physicochemical and hydroxymethylfurfural components of honey have been used as a means of differentiating fresh and newly prepared honey from aged and adulterated samples [7], [8].

The rheological characterization of polymers and polymers in dilute solutions is well established and so could be adopted to characterize honey since honey contains some oligomers. It has been reported that honey contains as high as 11% Melezitose which is an oligomer [3], [9]-[11]. This Melezitose content, therefore, easily supports rheological profiling required here since threshold for reflection of non-Newtonian behaviour starts from about 2% [12], [13].

A few studies have previously presented the rheological characterization of honey. Bera *and coworkers* [1] studied some physicochemical and rheological properties of irradiated honey. James *and coworkers* [14] worked on physical characterization of some honey samples from North-Central Nigeria. Also, DaCosta and Pereira, [15] undertook the rheological analysis of honey and propolis mixtures.

The objective of this work is to rheologically characterize, pure honey, adulterated honey to varying degrees and imitation honey samples at different temperatures to obtain their baseline behaviour and to analyze the data for compositional and structural information. Furthermore, is to establish a possible correlation of chromatographic and proximate characterization of honey with its rheological data.

II. THEORITICAL BACKGRAUND

This section presents the Carreau-Yasuda model (CYM) and Power Law model (PLM) used in the correlation of the effect of adulteration on rheology of honey.

A. Carreau-Yasuda Model [16]:

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_0 - \eta_{\infty}) [1 + (\lambda \dot{\gamma})^a]^{\frac{n-1}{a}} \quad (1)$$

This empirical model has five adjustable parameters, α , λ , n , η_0 , and η_{∞} .

This model describes non-Newtonian time dependent flow with asymptotic viscosities at zero shear rate (η_0) and infinite shear rate (η_{∞}), with no *yield stress*. The parameter λ is the viscous relaxation time that defines the location of the transition from shear-thickening to shear-thinning behaviour, while $1/\lambda$ is the critical shear rate at which viscosity begins to decrease. The power-law slope is $(n-1)$. The value of 'n' changes with the composition of the fluid. The parameter ' α ' is dimensionless parameter (sometimes called "the Yasuda constant" since it is a parameter added to Carreau equation by Yasuda) which describes the transition region between inception of flow and the power-law region and it is inversely related to the breadth of the zone.

B. Power Law Model

In most Polymeric fluids, the coefficient of viscosity is not constant, but is a function of the shear rate. Such fluids may be modeled by means of the Power Law equation [17]. Power law equation is given as:

$$\eta = \eta_0 \dot{\gamma}^n \quad (2)$$

where, η is the consistency coefficient or dynamic viscosity (mPa.s) while η_0 is the zero shear viscosity (mPa.s). n is the power law index (dimensionless).

III. MATERIALS

In our sample collection and preparation a wide variety of twenty samples of honey were collected from different geographical locations in Nigeria. Control samples A1 and A2 were harvested and processed to ensure purity. Other samples of "honeys" were purchased from Gauraka, Yola, Zuru, Oloru, Keffi, Lokoja, Kabba, Ondo, Afao- Ekiti, Ado-Ekiti Nsukka, and Lagos. Sucrose E1 (produced by heating to brown colour and then dissolving three parts of sucrose in one part of distilled water) was used during the adulteration of pure honey sample A1 to produce adulterated samples E2 (10% adulteration), E3 (50% adulteration), E4 (70% adulteration) and E5 (90% adulteration).

IV. METHODS

Characterisation of honey and adulterated samples were done using two models as given in this section.

A. Rheological Analyses

The rheological characterisation of the samples was carried out using Brookfield RV DV-III Ultra Programmable Rheometer. The measurements were done at room temperature of 27 °C and then at 35 °C. Room temperature was chosen because honey is eaten and stored at that temperature. Also 35 °C was chosen because heat destroys honey at temperatures above 40°C [19]. The equipment thermometer was always dipped inside the fluid before the measurements began for temperature control. The DV III Program mode was used. The shear rates of 0.0 to 2.45S⁻¹ were chosen at incremental steps of 0.1s⁻¹. The samples were allowed to stand in the container for at least 30 minutes before the measurements to allow for complete structural recovery from the structural distortion induced by flow into the container. The parameters of the Power Law model were extracted using least squares analysis. Carreau-Yasuda model was also used to correlate the results using non-linear regression iterations in Micro soft Excel solver. The experimental measurements were repeated after 24 hours to determine if the results were repeatable.

