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Short communication

Microscopic modeling of the rheological behavior of honey

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A B S T R A C T

The rheological behavior of honey fluid was model at molecular level using the trajectory of the sphericity of the particles in which the interactions are represented with a pairwise Leonard Jones potential. The honey fluid was subjected to perturbation ,and temperature variations was adjusted using Hoover thermostat with the simulation carried out in canonical ensemble, periodic boundary condition, and rheological property evaluated using Irvin and Kirkwood model. It was affirm that honey fluid exhibits shear thinning behavior because of particle re-arrangement. The rheological behavior is also a function of the molecular structure and composition in which the behavior of the honey fluid depends.

Keywords: Canonical ensemble, Rheology, Hoover thermostat, Perturbation, Pressure tensor

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1. Introduction

Honey is a sweet natural substance produced by Honey Bees. Bees are collected near nectar or honeydew, and are transported into the hive where began the processes that lead to their transformation into honey: the concentration and the enzymatic conversion of sugar. Honey composition is closely related to its botanical origin, and to the processing and environmental conditions (Abubakar et al., 2012).

When Honey fluid is subjected to shear stress, their response to the applied perturbation is at the heart of rheological testing (Anidiobu et al., 2019). However, the composition of the honey fluid plays a major factor on how it will behave under the application of external shear stress (Anidiobu et al., 2019).

Recently, the antioxidant in honey fluid has been characterized to have medicinal and domestic application (Jaganathan & Mandal, 2009). Therefore, guaranteeing honey quality was an important tool in maintaining market integrity, and ensuring the value added properties are not structurally altered (Anidiobu et al., 2019).

Rheology is an important tool for honey characterization because flow behavior follows closely with compositional changes in honey. Pure honey exhibits shear thinning flow pattern while sucrose solution displayed near Newtonian flow behavior at very low shear rate (Anidiobu et al., 2019).

Over the last 30 years molecular dynamics (MD) simulations have become one of the paramount tools to solve many of the complex problems been faced by rheologists and engineers. The advent of modern areas of science such as Nanotechnology, and the need to understand physical phenomena including rheology and tribology at the molecular scale have enhanced the growth of research both experimentally and computationally at Nano scale (Jabbarzadeh & Tanner, 2006).

Implementation of molecular dynamics to rheology have helped to comprehend the behavior of polymers qualitatively; In addition, important progress has been made in predicting quantitative rheological properties such as the viscosity of simple liquids. In particular, the application of Molecular dynamic to the behavior of confined fluids and lubricants at Nano-scales have revealed some important properties and the underlying physics of observed phenomena that include enhanced viscosity and relaxation times, as well as the role of normal stress differences in supporting large loads (Jabbarzadeh & Tanner, 2006).

Molecular dynamic has been an important tool in studying the relationship of the molecular structure and the rheological properties (Jabbarzadeh & Tanner, 2006). It is however very important to understand the molecular behavior of Honey at molecular scale because of its importance in predicting its quality assurance because, complexities, and the variations of its composition (Cianciosi et al., 2018).

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2. Material and Methods

2.1. Theoretical modeling

The honey fluid was conceived as hard spherical particles in which the potential between the particles are defined by the simple Lennard-Jones model. If both particles are far apart, the interaction potential is zero. However, they can be brought together with minimal energy in order for them to begin interacting. These particles can be continuously moved together until they are touching, At this point; it becomes increasingly difficult to further decrease the distance between the two particles. In order to bring the particle any closer together, we would need to add an increasing amount of energy and eventually, as the particles begin to invade each other space, they repel,-and the force of repulsion is far greater than the force of attraction.

2.1.1. Leonard-Jones potential model

The interactions between each atoms of honey fluid are represented using Leonard-Jones potential model in which the interactions are in pairwise.

$$f_i = -\sum_{j=1}^{N} \frac{48\varepsilon}{\sigma^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{14} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{8}\right]\left[x_{ije_x} + y_{ij}e_y\right] \; j \neq i \qquad (1)$$

where $x_{ij} = x_j - x_i, y_{ij} = y_j - y_i, and\ r_{ij} = r_j - r_i$ which represents the pairwise interaction. The atomic sphere are connected together to form a large molecule where $\varepsilon\ and\ \sigma$ indicates both the energy and length parameters which depends on the type of molecule present in the system. The length parameter σ is the distance between two interacting atoms when the potential energy is zero.

2.1.2. Unforced dynamic particle Model

The particulates system in honey fluid was represented by the displacement vectors of the Newton law under no external perturbation.

$$F_{ij} = m_i a = \frac{m_i\, d^2 x_{ij}}{dt^2} \qquad (2)$$

where the quantity F_{ij} represents the pair of interacting forces defined by Leonard Jones Potential (N), m_i is the mass of the honey fluid (kg), x_{ij} is the displacement vector (m), and t is the time (s).

