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MASTER'S degree in FOOD SCIENCE

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PRACTICAL FLUIDS FOR FOOD RHEOLOGY AND PROCESS CALIBRATION

by

Mitchell Hull

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Food Science and Human Nutrition

ABSTRACT

PRACTICAL CALIBRATION FLUIDS FOR FOOD RHEOLOGY AND PROCESS CALIBRATION

by

Mitchell Hull

Corn syrups were shown to have potential for use as Newtonian calibration fluids in some applications where established standard oils are not suitable. Applications include food industry pilot and plant calibration operations that require large volumes of test fluids and subsequent water-based cleaning.

Laboratory rheological analyses using both steady and dynamic shear conditions demonstrated that corn syrup viscosities are as constant as those of standard calibration oils. Some syrups showed significant elasticity that may be due to their tendency to dry upon exposure to air during analysis. The viscosities of some of the syrups did not significantly change during a five month period.

With careful attention to shelf-life and protection from air drying, corn syrups can be used in many food industry fluid equipment system calibration and evaluation operations. To Marie and Carolyn

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NOMENCLATURE

Α	= area of ideal parallel plate, m ²
F	= force required to maintain velocity \boldsymbol{v} of ideal parallel plate, N
G′	= storage modulus, Pa
t	= time, s
у	= distance between ideal parallel plates, m
γ	= angular dynamic strain, radians
γ _o	= angular strain amplitude, radians
Ý	= shear rate, s^{-1}
Ύ _{menx}	= maximum shear rate attained during a steady shear analysis
δ	= angle of the phase lag between the imposed stress and the resulting strain, degrees
ŋ	= Newtonian viscosity, Pa s
ካ '	= loss modulus or dynamic viscosity, Pa s
θ	= angle of cone, degrees
u	= kinematic viscosity, m ³ /s
υ	= ideal plate velocity, m/s
Ø	= density, kg/m ²
σ	= shear stress, Pa
σο	= shear amplitude, Pa
σ_y	= yield stress, Pa
ω	= angular frequency, radians/s

Chapter 1

INTRODUCTION

1.1. Calibration in Viscometry

1.1.1. Laboratory Applications

Calibration in viscometry is carried out to ensure that the analytical method being calibrated provides accurate results. Not only is calibration used in the design and manufacture of instruments (e.g., Brookfield) that measure true results only for ideal fluids, calibration is also performed by purchasers of "absolute" viscometers to assure themselves that the equipment is operating as designed (Delancy, 1988).

Calibration is the process of determining the response of a viscometer to known fluids. One, therefore, must have fluids whose viscosities are accurately known. The calibration procedure should be easy to conduct, thus permitting a proper statistical determination of the error of the viscometer.

1.1.2. Process Applications

The design and evaluation of process equipment that handle fluids is a continuing problem in food and other industries. Laboratory measurements of fluid flow behavior are sometimes used to design new equipment and to predict how a new fluid will behave in an existing fluid-handling system. Many process conditions cannot be accurately predicted, however, due to limitations in mathematical

description of complex geometries such as those found in pumps, filters, manifolds, heat exchangers, and extruders.

Process engineers therefore frequently prefer to evaluate a fluid handling system without having to conduct production-usage tests. Pilot scale production systems can be evaluated with a known fluid to determine the likelihood of success with the intended fluid. This pilot or process "calibration" can also be used to confirm operation of inline test transducers such as pressure sensors, thermocouples, and flowmeters. Finally, process calibration can help verify mathematical models of fluid flow in the process under study. These models are sometimes used to predict behavior of complex fluids in the process and therefore help guide manipulations of the process to better attain production objectives.

1.2. Justification for Study

Commercially available, certified viscosity standards are not suitable for many viscometer calibration needs, particularly those in the food industry. Costing \$30-\$40 per pint (Cannon Instrument Co., 1988), they are practical only for small volume viscometers found in the laboratory. All require organic solvents for cleaning, the higher viscosity standards being readily soluble only in halogenated hydrocarbons such as chloroform.

Many applications in the food industry requiring calibration fluids are not well served by the current recognized standard fluids. A partial list of applications includes

laboratory viscometers requiring substantial sample volume (e.g., some Brookfield instruments), tube viscometers beyond capillary size, process viscometers (Cheng et al., 1985), mixers, pumping equipment, manifolds, filters and screens, most heat exchangers, and extruders.

