

SOLUTION TO HONEY ADULTERATION IN NIGERIA: A RHEOLOGICAL METHOD

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Presentation Outline

- Introduction
 - Rheology
 - Statement of the Problem
 - Aim and Objectives
 - Significance of the Study
- Theoretical Background
 - Structural Kinetic Model
 - Improved Carreau Yasuda Model
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 - Rheological Modeling
- Results and Discussion
- Conclusion/Recommendations

Introduction

▶ Honey

- Formation
- Uses

▶ Rheology

- Simple fluid
- Structured fluid

Statement of the Problems

- Honey can only be produced by bees
- There is High demand for honey
- Honey is expensive
- Illicit Adulteration of honey to meet up with demands. The demand for honey in 2010 was 1.5 Million ton while the supply was 2 Million ton (FAO,2012).
- Conventional methods of Adulteration detection is expensive and time consuming
- Rheology

Aim and Objectives of the Study

▶ The aim of this study is to develop a test method based on rheology that can differentiate pure from adulterated honey.

▶ **Objectives of the Study**

- i. To explore the efficacy of utilizing honey rheology to assess its purity.
- ii. To extract structural and compositional information from the rheological data.
- iii. To validate the results of rheological characterization using established test methods.
- iv. To establish rheological characterization as a testing method for honey quality.

Scope and Delimitations of the Study

For this study, honey samples were collected from different regions in Nigeria between February 2010 and November, 2012 .

Significance of the Study

- i. High demands for honey and low supply for the product promotes adulteration.
- ii. Existing methods for honey quality assessment are expensive and time consuming.
- iii. The rheological method for quality assessment of fluids will be desirable being economical and simple.
- iv. This study establishes the efficacy of rheological assessment for honey.
- v. The test method deriving from this study will find application in the quality assessment of other fluids.

Theoretical Background

The Structural Kinetic Model

- Structured state \rightarrow Non Structured state (1)
- It is assumed that the change in the rheological behaviour is associated with shear-induced breakdown of internal structure of pure honey.
- This model will assume in accordance with the above equation that the structure of honey breaks down irreversibly under the effect of shear without significant buildup during the shearing, but recovers completely with time after shearing.
- $\theta = \theta(\gamma, t)$ (2)
- Equation (3) below was defined as follows according to Abu-Jdayil (2003)
- $\theta(\gamma, t) = \frac{\eta - \eta_{\infty}}{\eta_o - \eta_{\infty}}$ (3)
- $-\frac{d\theta}{dt} = k(\theta - \theta_{\infty})^n$ (4)

Structural Kinetic Model Continues...

- Where $k=k(\gamma)$ is the rate constant, and n (expected to take values in the range, 1 - 4) is the order of the structure breakdown process. Equation (4) may be solved subject to the boundary conditions noted above to give:

- $$\eta = \eta_{\infty} + (\eta_o - \eta_{\infty})[k(n-1)t + 1]^{1/(1-n)} \quad (5)$$

- $$\eta = KM^A \quad (6)$$

- $$\eta = \eta_{\infty} + (KM^A - \eta_{\infty})[kt(n-1) + 1]^{1/(1-n)} \quad (7)$$

- **Equation 7 is designated as Structural Kinetic Model for Nigerian Honey**

Amended Carreau-Yasuda and Power Law Models

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_o - \eta_{\infty}) \left[1 + (\dot{\gamma}\lambda)^a \right]^{\frac{n-1}{a}} \quad (8)$$

Putting Equation (6) to Equation (8)

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\mathbf{K}' \mathbf{M}^A - \eta_{\infty}) \left[1 + (\dot{\gamma}\lambda)^a \right]^{\frac{n-1}{a}} \quad (9)$$

$$\eta = \eta_o \gamma^{n-1} \quad (10)$$

Taking the natural logarithm of equation (10)

