Squeeze Flow Rheometry for Rheological Characterization of Energetic Formulations*

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The rheological characterization and the determination of the parameters describing the shear viscosity and wall slip behavior of energetic materials is a challenge. Some of the conventional rheometers including various rotational rheometers are not capable of deforming typical energetic formulations with their gel binders and high degrees of particulate fill. Other available rheometers are not conducive to rheological characterization of energetic formulations in the vicinity of the manufacturing operation with the data to be used immediately for quality control. Squeeze flow provides significant advantages in safety of materials handling and exposure as well as providing easy data generation for routine quality control of energetic formulations being processed. Here the basic hardware is reviewed along with the methods for the analysis of raw data to determine the parameters of the shear viscosity and the wall slip of energetic formulations. It is suggested that appropriate analytical and numerical analyses can indeed provide the basic wherewithal necessary for the solution of the inverse problem of squeeze flows to characterize the shear viscosity and the wall slip parameters provided that the issues of uniqueness and stability are properly addressed.

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I. Introduction

Energetic formulations are complex fluids, which present significant challenges for their rheological characterization [1-6]. This challenge stems from their viscoplasticity and concomitant wall slip behavior. Specialized techniques and multiple viscometers are employed to simultaneously characterize the parameters of the shear viscosity material function and wall slip versus the shear stress relationship [1-3]. Generally, the procedure for the characterization of the shear viscosity and wall slip involves systematic changes in the surface to volume ratio of the sample followed by the analysis of the flow curves [1-5]. When capillary flow is employed to generate flow rate versus pressure drop data, the procedure for wall slip corrected shear viscosity determination requires the use of multiple capillary dies involving systematically varied capillary lengths at constant diameter and different capillary diameters at constant length over the diameter ratio (for example, 12 capillaries were used in the study of the behavior of concentrated suspensions by Yilmazer and Kalyon [1]). In steady torsional flow between two parallel disks the procedure requires the systematic change of the gap of the rheometer or the imaging of the velocity distribution at the free surface of the fluid [1, 2].

The squeeze flow involves the unbounded compression of the energetic formulation (the energetic material is free to flow in the radial direction upon compression in the axial direction, i.e., an important positive safety aspect) that is kept under isothermal conditions and partially or completely filling the space between two parallel and rigid circular disks. One or both of the circular disks move in the axial direction at constant relative velocity, while the time-dependent force is being measured, or under constant normal force while the time-dependent relative velocity of the plate is measured [7]. In the analysis of the transport problem to derive the parameters of the shear viscosity and the wall slip of the energetic formulation, approximate solutions to this unsteady state problem can be obtained by assuming that the speed of travel of the disk is sufficiently slow so that the time derivatives in the conservation equations can be neglected, i.e., the "quasi-steady state assumption" [7,8]. A number of studies have been made on the squeeze flow for generalized Newtonian fluids [9-16]. Nevertheless, although its literature is rich, the squeeze flow has not been fully exploited to facilitate the identification of parameters of constitutive equations and wall slip behavior of energetic formulations. In this paper, first typical hardware suitable for the rheological characterization of energetic fluids is presented followed by the analysis of the transport equations which represent the dynamics of the squeeze flow for the determination of the parameters of the shear viscosity and wall slip behavior of energetic formulation. Analytical as well as FEM based numerical methods are used in our methodologies in conjunction with the solution of the inverse problem for the determination of the rheological parameters.

II. Squeeze Flow Hardware for Rheological Characterization of Energetic Materials

A schematic representation of the squeeze flow is shown in Figure 1. The energetic fluid sample is placed in between the two circular disks with a radius of R. Although different experimental configurations are possible, including the use of a constant normal force, our current configuration involves the top disk moving down at a constant speed of V, and the bottom plate being stationary. The time-dependent gap between the plates is designated as h, and the total force acting on the top plate is f.

The squeeze flow rheometer for energetics applications needs to have the following features:

- For safety the squeeze flow rheometer should be explosion proof.
- The unit needs to be run remotely, with no operator present during the characterization.
- The squeeze flow unit needs to be designed to be mobile and configured as a bench top unit.
- The rheometer needs to be sufficiently easy to use so that the plant operators can collect the rheological characterization data to be used for process and product quality control.
- The data analysis should be part of the data acquisition unit of the rheometer so that the operator/engineer need not be involved with data analysis.