There exists a need, therefore, for calibration fluids which are inexpensive, well-characterized, reasonably ideal in behavior and stability, can be easily cleaned with water, and are suitable for use in food processing.

1.3. Study Objectives

There are three basic objectives of this research: 1. Identify suitable materials for food industry use.

A fluid suitable for use in the food industry should have two main characteristics:

A. Ideal flow behavior.

A calibration fluid should conform to a simple model of behavior when undergoing a shear stress or strain. The simplest model is that of Newton, who described the force of shearing a fluid as directly proportional to the rate of shear. A so-called Newtonian fluid is not time-dependent and has a constant viscosity at any rate of shear. B. Ease of use.

A calibration fluid should be easy to use, to encourage a frequency of testing that is statistically significant. "Easy to use" ideally means that the fluid should be cleanable with water, safe, simple to prepare or ready for use as

purchased, stable during storage and use, easily disposable, and low in cost.

 Determine extent of Newtonian behavior of suitable fluids.

Viscometric analyses of a few fluids, determined to be suitable from the above survey, will be presented. The analyses will focus on the constancy of viscosity over a range of shear rates (experimental conditions). Comparisons will be made between currently accepted standards and potentially more practical alternatives.

3. Recommend fluids and procedures.

Fluids will be recommended, based on experimental evidence. Procedures for handling and storage will also be suggested for specific fluids.

Chapter 2

THEORETICAL CONSIDERATIONS

2.1. Description of Newtonian Fluid Behavior

The ideal Newtonian fluid will be described under steady and dynamic shear conditions.

2.1.1. Steady Shear Conditions

Conditions of steady shear can be most easily described in terms of the simple shear model depicted in Figure 1 (Boger et al., 1985). A fluid is held between two parallel infinite planes separated by a distance y.

The top plate of area A is moving to the right with a steady velocity, v. The fluid is sheared between the plates. The force required to maintain this velocity is F. This laminar flow field can be mathematically expressed by relating the force per unit area to the rate of shear:

$$F/A = \eta \cdot v/y \qquad [1]$$

where \P is a proportionality constant called viscosity. The shearing force per unit area is commonly called the shear stress and is denoted by σ . The rate of shear ν/γ is called the shear rate and is denoted by $\dot{\gamma}$. The above relationship is thus written:

$$\sigma = \eta \cdot \dot{\gamma} \qquad [2]$$

A Newtonian fluid has a linear relationship between shear stress and shear rate, passing through the origin of a plot of shear stress vs. shear rate, as shown in Figure 2. A Newtonian fluid has a constant viscosity at constant temperature.



Figure 1. Simple shear model.



Figure 2. Theoretical shear stress - shear rate plot for a Newtonian fluid.

Some analytical instruments, notably capillary viscometers, measure kinematic viscosity, u, directly:

$$u = \eta / \rho$$
 [3]

where ρ is the fluid density.

2.1.2. Dynamic Oscillatory Shear Conditions

This flow mode is often used to measure the behavior of viscoelastic fluids which exhibit properties between ideal solids and ideal liquids. By using this flow mode one can determine if there is any residual solid-like behavior in a candidate calibration fluid.

Consider the parallel plates discussed in section 2.1.1. Instead of imposing a steady linear velocity v on the upper plate, the plate is driven with a sinusoidally varying strain (distance the plate is moved) γ at a frequency of $\omega/2\pi$, where ω is the angular frequency (Whorlow, 1980). The shear stress,

$$\sigma = \sigma_0 \cdot \cos(\omega t)$$
 [4]

produces a strain,

$$\gamma = \gamma_0 \cdot \cos(\omega t - \delta)$$
 [5]

where δ is the angle of the phase lag between the imposed stress and the resulting strain, γ_0 is the angular strain amplitude, and t is time.

The storage modulus,

$$G' = \sigma_0 \cdot \cos(\delta) / \gamma_0 \qquad [6]$$

gives the in-phase stress amplitude, while the dynamic viscosity is expressed as

$$\eta' = \sigma_0 \cdot \sin(\delta) / \gamma_0 \qquad [7]$$

The dynamic viscosity η' approaches the steady viscosity η at very low frequencies. G' and η' are related to each other by

$$\tan (\delta) = \omega \eta' / G'$$
 [8]

The value of tan (δ) should be infinite for an ideal pure fluid, since G' << η' .