$$\ln \eta = \ln \eta_o + (n - 1) \ln \gamma \quad (11)$$

Honey Harvesting and Processing

1. Preparing To harvest our honey at Federal Polytechnic Ado-Ekiti

2. In the Apiary of the Polytechnic by 8:00pm on 29th Nov, 2012



3. Honey Harvesting Proper by 8:00pm 29-11-12

4. Apis Mellifera bees at Apiary Unit of Federal Polytechnic Ado-Ekiti



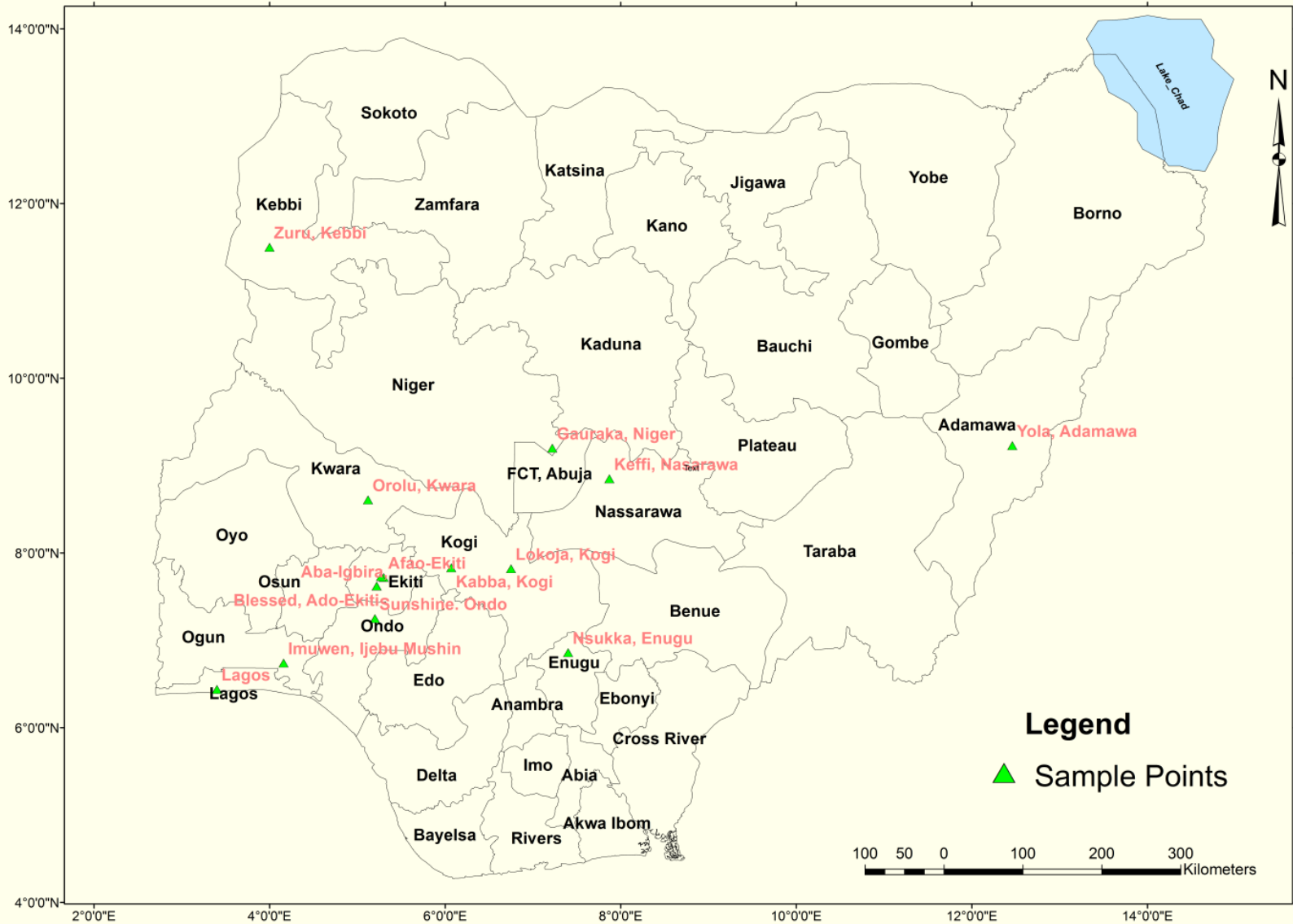
Table 1. Sample Details

S/N	Sample	Location	Collection Date	Location Coordinates	Production Date
1.	H	Federal Poly Ado-Ekiti	14-01-2012	7.6211°N, 5.2214°E	15-01-2012
2.	B1	Gauraka, Niger	June,2011	9.2000°N, 7.2167°E	
3.	B2	Yola, Adamawa	May,2011	9.2300°N, 12.4600°E	
4.	B3	Zuru, Sokoto	May,2011	11.5000°N, 4.0000°E	
5.	B4	Orolu, Kwara	May,2011	6.3833°N, 4.1833°E	
6.	B5	Keffi, Nasarawa	May,2011	8.8486°N, 7.8736°E	
7.	B6	Lokoja, Kogi	February,2011	7.8167°N, 6.7500°E	
8.	B7	Kabba, Kogi	May,2011	7.8333°N, 6.0667°E	
9.	C1	Sunshine, Ondo	May,2010	7.2500°N, 5.1950°E	
10.	C2	Real Oasis, Iworoko Ekiti		7.7267°N, 5.2667°E	15-03-2011
11.	C3	Blessed, Ado-Ekiti	February,2010	7.6211°N, 5.2214°E	
12.	C4	Nsukka, Enugu	November,2010	6.8567°N, 7.3958°E	
13.	C5	Abba Igbira Ekiti	February,2011	7.6211°N, 5.2214°E	
14.	C6	Lagos	March,2012	6.4351°N, 3.3958°E	

Table 1. Sample Details Continues...

S/N	Sample	Location	Collection Date	Production Date
14.	FS1	Fructose Syrup		01-12-2012
15.	FS2	10% Adulteration		01-12-2012
16.	FS3	50% Adulteration		01-12-2012
17.	FS4	70% Adulteration		01-12-2012
18.	FS5	90% Adulteration		01-12-2012

SAMPLE DEMOGRAPHY



Procedure For Rheological Characterisation

- Rheology of the samples was carried out using the Brookfield DV-III Ultra Programmable Cone and Plate Rheometer.
- All measurements were carried out with a cone radius of 24 mm and with a 0.8 cone angle; this gives the gap height of 0.1 mm at the circumference of the cone at shear rate of $0.01-4.16s^{-1}$.
- The samples were made to stand in the container for at least 30 minutes before the analysis. This is to allow for the complete structural buildup from shear-induced flow into the container.
- The principle of operating the DV-III Ultra is to drive a spindle(which is immersed in the test sample) through a calibrated spring. The spring deflection measures the viscous drag of the fluid against the spindle. Spring deflection is measured with a rotary transducer.

Correlation Tests

▶ **Hydroxymethylfurfural Determination**

- ▶ Hydroxymethylfurfural content was determined with high performance liquid chromatographic (HPLC) technique using Jeuring and Koppers, (1980) experimental procedure.

▶ **Antibacterial Properties of Honey**

- ▶ Stocked cultures of *Staphylococcus aureus* and *Pseudomonas aeruginosa* used in this study were obtained from the Microbiology Laboratory Unit, University Teaching Hospital Ado-Ekiti, Ekiti State. The isolates were identified based on standard microbiological techniques, and sub-cultured in nutrient agar at 37°C for 24hrs.

Antimicrobial Assay

- Antibacterial activity of different honey samples and a reference antibiotic (Cefoxitin) against *Staphylococcus aureus* and *Pseudomonas aeruginosa* were obtained from University Teaching Hospital Ado-Ekiti was tested by an agar diffusion method (CLSI, 2012).