B. Chromatographic and Proximate Analyses of Honey

A chromatographic analysis of honey was done to determine the quantity of hydroxymethylfurfural (HMF) in honey. The Jeuring and Kuppers [20] chromatographic experimental technique was used. Proximate and physicochemical characterization of samples was also performed as independent assessment such that the results can be compared with the rheological characterization. The determination of Carbohydrate content of samples was done using the method of Dreywood, 1946 [21]. The Protein Content of samples was determined by Kjeldahl analysis outlined by AOAC [22]. Determination of Vitamins A and C (Ascorbic Acid) was done by Revanasiddappa and Veena, [23] method.

The pH, Refractive Index, Density, and water content determination was done using AOAC [22] experimental methods. Elemental Analyses was carried out using Atomic Absorption Spectrophotometer with method outlined by International Atomic Energy Agency [24].

V. RESULTS AND DISCUSSION

A. Rheology

This characterization and modeling of rheological data of honey samples at low rates of shear using both Power law and Carreau Yasuda models is aimed at gaining more insight into the molecular and structural orientation of the samples through their deformational parameters. The rheological data obtained are used to distinguish pure from adulterated honey or to classify samples according to the level of their purity. The rheological signatures of pure honey samples A1 and A2, at 27 °C are shown in Fig 1. It can be seen that both samples followed a very similar pattern of flow. The samples first exhibited shear thickening behaviour at very low shear rate and then predominantly shear thinning behaviour as shear progresses. Kurzberck and coworkers, [25] suggested that the presence of chain branches gave rise to strain hardening which is a necessary property for stability of polymers undergoing deformation. Triantafillopoulos, [26] while interpreting rheograms of polymers in solutions suggested that at rest, or under low rates of shear, particles of the fluid fit into voids of adjacent layers of flow. As flow progresses, the particles begin to slide over the adjacent layers since they can no longer fall into the voids.

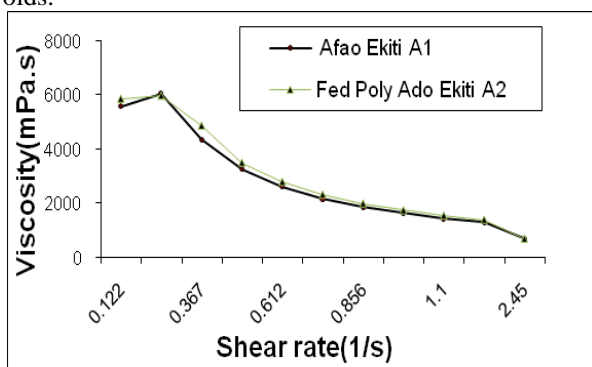


Figure 1. Pure honey samples A1 and A2 at 27 °C

Under this circumstance, resistance to flow increases, which causes the fluid to behave in a solid-like manner thereby inducing the shear thickening behaviour, isothermally and reversibly at the beginning of the rheological signatures. Likewise, suspension and colloidal structures resist deformation and sometimes flow does not even occur until reversible destruction of internal network is completed [2].

At a shear rate of 0.245 s^{-1} a peak was observed after which shear thinning behaviour commences. Franck, [2] suggested that viscosity peak is pronounced if the polymeric material at rest behaves in a viscoelastic manner and the viscosity build-up competes with viscosity decrease due to structural breakdown. At higher

shear rate, Triantafillopoulos, [26] explained the shear thinning behaviour to be as a result of isothermal and reversible breaking of structures in the fluid. The clusters and aggregates of particles originally present in colloids or suspensions are reversibly altered by shear. Some other researchers also reported cases of viscosity decrease with increase in shear rate. Adekunle, [27], Sopade *et al.*, [10], Olanrewaju, [28] and Anidiobu, [19] all reported cases of shear thinning behaviour of honey.

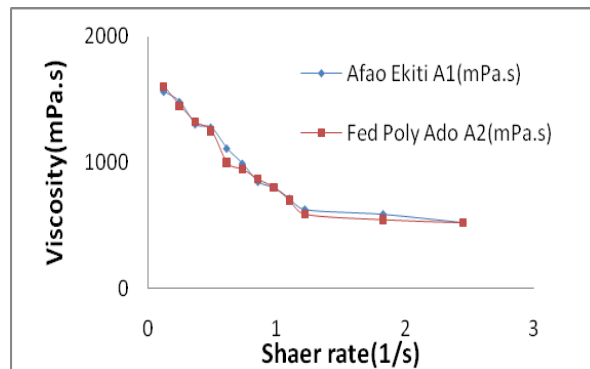


Figure 2. Pure honey Samples A1 and A2 at 35 °C

Fig. 2 shows the effect of high temperature on pure honey rheology. It can be observed that viscosity of the two pure honey samples decrease with increasing temperature. At shear rate of 1.22 S^{-1} and viscosity of 589 (mPa.s) the pure honey samples from Nigeria reached a breaking point at which the viscosity of honey tends towards Newtonian. This was why low shear rate rheology was chosen for these analyses where the observed rheology is governed by molecular interactions of the fluid during deformation so that the properties of the samples at the inception of deformation could be captured.