A purely solid (Hookean) material would be strained exactly in phase ($\delta = 0$), while a purely viscous fluid (Newtonian material) would be strained exactly 90° out of phase. This is because an imposed stress is directly proportional to the strain for a pure solid, whereas the stress is proportional to the rate of strain \dot{y} for a pure fluid.

From the above discussion, the behavior of a Newtonian fluid in dynamic oscillatory testing becomes clear. The experimentally determined value of G' should be zero, while the value for η' should be the same as the viscosity determined in steady shear:

η' = η

In fact, Boger et al. (1985) suggest that the accuracy of dynamic measurements can be checked with a Newtonian fluid of known viscosity.

Chapter 3

LITERATURE REVIEW

3.1. General Calibration Considerations

3.1.1. Definition

Analytical chemists understand calibration to mean the indexing of instrument or indicator response to the concentration of the analyte species of interest. Calibration may be thought of as relating a measured property of a sample to an estimate of the desired property of that sample (Wernimont, 1985).

3.1.2. Purposes

Calibration is done for one or both of the following reasons:

- a) when the analytical theory cannot readily predict quantitative instrument response from analyte concentration;
- b) when significant errors arise during an analysis based on quantitatively fundamental theory.

In practice, nearly all instrumental analyses use calibrations to assure the highest accuracy possible (Skoog and West, 1971).

3.1.3. General Procedure for Calibration

Calibration in analytical chemistry is typically carried out as follows (Miller and Miller, 1984):

The analyst takes a series of samples (normally at least three or four, and possibly several more) in which the concentration of the analyte is *known*. These calibration standards are measured in the analytical instrument under the same conditions as those subsequently used for the test (i.e., the "unknown") samples. Once the calibration graph has been established the analyte concentration in any test sample can be obtained by interpolation.

The calibration graph quoted above is a scatter (x,y) plot of the instrument responses to the known (calibration) samples versus the values assigned to the known samples.

3.1.4. Statistics of Calibration

There are several questions about a calibration graph that must be addressed (Miller and Miller, 1984). These include: 1) is the calibration graph linear or curved; 2) what is the best line through these points; 3) what are the estimated errors and confidence limits for the regression parameters that describe the line; 4) when using the calibration to measure test samples, what are the errors and confidence limits for the determined value; and 5) what is the limit of detection of the method?

The widely used statistical methods for computing a calibration regression are based on two assumptions: 1) the errors in the calibration graph occur only in the instrument response (y axis), i.e., the values assigned to the known calibration materials are assumed to have no error; and 2) the magnitude of the error in the instrument response is independent of the magnitude of the value assigned to the calibration material. Both assumptions are violated in most calibrations, but only the second has occasionally serious results. A detailed discussion of the statistics of calibration can be found in Miller and Miller (1984).

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3.1.5. Requirements of Calibration Materials

The most important characteristic a calibration material must have is credibility. The analyst must accept that the value assigned to the material accurately reflects the true value. The universally accepted strategy to attain this confidence is to obtain and properly use materials that are associated with a national standards organization program. The components of such a program are discussed in Section 3.2.

Other requirements typically made in calibration materials are: (1) independence from the method in question; (2) sufficient precision in the value ascribed to the material, so that none of the variability attributed to the instrument readings may be assumed to derive from the standards; and (3) inclusion of interfering "matrix" effects (i.e., non-ideal behavior such as elasticity, temperature sensitivity, and multiple phases) that might be encountered in actual samples (Wernimont, 1985).

3.2. Components of An Accuracy-Based Measurement System

The "systems approach" to assuring measurement compatibility, or accuracy, has been described (Uriano and Gravatt, 1977) as having six necessary technical components:

1. Basic Measurement Units

These provide self-consistent measurement scales that can be related to each other in exact physico-chemical equations. The Systeme International d'Unites (SI) are recognized by most nations as the basic units. There are seven base units in the SI system: mass, length, time, electric current, thermodynamic temperature, luminous intensity, and the quantity of substance (the mole). The SI units for viscosity and kinematic viscosity are Pa s ($[N/m^2]$ s) and m²/s, respectively. Commonly used units for viscosity are centipoise (cP), where 1 cP = 0.001 Pa s, and for kinematic viscosity, centistokes (cSt), where 1 cSt = 0.0001 m²/s (ASTM, 1983).