Results

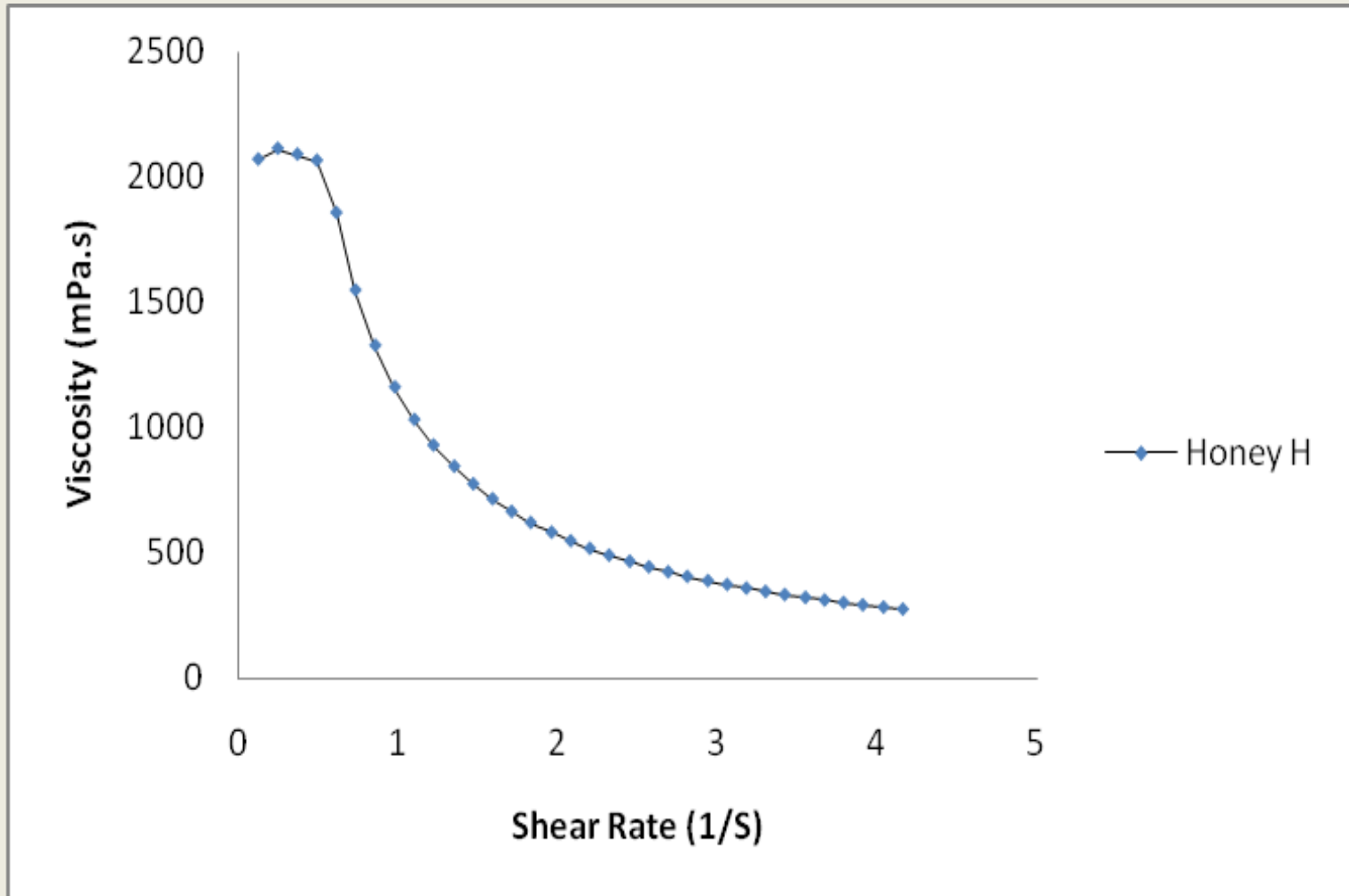


Fig.1 Rheology of Pure Honey at 27°C

RESULTS Continues...

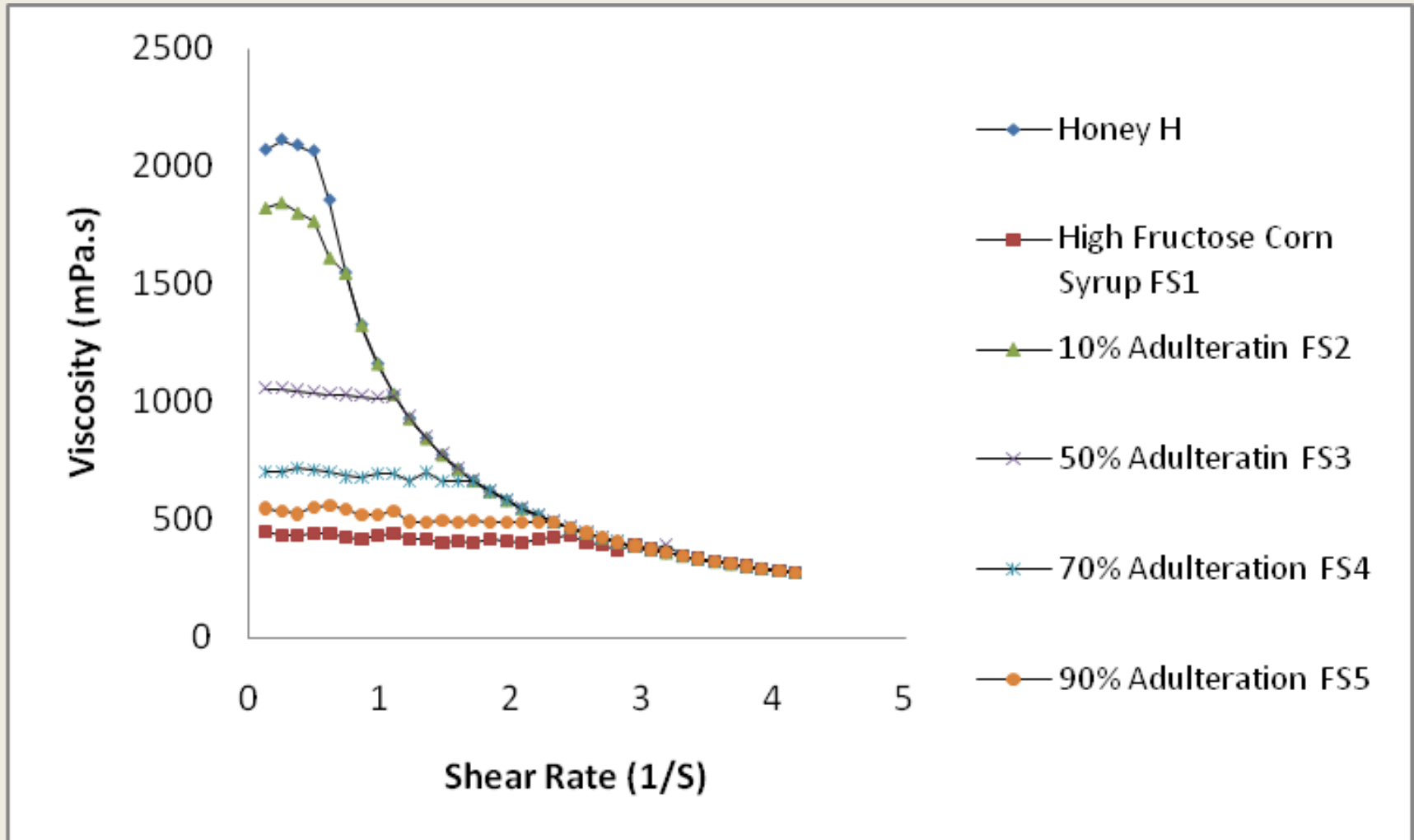


Figure 2. Rheological Profile of Honey Adulterated with High Fructose Syrup (FS)

Results Continues...