Fig. 3 shows the effects of adulteration with sucrose on the rheology of honey at 27 °C. It can be inferred from the plots that addition of different percentages of adulterant to pure honey (sample A1) led to decrease in the viscosity of the resulting samples up to sample E5. This simply shows that rheology of honey is dependent on its composition [1]. The rheograms show that the viscosity of sample E1 changed minimally with increase in shear rate. This suggests that the rheology of sucrose tends towards Newtonian.

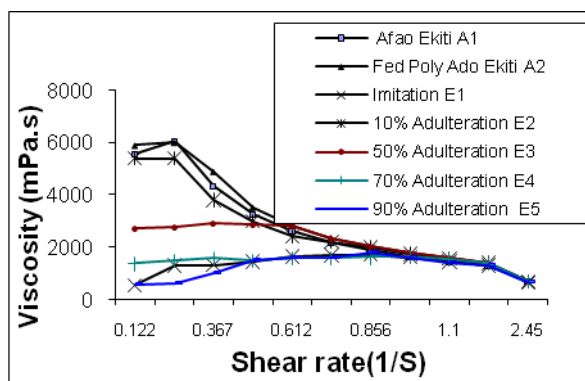


Figure 3. The Effect of Adulteration on the Rheology of Honey at 27 °C

Figs. 4 and 5 are the rheograms of “honey” from North and South of Nigeria. The results of Power law and Carreau-Yasuda curve fit in Tables I, II and III were extrapolated to characterize samples from Northern and Southern Nigeria at room temperature as shown in Table IV. Fig. 6 is the Power Law curve fit of sample A1 at 27 °C. In Power law model, the value of power law or behaviour index, n and zero shear viscosity η_o are very important rheological parameters since they have direct correlation with the structural and molecular orientation of the sample. The behaviour index was mainly utilized as the distinguishing factor for the samples in this analysis as suggested by DeLaney and Reilly, [12].

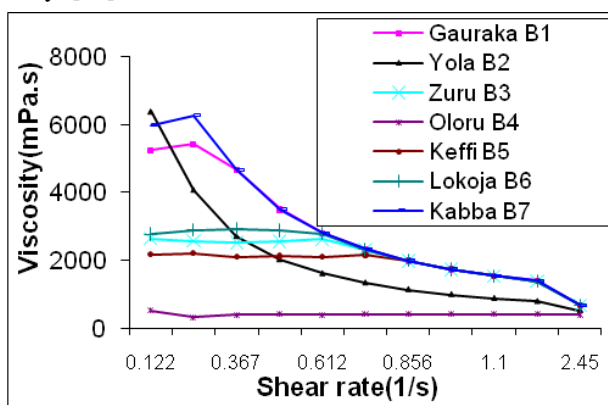


Figure 4. The rheograms of samples from northern Nigeria at 27 °C

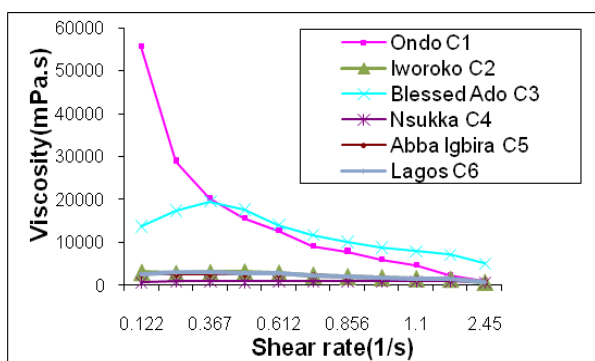


Figure 5. The rheograms of samples from southern Nigeria at 27 °C

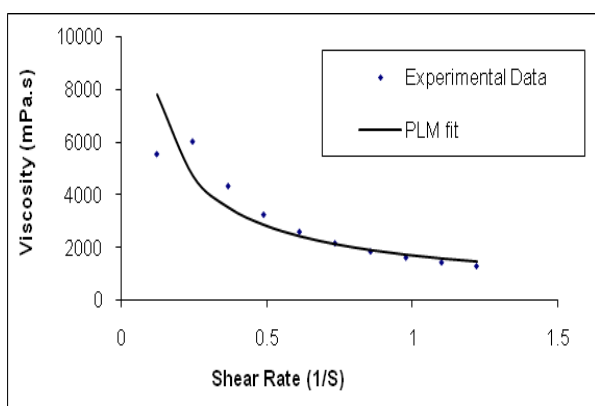


Figure 6. Power law curve fit of pure honey A1 at 27 °C

Fig. 7 is the Carreau-Yasuda correlation of pure sample A1 at 27 °C. The behaviour index in CYM depends also on the composition of the fluid. The value of 0.001 in table 2 suggesting a shear thinning behaviour was obtained for pure Sample A1 at 27 °C.