2.1.3. Non equilibrium molecular dynamics model

Non equilibrium molecular dynamics is the application of external perturbation to the equilibrium system in which the shear stress is applied. The quantity γ is the shear rate that depends on the direction in which the perturbation is applied.

$$\frac{d^2 r_i}{dt^2}\left(e_x + e_y\right) = f_i \frac{e_{x+e_{ey}}}{m} + \gamma \frac{dr_i}{dt}(e_y) \qquad (3)$$

This non- equilibrium molecular dynamic system is model as a perturbed equilibrium ensemble in which the statistical mechanics description prevents the system from relaxing to equilibrium and also helps to improve the efficiency of transport coefficient. (Jabbarzadeh & Tanner, 2006).

2.1.4. Periodic boundary condition

The periodicity is applied by introducing cell surrounded by the images in the periodic direction. When particle exists from one face of the primary cell, another image particles renter from the opposite cell. The interaction between the particles is governed by the minimum image convention where each particle interact with the closest periodic image of others particles including the one in the same cell (Fig. 1) (Jabbarzadeh & Tanner, 2006).

The initial position of particles and velocity are equally distributed in the simulation in order to have a well-defined easily reproducible configuration, and ensuring that atoms are not overlap. If atoms are overlap, the configuration resulted to highly repulsive forces which could make the system to blow off in the first few step of simulation.

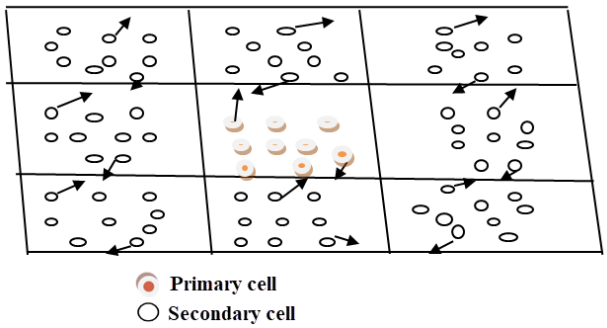

Fig. 1. Periodic boundary condition.

2.1.5. Macroscopic model

To derive relevant information from microscopic behaviour of a system, it is important to relate microscopic parameter with the macroscopic properties which can be achieved by using statistical equation of state. The statistical equation of state was derived by Irwin and Kirkwood to get these properties.

$$\sigma(r,t) = -\frac{1}{V}\sum_i \Big[m_i(V_{i,}t) - U(r_i,t)(V_i(r_i,t) - U(r_i,t) + \sum_i \sum_{j>i} r_{ij(t)} o_{ij}(t) F_{ij}(t)\downarrow \Big] r_{i=r} \qquad (4)$$

The first term is the kinetic contribution to the stress tensor, while the second term is the potential contribution to the stress tensor.

The shear viscosity is estimated from the fundamental relation.

$$\mu = \frac{\sigma}{\gamma} \qquad (5)$$

The σ is the x-y component of a stress tensor (N/m^2), while γ is the shear rate characterizing the shear field.

2.1.6. *Method of solution*

Predictor corrector was utilized to solve a second order particulate system numerically. This method was chosen as a result of its high accuracy, and the stability in the total energy of the system.

$$r^p(t+\Delta t) = r(t) + r^I(t)\Delta t + \frac{1}{2!}r^{II}(t)\Delta t^2 + \frac{1}{3!}r^{III}(t)\Delta t^3 + \cdots O(\Delta t)^4 \quad (6)$$

$$r_n(t+\Delta t) = r_n{}^p(t+\Delta t) + C_n[r_2{}^c(t+\Delta t) - r_2{}^p(t+\Delta t)] \quad (7)$$

$$r^p(t+\Delta t) = r^I(t) + r^{II}(t)\Delta t + \frac{1}{2!}r^{III}(t)\Delta t^2 + \cdots O(\Delta t)^3 \quad (8)$$

2.2. *Simulation method and experimental data*

Solution to the non-equilibrium molecular system was performed using predictor corrector method with a Matlab code for NEMD simulation. The dynamic model was integrated numerically with 1000 particles in which mass is located in a volume V with periodic boundary condition. The simulation is divided into initialization, equilibration and data production. The temperature of the system is kept constant using Hoover thermostat. The temperature of the system is kept constant using Hoover thermostat. The results were validated using the experimental data of (Anidiobu et al., 2019) honey gotten from different locations across Nigeria. Simulation is divided into Initialization, equilibration and data production.