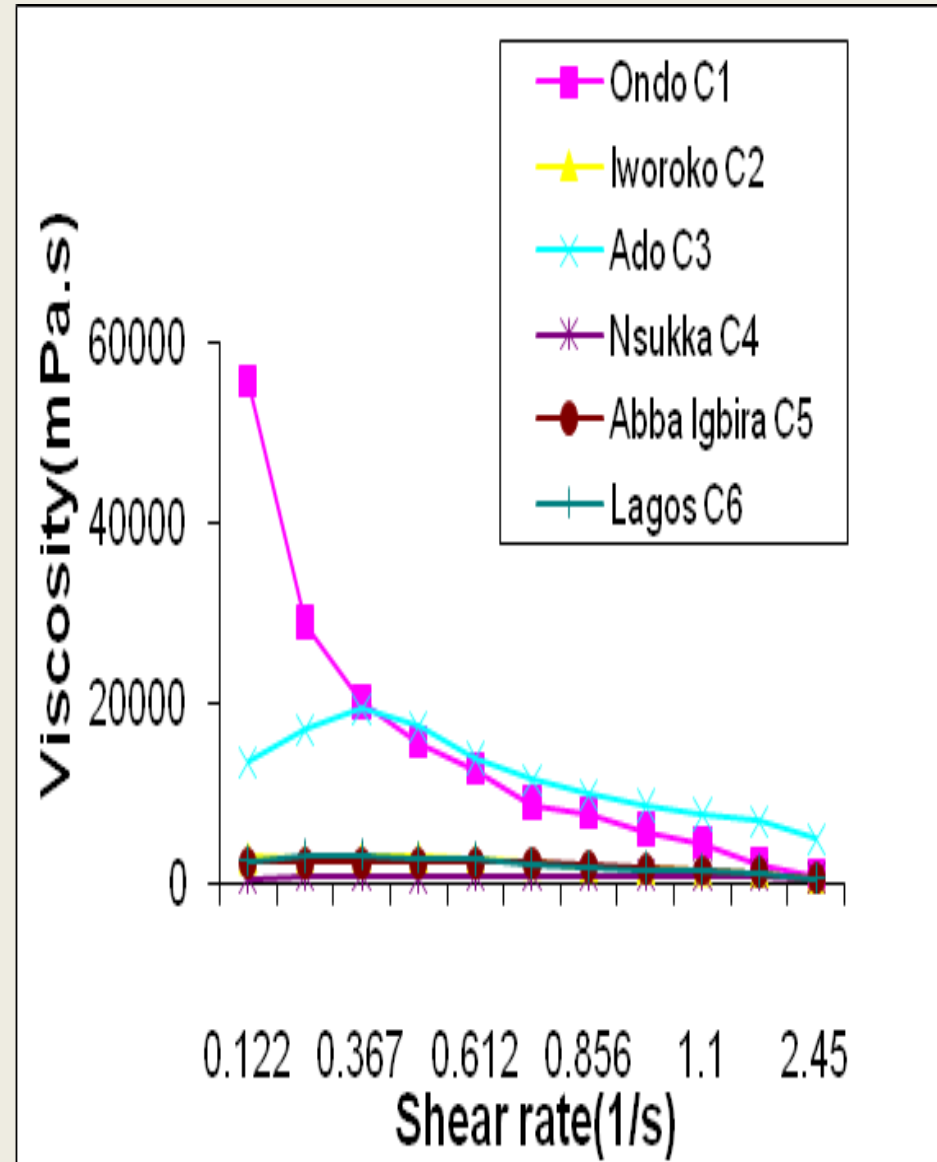
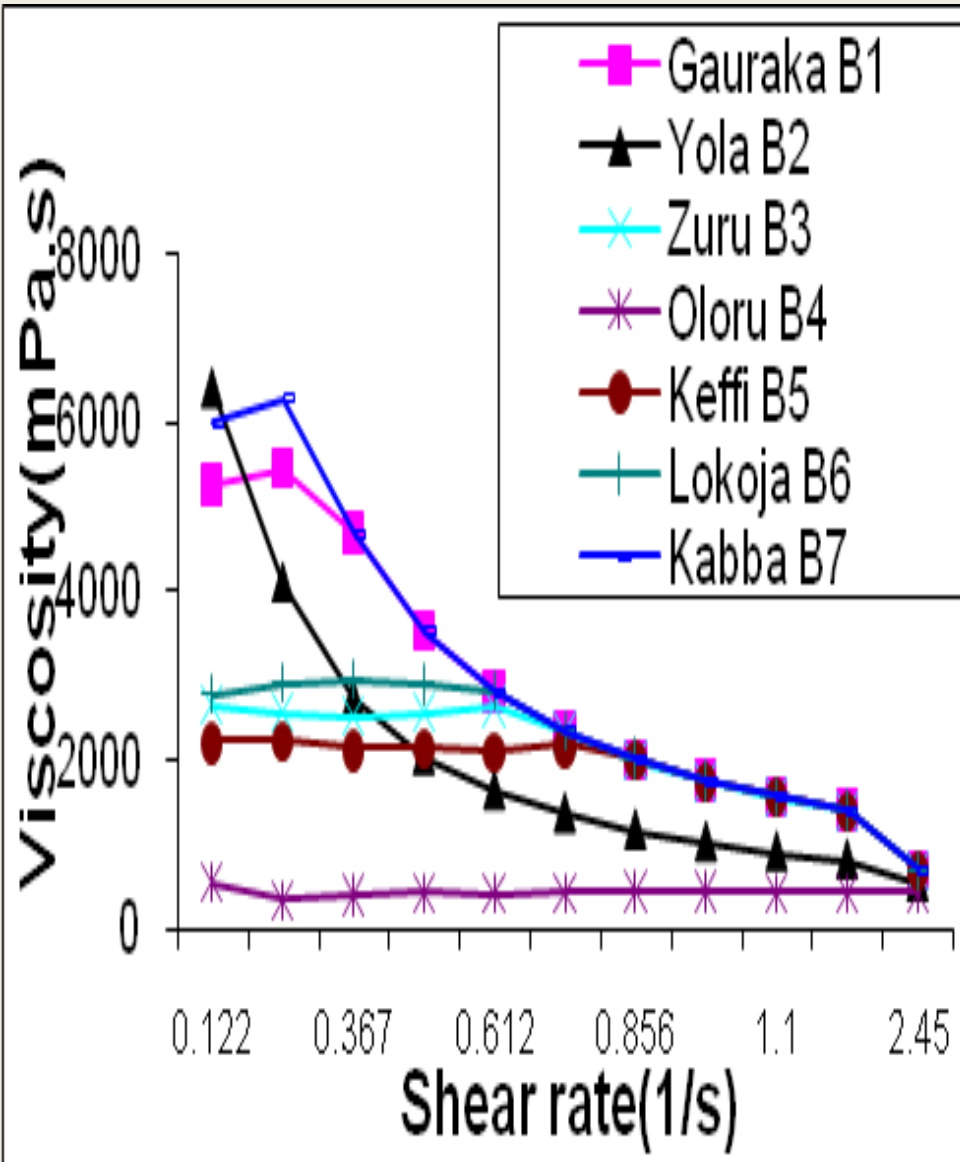


Fig 3. Rheology of Honey from Northern Nigeria at 27°C

Fig4. Rheology of honey from Southern Nigeria at 27°C

Results Continues...