A look at the plot shows that the difference between the experimental and correlated viscosities at the inception of deformation was negligible suggesting this model as a good tool to calculate the average molecular weight of samples from the rheological data when Mark Houink equation is incorporated to it. This was explored in our paper published earlier [29].

A comparison of Power Law and Carreau Yasuda models shows that the Carreau-Yasuda model better correlated the rheology of pure sample A1. Figs 8 through 11 are the Power law and Carreau Yasuda rheological correlation of some sucrose-adulterated samples and the details of the results are shown in tables 1 - 3. Table I is the rheological correlation results using Power Law model. The behaviour index of samples increases with increasing adulteration of honey. On the other hand, the zero shear viscosity decreases with increasing adulteration. Tables II and III are the results of rheological correlation using Carreau-Yasuda model at 27 °C and 35 °C respectively.

TABLE I. SUMMARY OF RHEOLOGICAL CORRELATION RESULTS USING POWER LAW MODEL

S/N	Samples	nat 27°C	η_o at 27°C	nat 35°C	η_o at 35°C
1	A1	0.29	1656.96	0.60	785.67
2	A2	0.27	1692.17	0.58	767.85
3	E1	1.30	1051.46	1.31	1054.17
4	E2	0.31	1629.00	0.75	560.32
5	E3	0.57	1503.40	0.95	1074.50
6	E4	0.82	1216.20	1.02	861.43
7	E5	1.12	964.65	1.33	1057.91
8	B1	0.29	1654.68	0.67	1410.39
9	B2	0.31	496.05	0.66	1387.20
10	B3	0.58	1470.01	0.95	1074.78
11	B4	1.02	420.50	0.88	292.21
12	B5	0.65	1400.16	0.95	1077.29
13	B6	0.56	1511.52	0.76	563.82
14	B7	0.26	1694.46	0.77	1284.62
15	C1	0.02	4180.63	0.59	787.60
16	C2	0.54	1530.63	0.76	565.86
17	C3	0.70	5697.20	0.30	1734.48
18	C4	0.25	1199.91	0.58	608.98
19	C5	0.62	1444.83	0.58	766.80
20	C6	0.56	1515.19	0.88	1121.68

After rheological characterization of the pure, adulterated and imitation honey using both Power law and Carreau- Yasuda models, it was observed that the results obtained followed a consistent pattern which was helpful in classifying other samples according to the level of their purity. If “ n ” is equal to 1, the fluid is Newtonian, if “ n ” is less than 1, the fluid is shear thinning and if “ n ” is greater than 1, it is then shear thickening. The results of serially diluted samples were extrapolated to classify samples from other locations in Nigeria as shown in Table IV. Samples B1, B7, and C4 are pure. This is so because in the Power law correlation at room temperature, the behaviour index which depends on the composition was found to be 0.29 for control sample A1. The results

of 0.29, 0.26, and 0.25 were also obtained for samples B1, B7 and C4 respectively which have the least deviations from the result of the control sample from Table I.

Likewise the behaviour index “n” for control sample A1 was found to be 0.60 at 35 °C which is quite close to (least deviation) 0.67, 0.77 and 0.58 obtained for B1, B7 and C4 respectively.

TABLE II. RHEOLOGICAL CORRELATION OF SAMPLES AT 27°C USING CARREAU-YASUDA MODEL

S/N	Samples	n at 27°C	η_0 at 27°C	η_∞ at 27°C	a at 27°C
1	A1	0.001	5788.20	60.00	144.88
2	A2	0.057	5943.96	67.26	74.60
3	E1	1.071	507.28	0.00	13.80
4	E2	0.127	5400.14	54.00	114.07
5	E3	0.250	2818.87	43.00	217.71
6	E4	0.500	1542.55	32.12	422.18
7	E5	1.002	219.11	12.18	55.88
8	B1	0.038	5341.60	56.69	15.09
9	B2	0.400	4637.92	0.00	10.00
10	B3	0.276	2579.28	0.00	323.07
11	B4	1.000	417.20	43.61	9.70881
12	B5	0.260	2164.79	381.70	238.83
13	B6	0.140	2881.26	198.72	160.80
14	B7	0.003	6138.99	6.51	106.36
15	C1	0.010	55591.17	718.66	103.92
16	C2	0.003	2944.43	2.30	103.87
17	C3	0.260	16452.84	28.64	184.24
18	C4	0.001	4941.43	80.56	166.78
19	C5	0.270	2406.58	23.40	97.68
20	C6	0.015	2955.68	19.19	56.29