2. Definitive Measurement Methods

Definitive methods of chemical analysis are those that have a valid and well-described theoretical foundation, give negligible systematic experimental errors and have high levels of precision. These methods evaluate the property in question either directly, in terms of the fundamental units of measurement, or indirectly relate the property to the fundamental units via exact mathematical equations. Such methods give "true results" with high reliability. The measurements obtained from these methods are said to be absolute measurements.

3. Primary Reference Materials

Reference materials are a class of well-characterized, stable, homogenous materials produced in quantity and having one or more physical or chemical properties experimentally determined within stated measurement uncertainties. Primary reference materials are those having properties certified by a recognized national standards laboratory. The measurement techniques used to certify primary reference materials are

the most accurate and reliable methods available: the definitive methods. The International Union of Pure and Applied Chemistry (IUPAC) and the International Organization for Standardization (sometimes referred to as the "International Standards Organization" and abbreviated hereafter as IOS) have recommended the use of the term "Certified Reference Material" (CRM) for primary reference materials; in the U.S., the National Bureau of Standards (NBS) uses the term Standard Reference Materials (SRM). CRMs are produced in relatively small amounts to the highest standards of accuracy, and are intended for use where accuracy is the most important requirement, regardless of cost. A primary use of CRMs is to serve as the foundation of accuracy for the development of reference methods.

4. Reference Measurment Methods

A reference method is defined as "a method of proven and demonstrated accuracy " (Cali et al., 1975). Reference methods represent the primary mechanism by which the accuracy of a definitive method or CRM is transferred into widespread use in the field. The reference method has proven accuracy, but may lack the direct or indirect relationship to fundamental units of the corresponding definitive method. The reference method, like the definitive method, may not be acceptable for routine field use when cost and/or speed are important.

5. Secondary Reference Materials

While primary reference materials are usually produced by a national standards laboratory such as NBS, secondary reference materials are usually developed for use in day-to-day field operations where cost and moderate accuracy are the most important requirements. The materials are usually produced by commerical or individual laboratories, and are meant for direct use as working standards.

6. Field Methods

These are routine methods typically used in normal, everyday operations requiring high throughput and low cost. Many of these methods are instrument-based and are based on comparative analytical principles, thus requiring the use of reference materials to correct for inherent systematic biases.

3.3. Accuracy and Precision in Viscometry

The accuracy of rheological analyses can only be firmly established for Newtonian fluids. For fluids of unknown behavior, accuracy is more elusive (Prentice, 1984):

The usual method of achieving accuracy is by cali-To the classical physicist this may seem bration. so axiomatic that it does not need to be stated. However, when dealing with rheologically interesting materials, the response of any instrument cannot be separated from the properties peculiar to the material. If a viscometer is calibrated, as it often is, by the use of a standard Newtonian fluid of known or predetermined viscosity, then its calibration can hold only for Newtonian fluids. Ideally, for use with a non-Newtonian fluid, it would be calibrated with one of similar characteristics. This, though, requires a knowledge of the very properties that are being sought. It is a circular argument and there is no way of breaking into it. One must therefore have recourse to calibration in

terms of the fundamental units. The fundamental quantities which are measured by a rheometer are usually a torque...and a velocity. However, a knowledge of the torque and velocity are only a means to an end for the rheologist. In order to define the properties of his materials properly, he needs to establish the relationship between stress and strain, and he requires his result to be uninfluenced by the instrumental means he uses to obtain Herein lies the problem of achieving accuracy. it. It has been shown that response of the instrument is conditional upon the properties of the sample material. Consequently, it is not possible to derive an unambiguous stress or strain....

Marvin (1972) also discusses this circular logic in viscosity measurement:

Stress, being defined in terms of forces acting across imaginary planes in a material, cannot be measured directly. It must be inferred from measurements made at a surface of the material, and its calculation implies some assumptions about the rheological properties of the material studied.