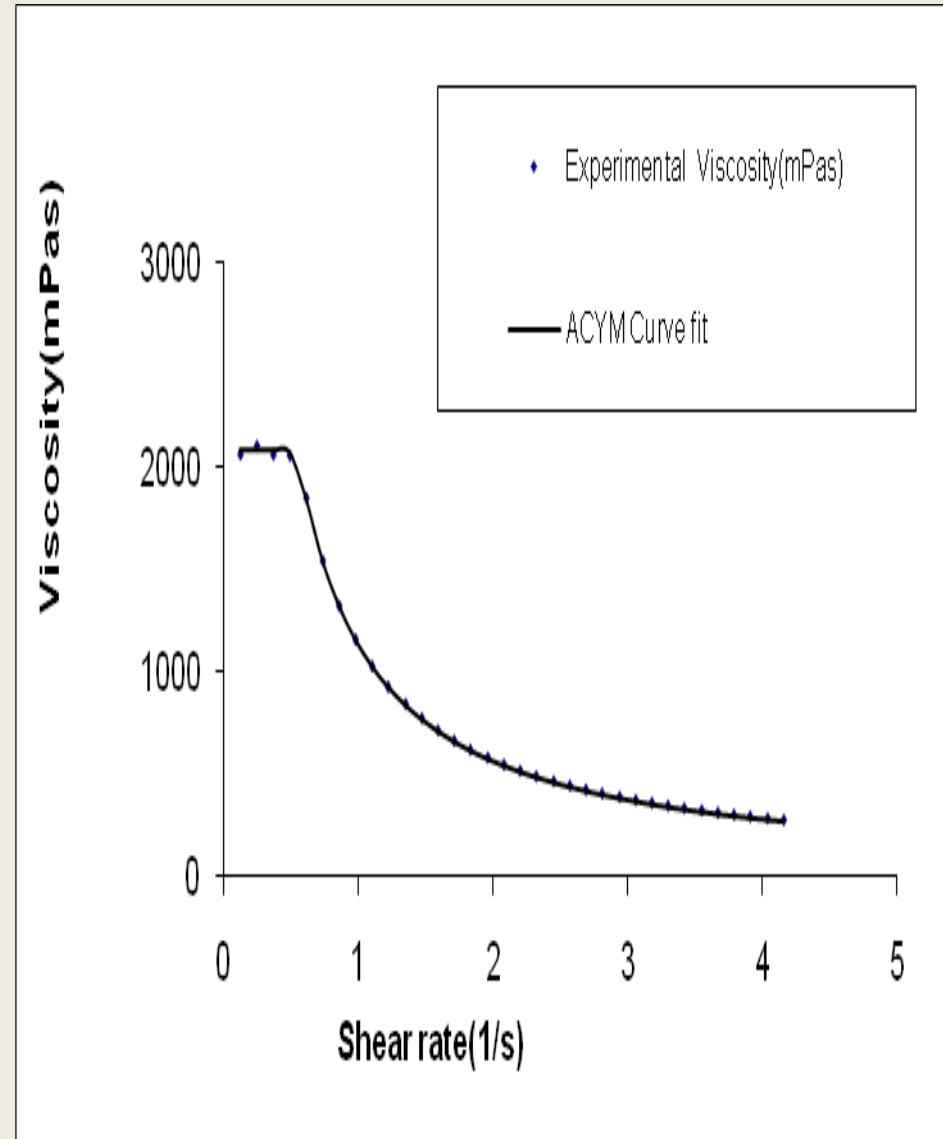
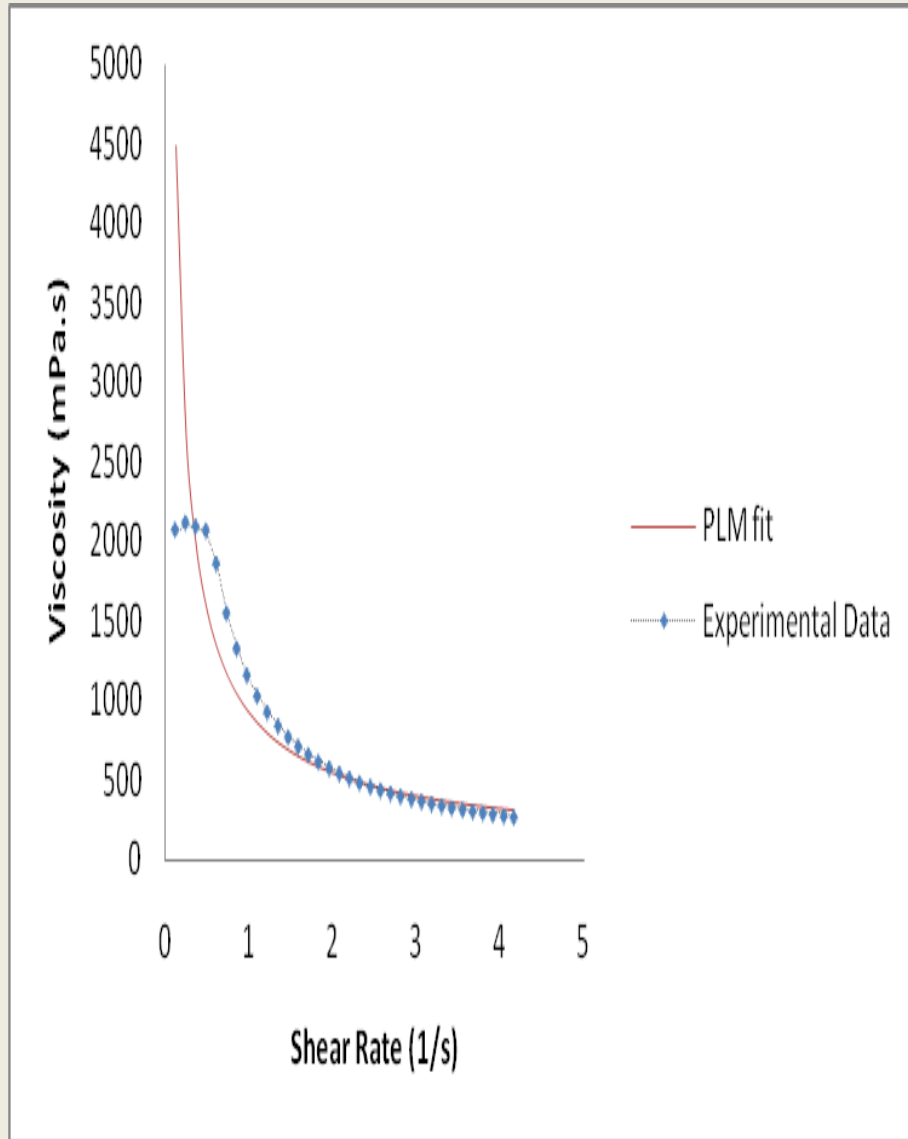