TABLE III. CARREAU-YASUDA MODEL PARAMETERS FOR SAMPLES AT 35°C

S/N	Samples	n at 35°C	λ (s)	η_0 at 35°C	a at 35°C
1	A1	0.687	3.62	13179.82	0.14
2	A2	0.680	4.85	15569.99	0.13
3	E1	1.700	0.01	845.0840	5.74
4	E2	0.705	18.00	1085.367	10.00
5	E3	0.900	0.50	1214.830	34.48
6	E4	1.001	26.30	804.8220	49.44
7	E5	1.656	0.00	833.7286	1.87
8	B1	0.402	1.28	2135.955	89.09
9	B2	0.975	123.74	7397.984	0.282
10	B3	0.939	0.70	1207.955	13.69
11	B4	1.451	4.69	349.3389	57.09
12	B5	0.923	0.79	1220.833	405.25
13	B6	0.719	18.13	1112.314	13.03
14	B7	0.600	0.99	1691.760	275.00
15	C1	0.670	0.11	2014.538	0.43
16	C2	0.799	194.45	1729.882	51.25
17	C3	-0.015	3.82	6765.380	7.655
18	C4	0.692	2.64	1458.703	0.74
19	C5	0.694	0.08	1569.537	0.54
20	C6	0.829	0.51	1326.444	14.20

TABLE IV. CLASSIFICATION OF HONEY SAMPLES BASED ON THE RESULTS OF POWER LAW AND CARREAU YASUDA MODEL

Standard	Classification	Samples
A1,A2	Pure	B1,B7,C4
E2	10% Adulterated	B2,C2
E3	50% Adulterated	B3,B5,B6,C1,C3,C5,C6
E4	70% Adulterated	
E5	90% Adulterated	
E1	Imitation	B4

In the rheological modeling using Carreau Yasuda model, the value of 0.001 was obtained for the control

sample A1 which is quite close to 0.038, 0.004 and 0.001 obtained for B1, B7 and C4. Following the same trend, Table 4 shows that samples B2 and C2 conform closest to 10% adulteration. Samples B3, B5, B6, C6, C3, and C5 conform to about 50% adulteration while sample B4 conform to 100% imitation (E1).