One indicator of the comparative lack of accuracy in the field of rheology is the value assigned to the viscosity of The viscosity of pure water at 20.00°C is the interwater. nationally agreed reference point for viscometry. The most recent fundamental measurement of the viscosity of water compared two independent analyses (Marvin, 1971). The accuracy for each method was estimated at 0.1%, yet the results of the two methods differed by 0.5%. While the uncertainty assigned to the value of the absolute reference was therefore declared to be \pm 0.25%, agreement between laboratories is better than 0.1% in many cases (IOS, 1977). The latter precision figure is for capillary viscometers used under very stringent protocols.

The uncertainty assignable to the accuracy of the best capillary measurements of high viscosity fluids cannot be less than one percent (Marvin, 1971). Most field methods, made with instruments rather than with capillaries, have considerably larger precision errors. R.S. Marvin, a retired NBS rheologist, has commented that few instruments, when presented with two fluids differing in viscosity by five percent, will detect any difference (Manning, 1987). Another rheologist (Tung, 1987), working in food science, called rheology "the five percent science."

3.4. Absolute and Relative Viscosity

Officials of NBS have written (Uriano and Gravatt, 1977) that

An absolute measurement of a chemical property such as composition is generally made by a method (either instrumental or manual in nature) in which the property in question is either directly evaluated in terms of the fundamental units of measurement or indirectly related to the base units via exact mathematical equations.

The above definition of an absolute method is restricted to very well-defined circumstances.

Absolute viscosity measurements are those conducted with a complete understanding of the interaction of fluid and instrument. In the strict sense of Uriano and Gravatt, absolute measurements have been published only a few times, mostly of water. All other measurements have been made in explicit or implicit relation to water.

More commonly in scientific literature the term "absolute viscosity" is used to mean "true" viscosity, as opposed to "relative" or "apparent" viscosity. Absolute viscosity in this context is the relationship between shear stress and shear rate. A necessary condition in deriving an absolute viscosity is that the shear field developed in the measuring device (called an "absolute viscometer") is well understood. This means that both the shear stress and the shear rate must be known with reasonable accuracy. A measured absolute viscosity will be the same regardless of the type of instrument used in the measurement. An absolute viscosity measured in a laboratory, for example, will therefore truly represent the viscosity of the same fluid in a defined process situation.

Relative viscosity generally refers to those measurements made on fluids that are repeatable only when using a specific instrumental configuration and technique. Another characteristic typical of relative viscosity measurements is that the conditions of shear stress and/or shear rate are unknown for the analysis. A relative viscometer can be calibrated with suitable (Newtonian) reference fluids so that the relative viscometer can give "true" or absolute viscosity when measuring Newtonian fluids, whose viscosities do not depend on shear rate.

An example of a relative viscosity analysis is one made using a Brookfield RV viscometer. The fluid-contacting sensors for this viscometer have complex geometries that make it difficult, or impossible, to accurately describe the shear field present in the fluid. The Brookfield's results

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can be compared with other identically obtained analyses to serve as a product development yardstick, for instance. The same results, however, cannot be used to predict fluid behavior under actual industrial processing conditions.

A cause of some confusion is the apparent paradox that instruments such as the Brookfield can also be used to measure the absolute viscosity of Newtonian fluids. This apparent contradiction is a consequence of the use of Newtonian reference materials to calibrate the torque-measuring response of the instrument. Because these calibration standards do not depend on a knowledge of the rate of shear, the calibration curve is able to successfully relate the torque to the viscosity of materials whose viscosity does not vary with shear.

3.5. Viscometry Calibration Materials and Methods

This section will discuss how standards of accuracy in viscometry are disseminated from the national standards laboratories to routine laboratory use. The components of this distribution system (units, analysis methods, and standard materials) were discussed in Section 3.2. The assignment of specific materials and methods to the components is the author's.

3.5.1. Definitive Methods

No one method is recognized to be the most definitive, most accurate method for measuring viscosity. Most absolute measurements attempting an accuracy of better than one percent when measuring the viscosity of water (the
internationally recognized primary reference material for viscometry) have been made using capillary flow (Marvin, 1971). Bingham and Jackson (1919) were the first to determine an internationally accepted value for the viscosity of water by evaluating published capillary results dating from 1840.

The currently accepted value for the viscosity of water was published by Swindells et al. (1952). The method used four different capillary viscometers, one pair having the same length but different radii, the other pair having the same radii but different lengths. The work was conducted over a twenty-year period.