Fig 5 Power Law Model Curve Fit of Sample H at 27°C

Fig 6. Amended Carreau-Yasuda Model Curve-fit of Sample H at 27°C

Results Continues...

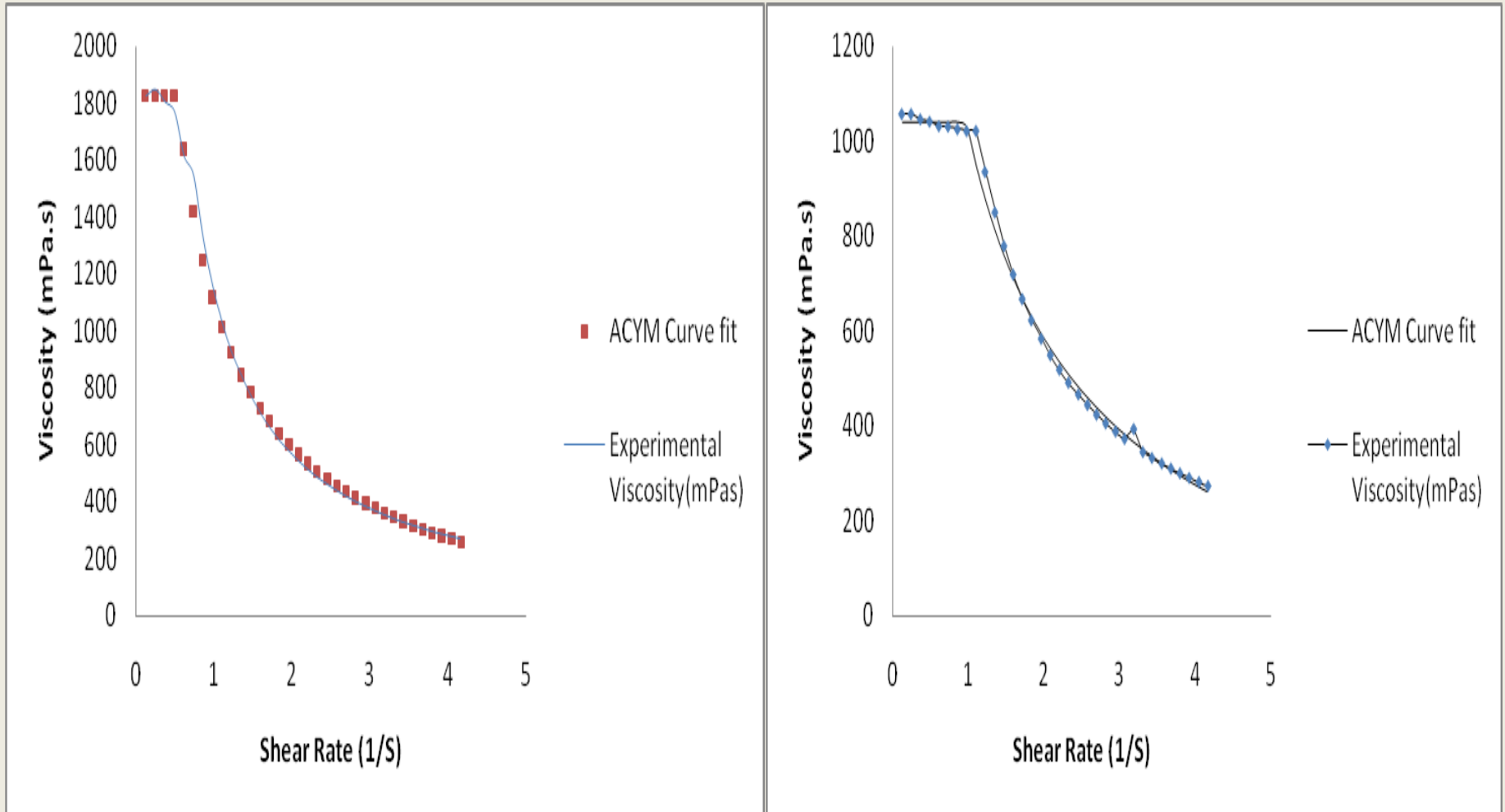


Figure 7. Amended Carreau-Yasuda Model Curve-fit of (10% Adulteration with FS) at 27°C Figure 8. Amended Carreau-Yasuda Model Curvefit of (50% Adulteration with FS) at 27°C

Results Continues...