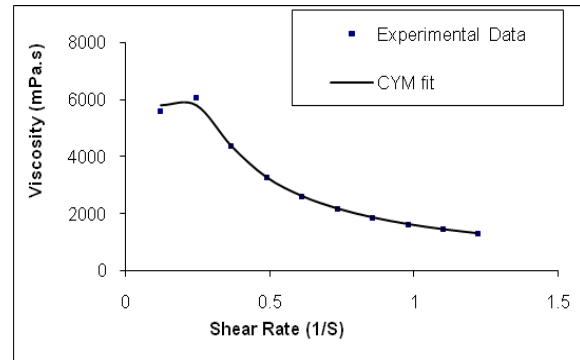


Figure 7. Carreau yasuda curve fit of pure honey A1 at 27 °C

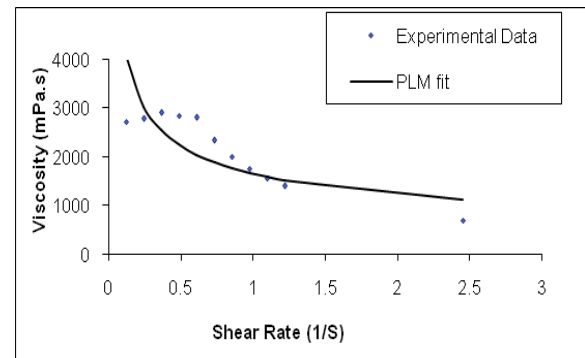


Figure 8. Power law curve fitting of sample E3 at 27 °C

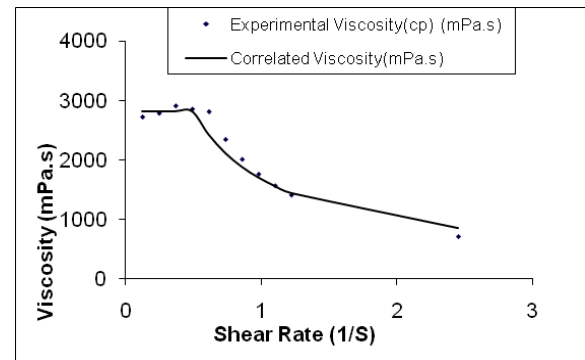


Figure 9. Carreau yasuda curve fitting of sample E3 at 27 °C

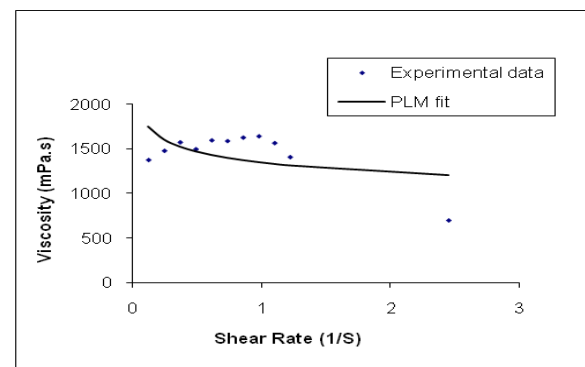


Figure 10. Power law curve fitting of sample E4 at 27 °C

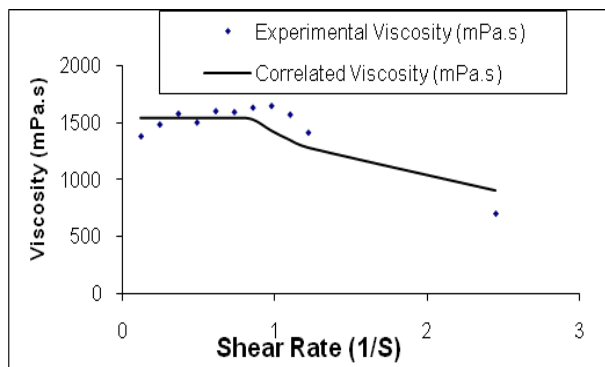


Figure 11. Carreau yasuda curve fitting of sample E4 at 27 °C

B. Chromatographic Characterization

EZChrom Elite Custom Report

Page 1 of 1

Sample ID: STD1
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 User: lab manager
 Acquired: 5/14/2013 2:16:01 AM
 Printed: 5/17/2013 12:16:35 AM

NAFDAC DAD REPORT

DAD-CHI 285 nm Results					
PK #	Name	Retention Time	Area	Units	concentration
2	HMF	4.073	2475945	mg/100ml	0.001 CAL

DILUTION FACTOR: 1
 MULTIPLIER: 1
 VIAL: 1

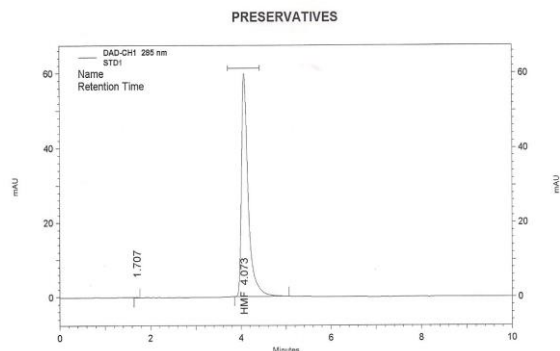


Figure 12. Chromatograph of pure hydroxymethylfurfural

This phase of study seeks to establish a possible correlation of chromatographic characteristics of honey with its rheological data. Figs 12 and 13 are the chromatographs of pure HMF and honey. In the chromatograph, absorbance is plotted against retention time of samples. Retention time is the time it takes for a compound to elute from the column after injection. The retention time of pure HMF in Fig. 12 is 4.073 minutes. In Fig. 13, the amount of HMF in pure honey is quantified by comparing the peak areas of HMF content in pure honey and standard HMF used. The result of 23.985mg/kg obtained is below the Codex Alimentary threshold of 80mg/kg confirming that sample A1 is pure honey. The 5-hydroxyl methyl furfuraldehyde content in honey samples is a measure of freshness, adulteration or heat treatment of honey. 5-hydroxyl methyl furfuraldehyde is formed in honey during acid-catalyzed thermal dehydration of hexoses (fructose and glucose) occasioned by disequilibrium introduced by the

adulterating material, storage or heat treatment of honey [30]. In Table Va, samples A2 (Federal Polytechnic Ado-Ekiti), B1, B7 and C4 all passed this test. Sucrose (E1) gave furfural content of 302.5mg/kg. The adulteration of pure honey sample A1 with 10% sucrose (E2) lead to higher furfural content of 88.91mg/kg. 50% adulteration of pure honey with sucrose raised the furfural content to 201.22mg/kg. Also, 70% adulteration further increased the furfural content to 220.34mg/kg while 90% adulteration with sucrose took the furfural concentration to 288.75mg/kg. This could be attributed to the rich hydroxymethylfurfural content in the sucrose used to serially dilute the pure honey. The high content of the furfural in sucrose adulterant could be attributed to enzyme, Invertase (Saccharase and α -glucosidase) which lead to decomposition of sucrose to glucose and fructose, thereby releasing hydroxymethylfurfural as a by-product of further dehydration of glucose and fructose in the presence of good acidic medium and high temperature. There is a need to look at the proximate composition of samples to gain more insight on their composition so as to correlate our earlier rheological results.