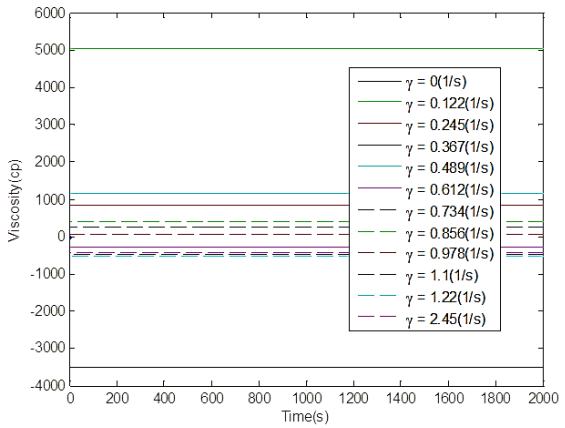

Fig. 2. Viscosity prediction of Ayo farm honey at 35°C.

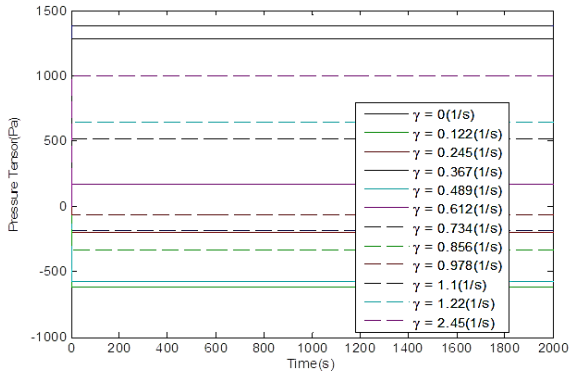

Fig. 3. Pressure tensor prediction of Poly farm honey at 27°C.

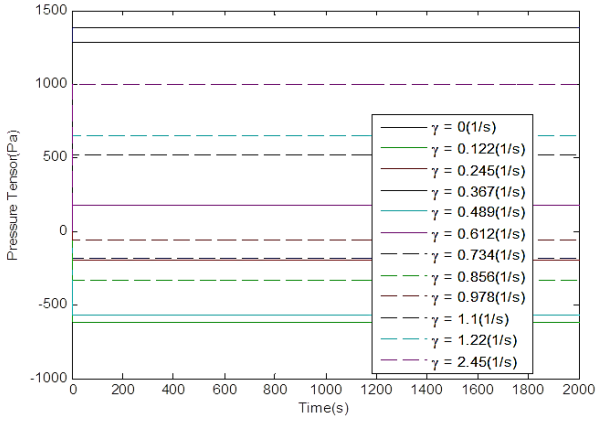

Fig. 4. Pressure tensor prediction of Ayo farm honey at 35°C.

3. Results and Discussion

The microscopic properties of the honey fluid were first of all converted into macroscopic pressure tensor. This is necessary in order to be able to evaluate the honey fluid pressure tensor when perturbation is applied.

3.1. *Pressure tensor and prediction*

The pressure tensor was evaluated from the particle trajectory using macroscopic equation of state proposed by Kirkwood and Irvin (Fig. 2-4).

The evaluation of local pressure tensors in the presence of many body interaction is helpful in simulation of chemically detailed systems with complex bonding (Heinz et al., 2005). The result of the pressure tensor indicates that there are no significant variations of pressure tensor with temperature, and also with viscosity. The pressure tensor indicates a propagation of pressure with change of shear rate. However, the viscosity of honey changed predominantly with shear rate, but the time dependent of honey fluid cannot be established.

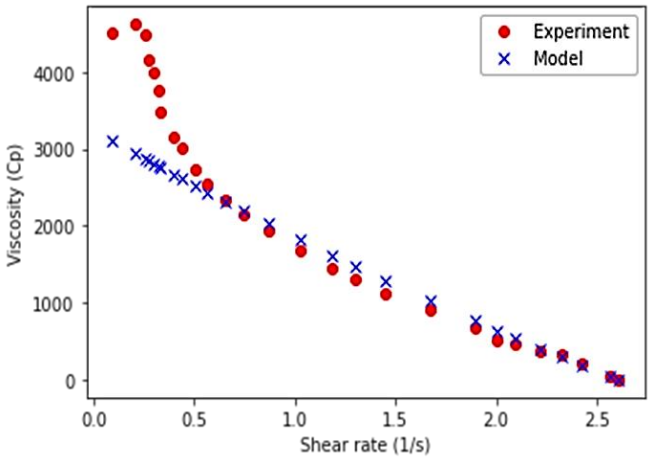

Fig. 5. Rheological prediction of Federal Poly farm honey at 27°C.