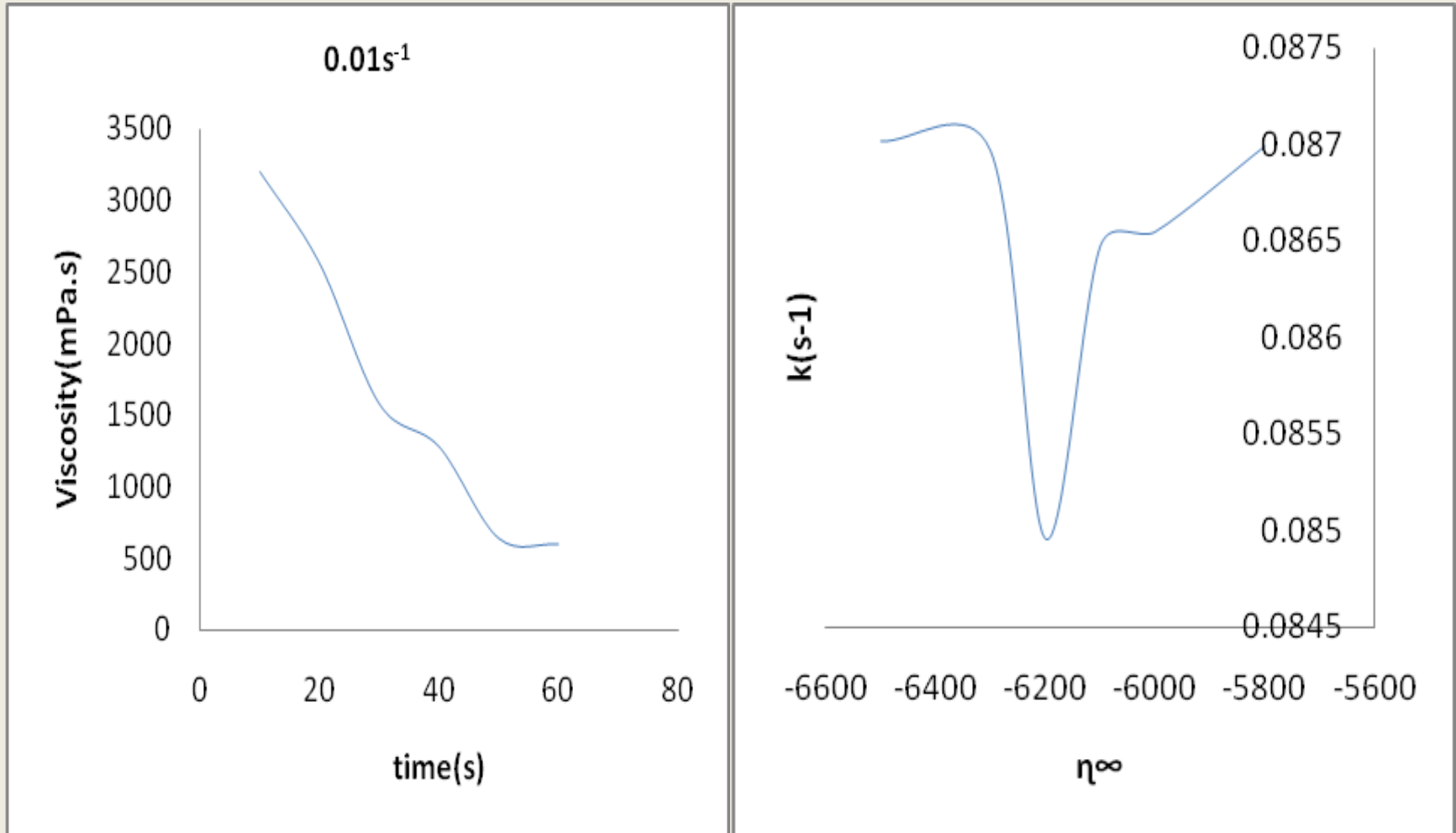


Fig. 9 Viscosity -Time Rheogram of Sample H at 27°C Fig. 10 Optimisation of k for Sample H

Results Continues...

Table 2. SUMMARY OF RHEOLOGICAL CURVE FITTING RESULTS USING POWER LAW

S/N	Samples	Samples Details	n at 27 °C	η_o at 27°C
1	H	Pure Honey	0.25	924.24
2	FS1	Fructose Syrup	0.89	433.03
3	FS2	10% Adulteration with FS	0.30	881.06
4	FS3	50% Adulteration with FS	0.51	722.39
5	FS4	70% Adulteration with FS	0.68	579.20
6	FS5	90% Adulteration with FS	0.80	476.35

Results Continues...

Table 3. SUMMARY OF RHEOLOGICAL ACYM CORRELATION OF SAMPLES AT 27°C USING AMENDED CARREAU-YASUDA MODEL

S/N	Samples	Sample Identity	n	Molecular Weight (g/mol)	λ (s)	η_0	a
1	H	Pure honey	0.23	205	2.09	2084.06	131.60
2	FS1	Fructose Syrup	0.99	159	242.60	739.47	59.14
3	FS2	10% Fructose Syrup Adulteration	0.30	200	1.87	1822.33	54.02
4	FS3	50% Fructose Syrup Adulteration	0.51	182	1.03	1039.50	58.65
5	FS4	70% Fructose Syrup Adulteration	0.68	172	1.42	642.25	57.41
6	FS5	90% Fructose Syrup Adulteration	0.80	162	0.89	532.46	28.17

Results Continues...

Table 4. SUMMARY OF RHEOLOGICAL CURVE FITTING USING THE SKM AT 27°C

Sample Code	Sample Identity	Molecular Weight (g/mol)	n	k(S ⁻¹)
H	Pure honey	202	3.00	3.26
FS1	Fructose Syrup	145	1.50	5.22
FS2	10% Fructose Syrup Adulteration	197	2.50	3.50
FS3	50% Fructose Syrup Adulteration	174	2.50	3.26
FS4	70% Fructose Syrup Adulteration	162	2.00	4.06
FS5	90% Fructose Syrup Adulteration	151	1.50	4.12

Results Continues...

Table 5. CLASSIFICATION OF HONEY SAMPLES BASED ON THE RESULTS OF POWER LAW AND CARREAU YASUDA MODEL ON SERIAL DILUTION OF HONEY WITH

	CLASSIFICATION	SAMPLES
H	Pure	B1,B7,C4
FS2	10% Adulteration	B2,C2
FS3	50% Adulteration	B3,B5,B6,C3,C5,C6
FS4	70% Adulteration	
FS5	90% Adulteration	
FS1	100% Imitation	B4

Results of Correlation Tests

EZChrom Elite Custom Report

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A₉

Sample ID: STD1
 Filename: C:\EZChrom Elite\HONEY\Data\13-05-13\019dat-Rep1
 Method: C:\EZChrom Elite\HONEY\Method\13-05-13\HMF13-05-13B.met
 User: lab manager
 Acquired: 5/14/2013 2:16:01 AM
 Printed: 5/17/2013 12:16:35 AM