- The parameters of constitutive equations and wall slip need to be generated immediately upon the testing of the sample to allow the use of the data in product quality control.
- The unit needs to be easy to clean and the surfaces that come into contact with the energetic material can be easily replaced.

The squeeze flow rheometer, which satisfies all of these objectives, is shown in Figure 2-4 (available from Material Processing & Research, Inc. of Hackensack, NJ [17]). The mechanical displacement to achieve the squeeze motion is generated by compressed air pressure (90 psi is sufficient). The squeeze flow rheometer is incorporated with an embedded computer, which allows real-time data to be collected and concomitantly analyzed. There are two sensors on the unit, a pressure transducer and a linear variable displacement transducer. The rheometer is designed to press specimens, which are collected from mixers and processors that are located in the immediate vicinity of the rheometer so that solvent loss and temperature control are not issues. Especially with viscoplastic, structured fluids resting the specimens during relatively long periods of thermal stabilization alters the rheological behavior by building up a yield stress.

The source code for the data analysis is burnt into the chip so that the data analysis is immediate. The data can be transferred or stored on a flash card, which can then be immediately downloaded to another PC or using field point technology, the rheometer can be run wireless, or through the internet. A web camera is integrated so that the squeeze test not only can be run remotely but also can be monitored remotely. One explosion-proof version, which is being used in the gun propellant industry, is driven only through three buttons and the parameters are displayed on an intrinsically safe LCD display (Figure 4). In the following the analysis of the data emanating from the squeeze flow rheometer is discussed in conjunction with the data emanating from the unit.

III. Squeeze Flow and Method to Determine Rheological Parameters of Energetic Materials

Energetic suspensions and gels generally exhibit relatively high shear viscosity values to give rise to creeping flow conditions upon being subjected to squeeze flow. Under the resulting typical relatively low Reynolds number conditions the inertial terms in the equations of motion can be neglected. The governing equations for axisymmetric flow of incompressible fluids and under quasi-steady state and isothermal conditions become:

$$\frac{1}{r}\frac{\partial r v_r}{\partial r}+\frac{\partial v_z}{\partial z}=0, \qquad (1)$$

$$\frac{1}{r}\frac{\partial r \tau_{rr}}{\partial r}+\frac{\partial \tau_{rz}}{\partial z}-\frac{\tau_{\theta\theta}}{r}+\frac{\partial p}{\partial r}=0, \qquad (2)$$

$$\frac{1}{r}\frac{\partial r \tau_{rz}}{\partial r}+\frac{\partial \tau_{zz}}{\partial z}+\frac{\partial p}{\partial z}=0. \qquad (3)$$

Here v_r and v_z are the velocity components in the radial and axial directions, i.e., r and z, respectively, p is the pressure, and τ_{rr}, τ_{zz}, $\tau_{\theta\theta}$ and τ_{rz} are components of the deviatoric stress tensor. If the rate of movement of the plate, V, is sufficiently slow to allow viscoelastic effects to be considered to be negligible, generalized Newtonian fluid constitutive behavior is applicable, i.e., $\underline{\underline{\tau}}=-\eta(II)\underline{\underline{\Delta}}$, where $\underline{\underline{\tau}}$ and $\underline{\underline{\Delta}}$ are the stress and rate of deformation tensors. $\eta(II)$ is the shear viscosity material function varying as a function of the second scalar invariant of the magnitude of the rate of deformation tensor, $\dot{\gamma}$, i.e., $\dot{\gamma}=\sqrt{II/2}$. The squeeze flow is subject to the following non-linear wall slip condition, i.e., slip velocity, U_s, versus the shear stress, τ_{rz}:

$$U_s=\beta\ |\tau_{rz}|^{sb}, \qquad (4)$$

where the Navier slip coefficient, β, and the slip exponent, sb, are parameters of the wall slip behavior, which are related to the shear viscosity material function of the binder of the suspension and the apparent slip layer thickness for concentrated suspensions [5].