A₄

EZChrom Elite Custom Report

Page 1 of 1

Sample ID: FC13944
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 Acquired: 5/14/2013 4:53:10 AM
 Printed: 5/17/2013 12:12:23 AM

NAFDAC DAD REPORT

DAD-CHI 285 nm Results					
PK #	Name	Retention Time	Area	Units	concentration
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DILUTION FACTOR: 1
 MULTIPLIER: 4994.36
 VIAL: 6

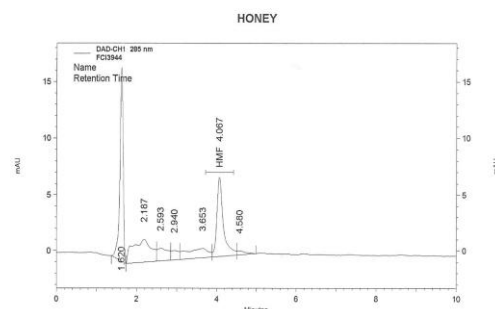


Figure 13. Chromatograph of honey from sample A1

C. Proximate and Physicochemical Characterization

Tables Va and Vb contain the proximate and some physicochemical parameters of samples. The protein content of honey has been used for a long time as an index of quality [31], [32]. This trace quantity of protein was introduced into the honey from pollens from the flowers and during regurgitation of nectar in the stomach of bees while processing in the comb. Bognadov and coworkers, [30] recommended a minimum protein content of 1.25 wt.% for pure honey. Looking at the results in table 5a, pure samples A1 and A2 gave protein content values of 1.869 and 1.825 wt.% suggesting that they are pure. These results also conform

to that of Odeyemi *and coworkers*, [31] that gave the protein concentration of the Nigerian honeys from 1.625 to 3.375 wt%. Likewise, Agunbiade *and coworkers*, [32] gave the protein concentration of the Nigerian honeys as 1.43 to 2.72 wt. %. In the rheological characterization of samples, it was concluded that samples B1, B7 and C4 behaved rheologically like our pure samples. The results of protein content of these three samples coincidentally were 1.956 wt% and so falls within the standard recommended [30].

On the other hand, honey samples B2 and C2 were adjudged to be 10% adulterated by rheological characterization. The results below show that samples B2 and C2 have protein contents of 1.563 and 1.563% respectively. These results though they are lower than the pure samples are still within the protein content limit for pure honey. This simply suggests that rheology could be a bit more sensitive than the protein content analyses in honey as it detects adulteration where protein content analysis is slightly blind or insensitive. It is hereby suggested that the standard be changed for the Nigerian honey to 1.800 to 3.125 wt% based on the results in Table Va. Samples B3, B5, C6, C3, and C5 were adjudged to be 50% adulterated. Their protein content values of 1.237, 1.094, 1.244, 1.169 and 1.093 wt.% were off the minimum standard of 1.25wt.%. Similarly it was shown rheologically that sample B4 was an imitation honey. Therefore the value of 0.256 wt. % obtained is similar to that of sucrose (E1): 0.394 wt.%. These results have corroborated the rheological characterization results earlier obtained and show that rheology is an effective tool to determine quality in honey.

TABLE VA. CHROMATOGRAPHIC, PROXIMATE ANALYSES AND PHYSICOCHEMICAL PROPERTIES RESULTS

S/N	Sample Code	Sample Name	HMF	%NH ₂	%CHO	%Vit A
1.	A1	Ayo Bee Farm Ado-Ekiti	23.99	1.869	80.41	0.01
2.	A2	Federal Poly Ado-Ekiti	60.90	1.825	78.63	0.02
3.	B1	Gauraka Niger State	23.98	1.956	81.44	0.01
4.	B2	Yola Adamawa	59.22	1.563	82.33	0.02
5.	B3	Zuru Sokoto	66.10	1.237	81.21	0.01
6.	B4	Oloru Kwara	1469.50	0.256	74.33	0.03
7.	B5	Keffi Nasarawa	6.93	1.094	79.34	0.02
8.	B6	Lokoja Kogi	55.50	1.406	82.64	0.04
9.	B7	Kabba Kogi	35.31	1.956	81.56	0.03
10.	C1	Sunshine honey Ondo	18.58	3.125	79.33	0.02
11.	C2	Real Oasis Ekiti	7.45	1.563	79.78	0.02
12.	C3	Blessed Ado-Ekiti	111.27	1.169	79.88	0.03
13.	C4	Nsukka Enugu	75.74	1.956	77.32	0.03
14.	C5	Abba Igbira	86.37	1.093	80.78	0.04
15.	C6	Lagos	53.74	1.244	79.33	0.03
16.	E1	Sucrose	302.50	0.394	77.99	0.04
17.	E2	10% Sucrose Adult.	88.91	1.250	79.40	0.02
18.	E3	50% Sucrose Adult.	201.22	0.919	78.75	0.03
19.	E4	70% Sucrose Adult.	220.34	0.575	78.23	0.03
20.	E5	90% Sucrose Adult.	288.75	0.444	78.09	0.04