Between 1952 and 1971, only three attempts were made to measure the absolute viscosity of any liquid. Roscoe and Bainbridge (1958) suspended a water-filled glass sphere from a torsion wire, and measured decrement in the oscillation period. Maliarov (1959) measured pressure drops across two capillaries connected in series through a central water--filled reservoir. Finally, Kawata, Kurase, and Yoshida (1969) used a capillary, essentially the same as that of Swindels et al. (1952), to measure the viscosity of a hydrocarbon liquid.

Most recently, Marvin (1971) discussed absolute viscosity measurements made by colleagues at NBS on water using two independent methods. White and Kearsley (1971) used a torsional pendulum to measure the period of oscillation of a sphere through water. Penn and Kearsley (1971) measured

pressure drop through taps in the walls of a channel through which water was pumped. The channel was a novel design formed from two accurate cylinders and an optical flat, yielding a triangular cross-section with one side flat and the other two sides circular arcs. Both methods had an estimated accuracy of 0.1 percent, yet the two results differed by 0.5 percent.

3.5.2. Primary Reference Material

IUPAC (Marsh, 1980) and IOS (1977) have stated that "the internationally recognized reference material is water in equilibrium with air at 293.15 K and atmospheric pressure," where the value of atmospheric pressure is 101.325 kPa. The recommended method of preparation cited by IUPAC is "purification by double distillation and passing through a fine sintered glass frit (to saturate the sample with air) just prior to use (Swindells et al., 1952)."

IUPAC (Marsh, 1980) and IOS (1977) have accepted the recommendation of Marvin (1971):

...that viscometer calibrations be based on the following value for the viscosity of water = 0.001002 Pa s [at 293.15 K] with the proviso that when only agreement between measurements made in different laboratories is important, the uncertainty associated with this value be ignored but that when a true value of the viscosity is required, an uncertainty of ± 0.25 percent be assigned to this value (Marsh, 1980).

3.5.3. Reference Measurement Methods

Recall that a reference method is defined as "a method of proven and demonstrated accuracy " (Cali et al., 1975). These methods are used to transfer the accuracy of a defini-

tive method or certified reference material (CRM) into widespread use in the field.

In the U.S., the American Society for Testing Materials (ASTM) has specified the reference method for transferring the result of the absolute viscosity measurements of water into widespread field use. The method (ASTM, 1987) uses a series of "master viscometers" with different calibration constants to successively measure water and oil standards. The master viscometers are capillary instruments, either of the Cannon (1944) or Ubbelohde (1936) type, specially designed to minimize errors due to surface tension, kinetic energy, and capillary end effects.

Capillary viscometers are apparently the universal choice for viscosity measurement where high precision is required. Temperature control is often the factor limiting the precision attainable in the measurement of viscosity. The percentage change of viscosity for many fluids typically ranges from about 2 percent per 'C at 0.001 Pa s to 10 percent per 'C at 10 Pa s. For accurate viscosity measurement the temperature must therefore be controlled to ±0.01'C or better. This level of control is most easily realized with a viscometer that can be completely immersed in a thermostatic bath. A capillary viscometer is one of the few viscometers easily usable in such a bath.

The first part of the ASTM method uses two master viscometers, referred to as "master class" instruments by IUPAC (Marsh, 1980), with calibration constants in the range of

0.001 to 0.003 cSt/s. Water under the primary reference material conditions at 20°C is used to determine the calibraton constant of the two instruments.

The calibrated master class viscometers are then used to measure two Newtonian oils (see Secondary Reference Materials, Section 3.5.4.) at 40°C. The first oil must have a kinematic viscosity of about 3 cSt at 40°C, the second a kinematic viscosity of about 8 to 9 cSt. The now-calibrated oils are then used to determine the calibration constant of a third master viscometer in the range of approximately 0.003 to 0.009 cSt/s corrected to 20°C.

Additional master viscometers and additional viscosity oil standards can be calibrated by extending this "step-up" procedure until the desired viscosity range is achieved. Steps between successive viscosities or calibration constants must increase by a factor of three or less. Oils are calibrated at other temperatures using the average result from two master instruments. Corrections must be made, where applicable, for differences in acceleration due to gravity, temperature, buoyancy, density, and surface tension.