The slip coefficients for the top and bottom disks, i.e., β_t and β_b respectively, can be different due to differences in roughness or the materials of construction of the two plates. For 1-D flow the shear stress for the Herschel-Bulkley type viscoplastic constitutive equation becomes $\tau_{rz} = \pm\tau_y - m\,|\,dv_r/dz\,|^{n-1}\,(dv_r/dz)$ for $|\tau_{rz}| \geq \tau_y$ (- sign is used for negative shear stress, τ_{rz}) and the shear rate $(dv_r/dz) = 0$ for $|\tau_{rz}| < \tau_y$ (Herschel and Bulkley [18]). Here, m is the consistency index, n is the power-law index, and τ_y is the yield stress. Thus, for energetic suspensions the shear viscosity of which is represented by the Herschel-Bulkley fluid subject to wall slip there are five parameters $\{m, n, \tau_y, \beta, sb\}$ that need to be determined for representing the shear viscosity along with the wall slip condition. For energetic suspensions, sb can be estimated from the shear viscosity material function of the binder and the concentration and properties of the rigid particles [5]. The solution of the squeeze flow problem for the Herschel-Bulkley fluid also provides the solutions for Newtonian fluid with n=1 and τ_y = 0; Bingham fluid with n=1; power-law behavior with τ_y = 0; all subject to either no slip or slip at the wall.

The force acting on the top plate is:

$$\begin{aligned} f &= \int_0^R 2\pi(p+\tau_{zz})\,|_{z=h}\; r\,dr \\ &= \int_0^R \pi\left(\left(-\frac{dp}{dr}\right)r^2 + 2\tau_{zz} r\right)\Bigg|_{z=h} dr. \end{aligned} \tag{5}$$

The problem (1)—(5) can be solved either numerically or analytically to determine the normal force, f, acting on the moving plate (i.e., [8-16]).

Reasonable agreement between FEM [13] and the analytical solution [11] of the squeeze flow subject to the lubrication assumption was found under certain conditions. For example, for the modified Bingham number ($\tau_y/m(V/R)^n$) range of 0 to 100, the percentage deviation of the total normal force, *f,* calculated on the basis of the lubrication assumption differed by less than 10% of the total normal force determined with the FEM analysis for the no-slip condition. However, the agreement between the total normal force values determined with FEM versus the analytical solution using the lubrication assumption was shown to deteriorate with inclusion of wall slip versus the no-slip condition, with increasing wall slip coefficient and upon increasing the yield stress value of the fluid [13]. It was suggested that FEM analysis or experimental data are necessary to determine the conditions under which the lubrication assumption can be assumed to be valid for squeeze flow.

IV. Squeeze Flow and Inverse Problem Solutions for Determination of Rheological Parameters: Herschel-Bulkley Fluid with Wall Slip

As indicated earlier the inverse problem solution of the isothermal squeeze flow for the Herschel-Bulkley fluid subject to wall slip outside of the lubrication flow region requires a numerical solution. Here, the FEM approach is followed to solve the governing equations, and a combination of the steepest descent and the conjugate gradient methods [20] is employed to carry out the minimization required for the solution of the inverse problem. Starting from an initial guess, the minimization begins with the steepest descent method and, after certain number of steps in searching, switches to the conjugate gradient method. The FEM code was validated using experimental data, and the effectiveness of the minimization program has been tested (see Tang and Kalyon [21]).

The validity of the inverse problem solution methodology was probed directly by employing the FEM solution for both the linear and non-linear wall slip conditions (Kalyon and Tang [22]). The investigation in [22] suggested that the parameter domain was subdivided into multiple subdomains and initial points pertaining to each subdomain were taken to arrive at the global minimum, which was considered to represent the solution of the problem for all four parameters.

This approach of parameter domain division is based on the observations from extensive numerical experimentation, which suggested that when the number of parameters sought is equal to or greater than three, reasonable estimates could only be made if the initial guesses for parameters sought are relatively close to the true values. However, how do we know where the true solution lies, prior to the characterization of the fluid, so that the initial guesses are made to approach the true values of parameters? The method involves the division of the parameter space spanned by {m, n, τ_y, β} into subdomains and starting the minimization with multiple initial conditions belonging to each subdomain. In conjunction with this method the objective function arising from each subdomain can be compared with the others and a global minimum can be determined. To illustrate, let us suppose the smallest possible values for m, n, τ_y, and β are respectively $m_{\min}, n_{\min}, \tau_{y_{\min}}$, and $\beta_{\min}$, and the largest possible values are respectively $m_{\max}, n_{\max}, \tau_{y_{\max}}$, and $\beta_{\max}$. We divide the whole possible domain of parameters $[m_{\min}, m_{\max}] \times [n_{\min}, n_{\max}] \times [\tau_{y_{\min}}, \tau_{y_{\max}}] \times [\beta_{\min}, \beta_{\max}]$ into multiple subdomains (with the total number of subdomains given as $L_m \cdot L_n \cdot L_{\tau_y} \cdot L_\beta$) as:

$$m = m_{\min} + (I-1)\Delta m, \quad 1 \le I \le L_m + 1, \tag{6}$$

$$n = n_{\min} + (J-1)\Delta n, \quad 1 \le J \le L_n + 1, \tag{7}$$

$$\tau_y = \tau_{y_{\min}} + (K-1)\Delta \tau_y, \quad 1 \le K \le L_{\tau_y} + 1, \tag{8}$$

$$\beta = \beta_{\min} + (M-1)\Delta \beta, \quad 1 \le M \le L_\beta + 1, \tag{9}$$

where $\Delta m = (m_{\max} - m_{\min}) / L_m$, $\Delta n = (n_{\max} - n_{\min}) / L_n$, $\Delta \tau_y = (\tau_{y_{\max}} - \tau_{y_{\min}}) / L_{\tau_y}$, $\Delta \beta = (\beta_{\max} - \beta_{\min}) / L_\beta$, and L_m, L_n, L_{τ_y}, and L_β are the numbers of subdomains in directions of m, n, τ_y, and β, respectively. We start the minimization from each {I, J, K, M}, and upon obtaining all of the solutions pertaining to different sets of initial conditions the global minimum is obtained and the corresponding set of parameters obtained is considered to represent the solution. Provided that the division is sufficiently fine and the objective function is continuous and smooth, it is anticipated that the procedure will find the global minimum. Additional information on the methodologies utilized can be found in the Appendix.

V. Concluding Remarks

The squeeze flow rheometer is introduced as a convenient method for the rheological characterization of energetic formulations. The hardware needs to be used in conjunction with software and source codes developed for the solution of inverse problem for the determination of the parameters of viscoplastic constitutive equations and wall slip of the energetic formulation. If the parameter space is divided into multiple subdomains so that initial conditions would coincide with each subdomain, the reliability of the search method increases and reasonable estimates for obtaining up to four parameters can be obtained. The advantage of the squeeze flow in conjunction with inverse problem solution for the determination of the parameters becomes apparent upon considering that the squeeze flow test takes only a few minutes versus the weeks of work generally involved in collecting conventional rheological characterization data, for example, capillary flow using multiple capillaries and multiple apparent shear rates run for each capillary for the characterization of energetic fomulations.

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Appendix A Inverse Problem for Parameter Estimation

Given a set of experimental data for the forces $0 < f_1^e < f_2^e < \cdots < f_M^e$ exerted on the top plate to drive the flow at gaps $h_1 > h_2 > \cdots > h_M > 0$, the least square objective function becomes:

$$J(F,F^e) \equiv \frac{1}{M}\sum_{i=1}^{M}(1-\frac{f_i}{f_i^e})^2 , \tag{A1}$$

where $F^e = \{f_1^e, f_2^e, \cdots, f_M^e\}$, $F = \{f_1, f_2, \cdots, f_M\}$, and the latter represents the total normal forces on the plates given by an analytical or a numerical solution.

Let m, n, τ_y, and β be real numbers and $\alpha=\{m,n,\tau_y,\beta\}$. The parameter estimation can be formulated as the following inverse problem:

$$Find \quad \{\alpha\} = \{\alpha \mid J(F,F^e) = \min_\alpha J(F,F^e)\}, \tag{A2}$$

$$Subject \quad to \quad f_i = \int_0^R 2\pi(p+\tau_{zz})_i \mid_{z=h} rdr, \quad i = 1,2,\cdots,M. \tag{A3}$$