TABLE VB. PROXIMATE ANALYSES AND PHYSICOCHEMICAL PROPERTIES RESULT

S/N	Sample Code	Sample Name	%Vit C	%H ₂ O	Density (kg m ⁻³)	pH
1.	A1	Ayo Bee Farm Ado-Ekiti	0.09	18.2	1420.0	3.3

2.	A2	Federal Poly Ado-Ekiti	0.11	20.9	1409.8	3.4
3.	B1	Gauraka Niger State	0.15	17.8	1403.8	3.9
4.	B2	Yola Adamawa	0.06	16.2	1410.4	3.9
5.	B3	Zuru Sokoto	0.11	18.2	1410.8	3.9
6.	B4	Oloru Kwara	0.02	24.6	1380.2	3.5
7.	B5	Keffi Nasarawa	0.08	19.4	1425.4	4.3
8.	B6	Lokoja Kogi	0.07	15.5	1400.0	3.9
9.	B7	Kabba Kogi	0.06	17.8	1435.0	4.0
10.	C1	Sunshine honey Ondo	0.25	19.8	1396.4	3.9
11.	C2	Real Oasis Ekiti	0.11	19.4	1396.4	3.7
12.	C3	Blessed Ado-Ekiti	0.23	17.8	1439.0	3.6
13.	C4	Nsukka Enugu	0.04	22.6	1408.7	3.7
14.	C5	Abba Igbira	0.23	18.6	1396.4	3.9
15.	C6	Lagos	0.16	20.2	1309.6	3.4
16.	E1	Sucrose	0.84	19.4	1398.0	4.4
17.	E2	10% Sucrose Adult.	0.20	19.4	1400.0	3.9
18.	E3	50% Sucrose Adult.	0.34	19.4	1409.0	3.9
19.	E4	70% Sucrose Adult.	0.53	19.4	1404.0	4.1
20.	E5	90% Sucrose Adult.	0.79	19.4	1400.2	4.2

The total carbohydrate content of samples in Table Va did not follow any definite pattern and cannot be said on its own to be an index of quality. However Codex Alimentarius [33] recommended that reducing sugars in honey should be more than 60%. This cannot be used as an index of quality here since all the samples passed this test. Likewise the vitamin A and C contents of samples did not follow a definite order.

According to [33], the moisture content of honey should not be above 21%. In table 5b almost all our samples conform to this specification with the exception of samples B4 (Oloru, Kwara) and C4 (Nsukka, Enugu). It will be recalled that B4 was adjudged earlier to be a fake honey. The value of 22.6% recorded for sample C4 suggests that it has more water than it should have. It is good to point out that every case like this may not be that of water adulteration but the season of harvest, ripening level and climate of region can have impact on the water content of honey.

The density of honey is another reflection of intrinsic quality of the sweetener. The density of pure honey is from 1403.8 to 1420 kg/m³. A similar result was obtained for the Pakistani honey (1400 to 1500 kg/m³) by Rehman *and coworkers*, [34]. When the density profile of honey in a particular region is noted, it could be easy to tell by aid of density measurement whether honey is adulterated or not. However one limitation of this method is water content which equally influences the density of samples.

The pH of our samples ranges from 3.3 to 5.1 in Table Vb. This is similar to standard recommended by Codex Alimentarius which ranges from 3.2 to 5.5. Rehman *and coworkers*, [34] also obtained similar results which is from 3 - 5 for the Pakistani honey. It can be seen that all the samples passed this test including the suspected adulterated samples. However, it was observed that the pure samples have lower pH than the suspected adulterated ones. Also, it was observed that the higher the levels of adulteration of honey with sweeteners, the higher the pH of the resulting fluids.

VI. CONCLUSION

Rheology is a sensitive tool for honey characterization since flow behaviour correlates closely with

compositional changes in honey. The viscosity of honey decreases as shear rate increases over time. Pure honey exhibited shear thinning flow pattern, while sucrose solution exhibited near Newtonian flow behaviour at very low shear rate. The increase in sucrose content in honey drags its viscosity towards Newtonian. The rheology of honey is a function of temperature as flow became linear at high temperature up to a point when the flow tends towards Newtonian. Two rheological models, Power law and Carreau Yasuda models were employed to fit the rheological parameters of honey samples. The Carreau Yasuda model correlated better with the rheology of honey. The protein content of honey decreased sequentially with increase in adulteration in the serial diluted samples. Therefore protein content results of pure, adulterated and fake samples have further correlated the earlier rheological results confirming that indeed rheology can serve as an index of quality in honey.

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