The repeatability (difference between repeated tests) of the method is such that the difference between successive test results should exceed 0.1% of their mean in less than 1 case out of 20. The reproducibility of the method (different operators and laboratories) is better than 0.35%, analogously defined. The accuracy of standards over 0.1 Pa s

calibrated by this method should be assigned a value of $\pm 0.3\%$, the uncertainty arising from the error in the multi-step and in the limited stability of the oils (Marvin, 1972).

Other nations use an essentially identical approach to that of the United States. According to Marsh (1980):

...reference materials with certified values are used to calibrate viscometers. The certified values of these reference materials are always determined by comparison with a viscosity of water, either directly or indirectly, through a chain of intermediate reference liquids and master class instruments. The consistency of the various national viscosity scales is checked by a continuing programme of direct international comparisons made by the exhcange of both master viscometers and reference materials between the various suppliers.

The ASTM methods are apparently well-respected in the international community. As an example, consider the work of Bauer and Meerlander (1984). They used ASTM method D 2162 (1973) to measure water as the basis for an investigation of low-viscosity calibration materials. See Section 3.6.2. for further discussion. The authors were with the Physikalisch-Technische Bundesanstalt, the national standards laboratory of the Federal Republic of Germany.

3.5.4. Secondary Reference Materials

IUPAC has published a survey of secondary reference materials: "Recommended Reference Materials for Realization of Physicochemical Properties. Section: Viscosity" (Marsh, 1980). The recommendation concerns only reference liquids which are Newtonian. One may infer that non-Newtonian fluids are not recommended by IUPAC as viscosity reference materials.

3.5.4.1. Survey of Internationally Recognized Materials

The fluids from the 10 international suppliers cited in the IUPAC survey include petroleum oils, polyisobutenes, silicone oils, undefined polymers and asphalts, and molten glasses. One reason that pure materials are not used as reference materials is that viscosity usually depends "significantly and indeterminately on the purity of the material." Any pure material would therefore require purification immediately prior to use as a viscosity standard (e.g., water in ASTM method D 2162). Unfortunately, those materials that can be sufficiently purified without elaborate equipment have viscosities of the same order of magnitude as water (Marvin, 1972).

Marsh states that "it is necessary that the (calibration) materials show Newtonian behavior, that they are non--corrosive, and except for molten glasses, have a high solubility in at least two readily available organic solvents so as to enable appropriate cleaning." Further requirements are stability of viscosity during storage and use, reasonable cost, and safety.

The suppliers surveyed included the national standards laboratories of Australia, France, the Federal Republic of Germany, Hungary, Japan, the Netherlands, Poland, the United Kingdom, the United States, and the U.S.S.R. One private laboratory (Cannon Instruments, U.S.) was also included. The viscosities of CRMs available from the 10 suppliers ranged from 10^{-3} to 10^{11} Pa s, though the most common range was from 10^{-3} to 30 Pa s.

The uncertainty of the values assigned to standards in the 0.1 to 10 Pa s range, and above 10 Pa s, is about 0.3 percent and 1 percent, respectively. Temperature control necessary to use the standards is generally within 0.01°C for the lower range, and 0.02°C for those standards above 10 Pa s.

3.5.4.2. Reference Materials in the United States

The U.S. NBS supplies three reference materials with viscosities ranging from 10 to 10^{11} Pa s. These materials are designed for calibrating rotating cylinder instruments and fiber elongation equipment, and are certified in the temperature range of 464°C to 1545°C.

The other major source of certified viscometer calibration materials in the U.S. is provided by the Cannon Instrument Company (State College, PA) under contract with ASTM Committee D-2. The materials supplied by Cannon ranges from 0.003 Pa s to 900 Pa s.

A discussion of the composition and properties of the Cannon materials is instructive in discerning important properties of calibration fluids. The 0.11 to 1.4 Pa s materials, highly refined petroleum oils without additives, are of mixed composition, include naphthinic molecules, and are highly paraffinic. The materials have a narrow, but unspecified, molecular weight distribution.