Minimization of the inverse problem (A2) and (A3) can be carried out using various methods including the steepest descent method, the conjugate gradient method or combinations of multiple methods [19]. In the search for the minimum, the derivatives of the objective function are evaluated using central differences, for example for searching four parameters:

$$\frac{\partial J}{\partial m} \approx \frac{J_{m+\Delta m,n,\tau_y,\beta} - J_{m-\Delta m,n,\tau_y,\beta}}{2\Delta m}, \tag{A4}$$

$$\frac{\partial J}{\partial n} \approx \frac{J_{m,n+\Delta n,\tau_y,\beta} - J_{m,n-\Delta n,\tau_y,\beta}}{2\Delta n}, \tag{A5}$$

$$\frac{\partial J}{\partial \tau_y} \approx \frac{J_{m,n,\tau_y+\Delta\tau_y,\beta} - J_{m,n,\tau_y-\Delta\tau_y,\beta}}{2\Delta\tau_y}, \qquad \text{(A6)}$$

$$\frac{\partial J}{\partial \beta} \approx \frac{J_{m,n,\tau_y,\beta+\Delta\beta} - J_{m,n,\tau_y,\beta-\Delta\beta}}{2\Delta\beta}. \qquad \text{(A7)}$$

LIST OF CAPTIONS

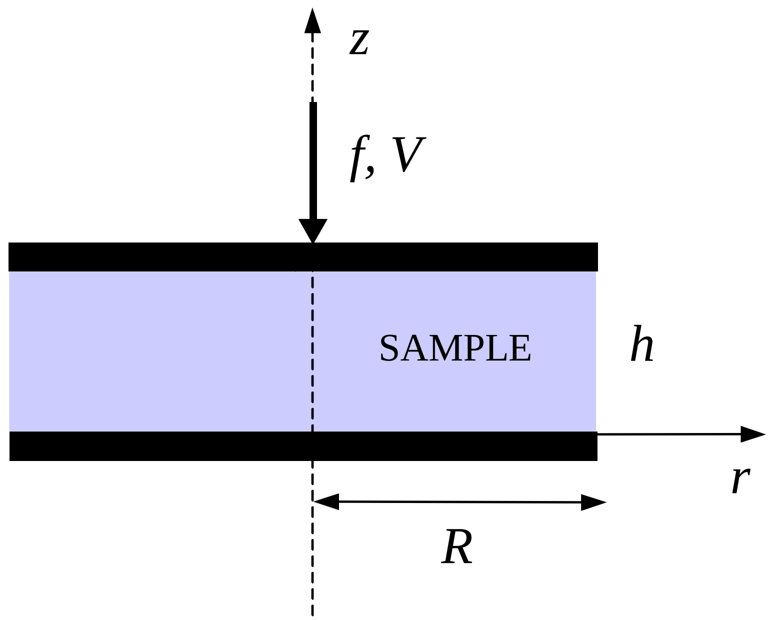

Figure 1

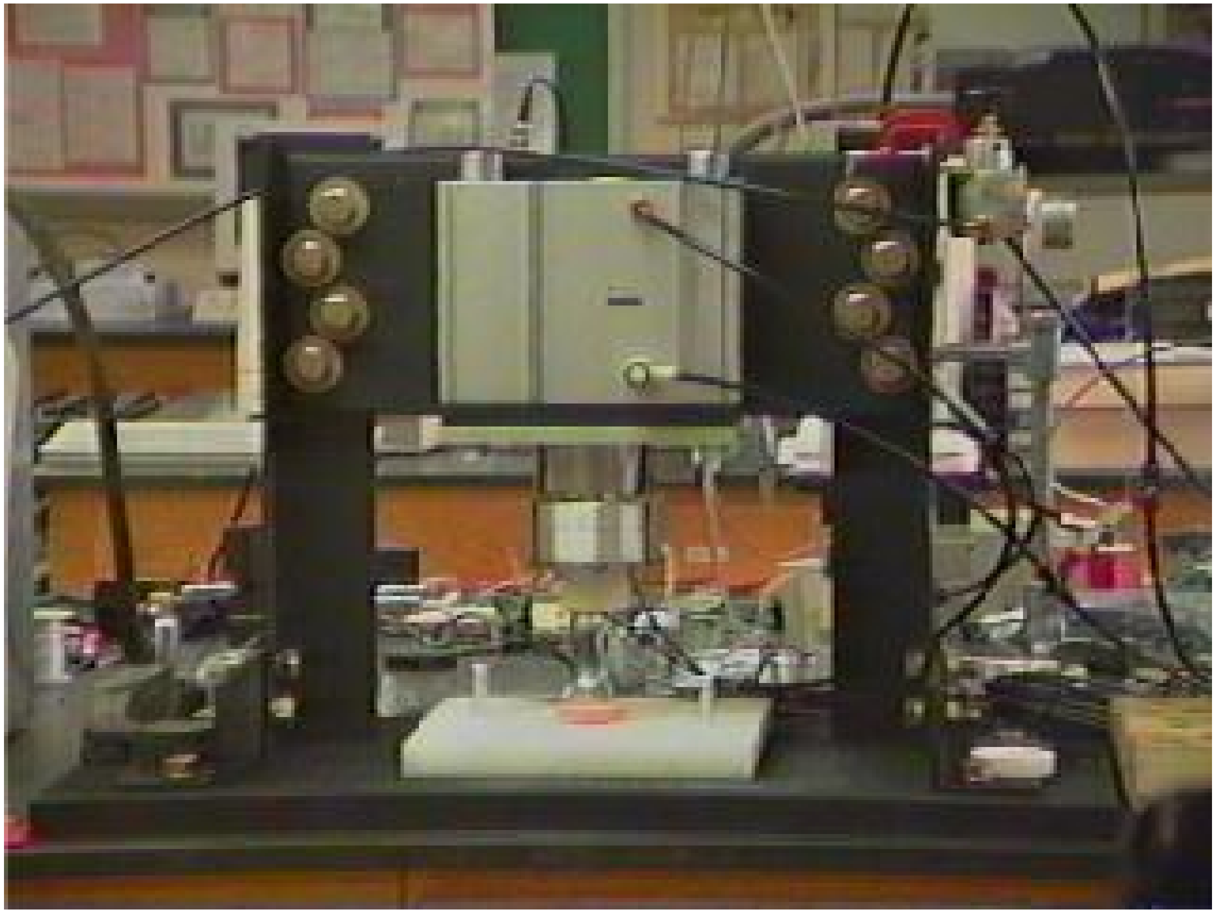

Figure 2

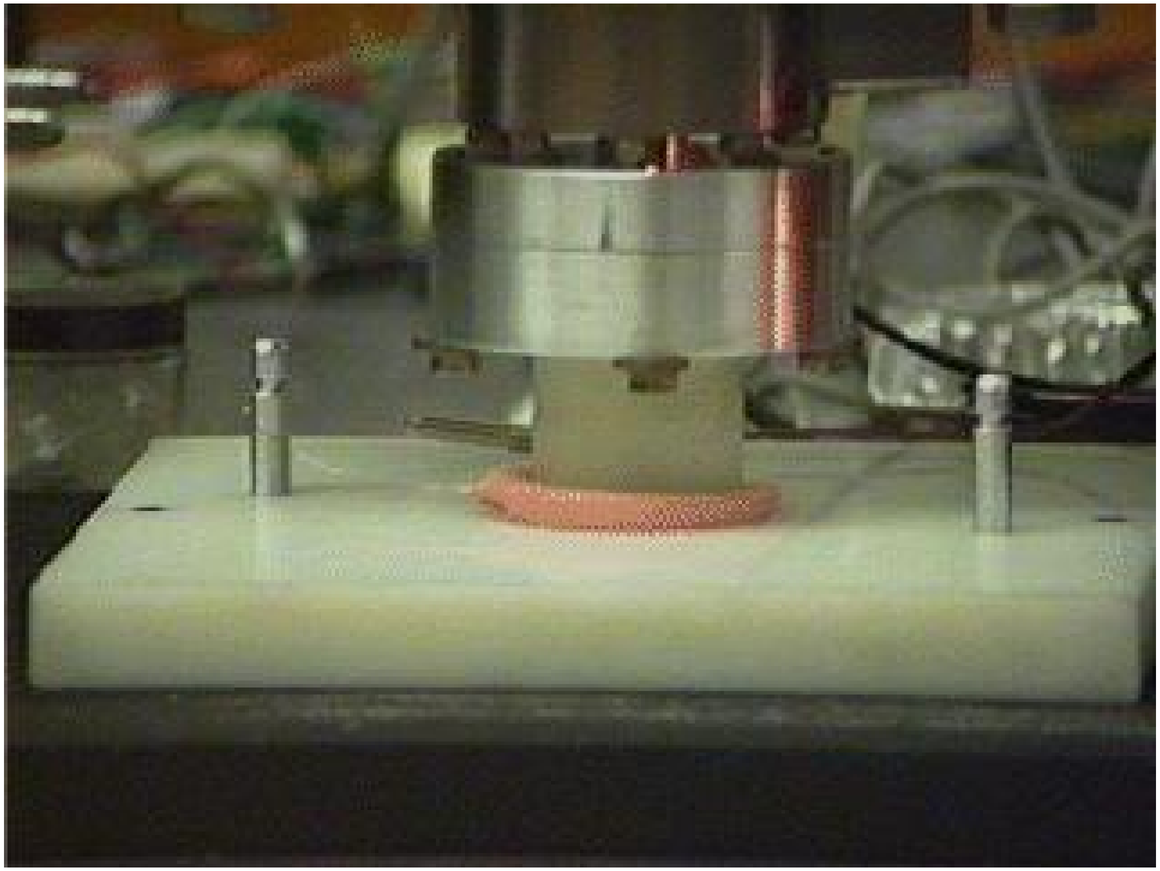

Figure 3

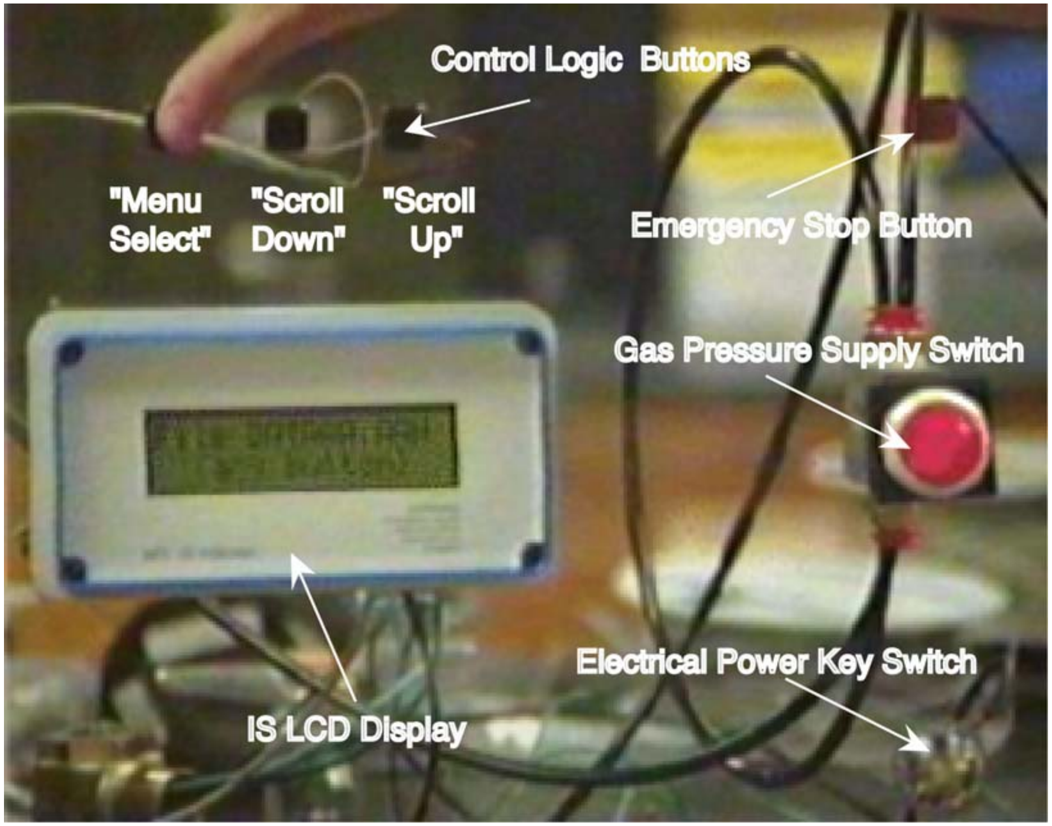
Control Logic Buttons
"Menu Select"
"Scroll Down"
"Scroll Up"
Emergency Stop Button
Gas Pressure Supply Switch
IS LCD Display
Electrical Power Key Switch

Figure 4