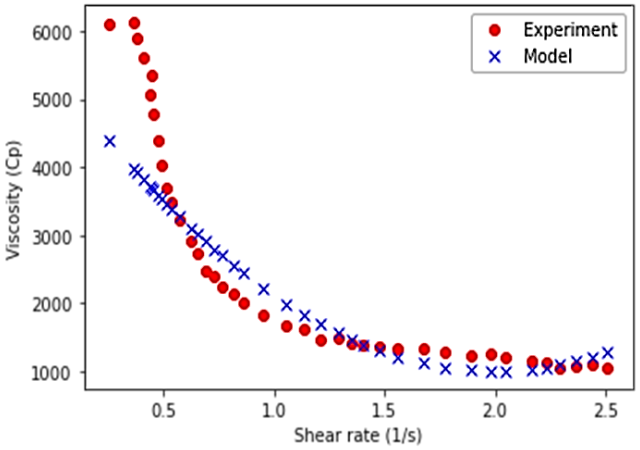

Fig. 6. Rheological prediction of Ayo Bees farm honey at 27°C.

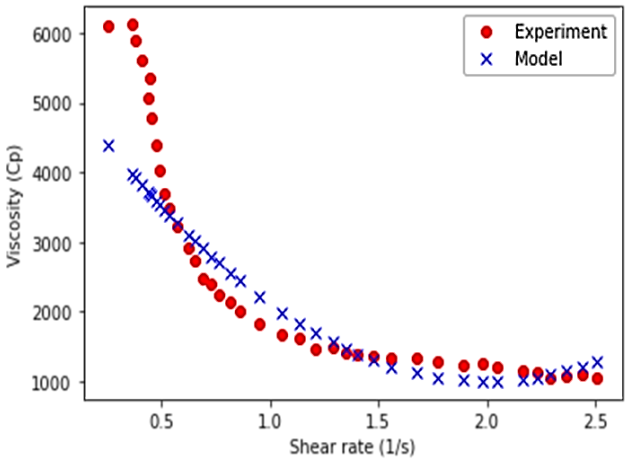

Fig. 7. Rheological Prediction of Ayo Bess Farm Honey at 35°C.

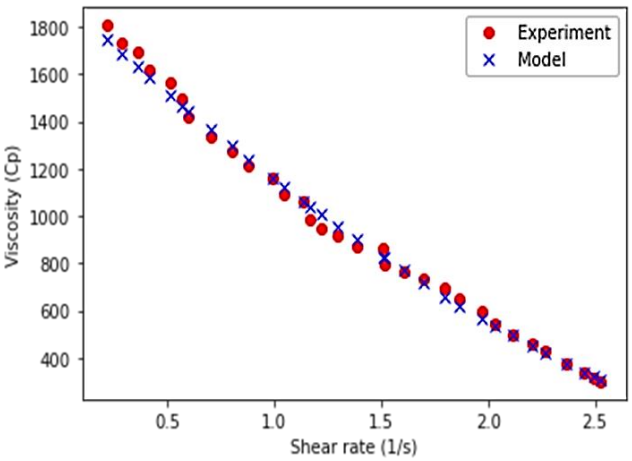

Fig. 8. Rheological prediction of Fed Poly Honey at 35°C.

3.2. Pressure tensor and viscosity prediction

The rheological property is an important tool for rheological characterization since flow behaviour correlates with molecular structure (Anidiobu, 2014).

An important advantage of this numerical microscopic numerical simulation is the ability to resolve which component of the forces contributes to viscosity. The model demonstrates that the ubiquitous shear thinning in honey fluid is a direct consequence of particle re-arrangement due to apply shear.

The microscopic behavior of honey fluid to predict its rheological behavior is an important model since honey fluid exhibits non Newtonian characteristics. The behavior of honey as shown in the result depicts that there is a change of viscosity as the shear rate increases. The viscosity decreases with increase of shear rate and therefore honey fluid exhibits shear thinning behavior. This behavior can be explained from the molecular perspective due to inter chain entanglement which increases the viscosity at low shear rate. As shear rate increases, individual chains became more oriented along the lines of flow thereby reduces viscosity.

From Fig. 5-8, the honey behavior indicates different molecular structural changes among the two honey sources that were model. These imply that the source of honey plays an important role in its molecular structural interactions.

4. Conclusion

The use of microscopic model is an important tool to predict the behaviours of complex fluid under perturbation. The accuracy of the modelling equation depends largely on the choice of boundary conditions, and numerical solution. Honey fluid under perturbation exhibits non Newtonian shear thinning behaviours, and it can be concluded that the rheological behaviours of honey follows this pattern provided there is no any other contaminant like sucrose that can microscopically distort this pattern of way of behaviour, although there may be slight different between different honey source when perturbation is applied.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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