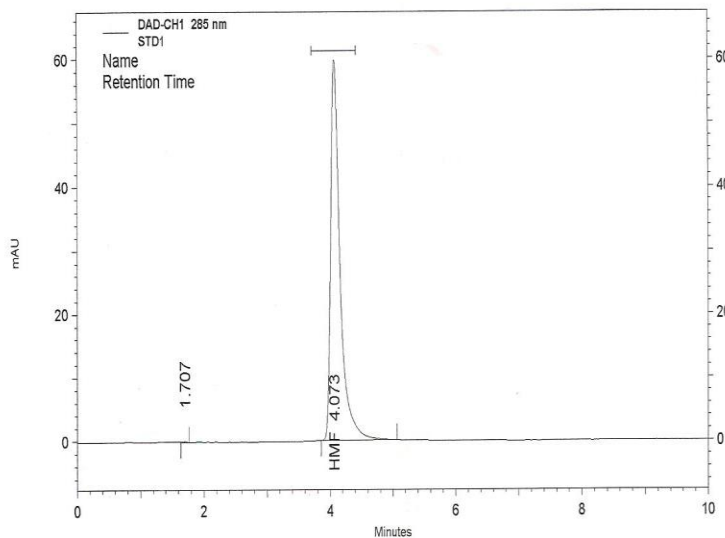
NAFDAC DAD REPORT

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

PRESERVATIVES



EZChrom Elite Custom Report

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Sample ID: FCI3944
 Filename: C:\EZChrom Elite\HONEY\Data\13-05-13\028.dat
 Method: C:\EZChrom Elite\HONEY\Method\13-05-13\HMF13-05-13B.met
 User: lab manager
 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
6	HMF	4.067	319771	mg/L	$\frac{0.287}{10} \times 50$ 1.435 mg/L

DILUTION FACTOR: 1
 MULTIPLIER: 4994.36
 VIAL: 6

HONEY

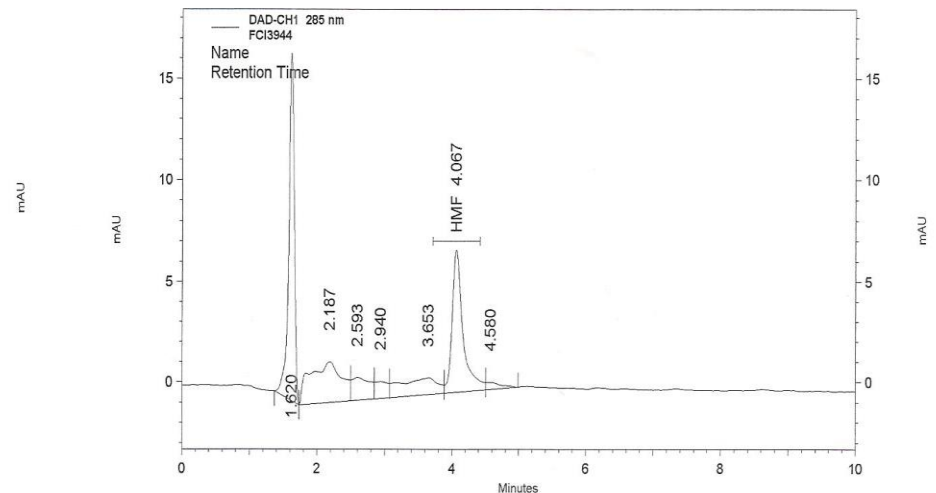


Fig 11 Chromatograph of Pure Hydroxymethylfurfural

Fig 12 Chromatograph of Pure honey From Fed Poly Ado

Table 6. Summary Of Chromatographic Analyses Results

S/N	Sample Code	Sample Name	HMF(ml/kg)
1.	H	Federal Polytechnic Ado-Ekiti	1.44
5.	B1	Gauraka Niger State	23.98
6.	B2	Yola Adamawa	59.22
7.	B3	Zuru Sokoto	66.10
8.	B4	Oloru Kwara	1469.50
9.	B5	Keffi Nasarawa	35.31
10.	B6	Lokoja Kogi	55.50
11.	B7	Kabba Kogi	6.93
12.	C1	Sunshine honey Ondo	18.58
13.	C2	Real Oasis Ekiti	75.74
14.	C3	Blessed Ado-Ekiti	111.27
15.	C4	Nsukka Enugu	7.45
16.	C5	Abba Igbira	86.37

Table 6. Summary Of Chromatographic Analyses Results Continues...

17.	C6	Lagos	53.74
18.	FS1	Fructose Syrup	202.50
19.	FS2	10% Fructose Adulteration	60.91
20.	FS3	50% Fructose Adulteration	81.22
21.	FS4	70% Fructose Adulteration	120.34
22.	FS5	90% Fructose Adulteration	188.75

Validation of Results

Table 8: The Antibacterial Effect of Honey on *Staphylococcus aureus*

S/	Sample	Description	Zone of
N	Code		Inhibition(mm)
1.	H	Federal Polytechnic Ado- Ekiti	25
2.	FS1	Fructose Syrup	-
3.	FS2	10% Fructose Adulteration	11
4.	FS3	50% Fructose Adulteration	9
5.	FS4	70% Fructose	-

Validation of Results

Table 9: The Antibacterial Effect of Honey on *Pseudomonas aeruginosa*.

S/ N	Sample Code	Samples	Zone of Inhibition(mm)
1.	H	Federal Polytechnic Ado-Ekiti	26
2.	FS1	Fructose Syrup	-
3.	FS2	10% Fructose Adulteration	9
4.	FS3	50% Fructose Adulteration	9
5.	FS4	70% Fructose Adulteration	-
6.	FS5	90% Fructose Adulteration	-

Conclusion

– The objectives of this study were achieved and from the results of the investigations conducted, the following conclusions can be made:

- At room temperatures pure honey exhibits shear thinning flow pattern at low shear rate.
- Compositional changes in honey due to the addition of common adulterants reflect in the sample's rheogram suggesting rheological characterization as a method for detecting adulteration of honey. By extension rheological characterization can serve to detect the faking of this product.

Conclusion Continues...

- Power law and Carreau Yasuda models can measure the degree of honey adulteration in Nigerian honey.
- Structural Kinetic model developed in this study produced plausible estimates for the average molecular weight of the samples studied by this suggest itself as a sample quality tracker.
- The results from the amended Carreau Yasuda model compared relatively well with those from our new structural kinetic model.
- The results of physicochemical characterization of honey correlated well with this new rheological method.

Contributions To Knowledge

- A novel test method has been devised for rheological authentication of honey and classification of honey adulterated with, fructose syrup.
- A structural kinetic model was derived from first principles for the extraction of structural information and average molecular weight of honey from rheological data.
- This study for the first time suggests that a 3rd order breakdown kinetics adequately describes honey deformation under shear which perhaps accounts for the three main constituents of the fluid.
- By covering the low shear rate zone of honey deformation, this work established that honey exhibits shear thinning behaviour at low rates of shear but becomes Newtonian as shear rate increases.

Recommendations

- In view of the limited number and source distribution of samples used in this study, the conclusions drawn can be augmented to a more general applicability by including and analyzing more samples from locations outside Nigeria.
- The results of this study should inspire the design and manufacture of a simple test apparatus for the rheological screening of samples of honey for authenticity and quality.

Thank You For Listening

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