Cannon's 4.9 Pa s to 72 Pa s materials are polybutenes or polyisobutenes. Butene is polymerized to the degree necessary to give the appropriate viscosity; they are not blended and do not contain additives. While many polymers are non-Newtonian, polybutenes below about 17000 daltons have been shown to be Newtonian (Porter and Johnson, 1960). The Cannon fluids are probably below 5000 daltons, but may have some slight deviations in Newtonian behavior in the generation of stress normal to that of shear. These deviations, however, are too slight to be demonstrated with respect to shear rate (Hardy, 1962).

Cannon's materials have a very temperature-dependent viscosity: a 1°C change in temperature will result in a viscosity change ranging from two to nine percent, depending on the specific oil. The stability of these materials is such that viscosity changes less than 10% per year. While most standards are good for three to five years, Cannon claims a one year shelf-life. The stability estimates are for unopened jars only; an opened jar of oil can pick up solvent vapors and change viscosity (Manning, 1987).

A third source, Brookfield Laboratories (Stoughton, MA), supplies silicone oils "traceable to NBS." The oils are purchased in bulk from General Electric Corporation (Waterford, NY), calibrated, and repackaged. However, Marvin (1972) stated that: "Other series [besides the ASTM-Cannon series]...are available...but none are measured with the degree of precision and control of the ASTM series." Two

undesirable properties of silicone oils are that they are difficult to remove from viscometers (Marvin, 1972, and Hardy, 1962), and that their viscosities are "widely known to be slightly shear-thinning" (Manning, 1987). However, Walker (1989) claims that silicone is less likely to become contaminated than petroleum oils, that "chlorothane" effectively cleans these fluids from instruments, and that the real shelf-life is 5-10 years for some of the Brookfield silicones. One must note that the Brookfield standards are not part of the national standards organizations' programs in the U.S.

3.5.5. Rheometer Manufacturers' Recommendations

Several instrument suppliers have recommended different practices for assuring the user of the accuracy of measurements made with their rheometers. The manufacturers' advice falls into two categories, described below.

3.5.5.1. Hanging Weights

Rotary rheometers constitute a very popular class of instrument sold for viscosity measurement. The instruments' basic principle of operation is as follows. The sample is held between two independent parts of a sample cell. The most popular geometries are: 1) cone (or plate) and plate, and 2) coaxial cylinders (also referred to as "concentric cylinders,", consisting of a "cup" and a "bob"). One part of the cell is held stationary while the other part is rotated. The resistance of the fluid, held between the two cell components, to this rotation is measured as torque versus the angular velocity of rotation. The viscosity is then calculated from a theoretical understanding of the flow field created in the sample by the sample cell. Either the speed or the torque may be controlled in a rotary rheometer and the other parameter measured. Both the angular velocity and the torque must be accurately known for the resulting viscosity to be accurately calculated. The manufacturers of at least two rotary rheometers (Rheometrics and Haake) recommend that the torque sensor in their instruments be calibrated using "hanging weights."

The hanging weight method employs a weight connected to the torque sensor via a thin nylon line which is draped over a suitable disk or cylinder of known radius. The resulting torque can be accurately calculated and related to the instrument torque response. A series of weights and resulting responses are used to construct a calibration graph. A linear regression of the graph can then be used to translate the instrument readings taken during sample measurement into torque.

3.5.5.2. Calibration Fluids

Manufacturers of both relative and absolute viscometers recommend that their instruments be checked occasionally using a standard fluid. Brookfield Laboratories (Stoughton, MA) used a series of calibration fluids to develop the calculation factors for their popular RV series of relative viscometers. Fisons Instruments (Saddle Brook, NJ) sells German-made calibration fluids to those users of Haake

viscometers who wish to check the accuracy of their instruments.

Mitech, Inc. (Willoughby, OH), distributors of the Carrimed Controlled Stress Rheometer (Carrimed Ltd., Dorking, England), have used Brookfield calibration oils to check the accuracy of the instrument during installation, particularly with regard to the accurate setting of the gap when using the cone and plate geometry. This approach is confounded by the difficulty of temperature calibration at the plate surface for this instrument. Accurate knowledge (within 1% of the true value) of the cone angle and gap between the cone and plate for the Carrimed is exceedingly difficult to obtain, however.

3.6. Alternative Secondary Reference Calibration Materials 3.6.1. Relationship of Fluid Structure to Rheological Properties

There has been considerable interest in relating viscosity of liquids to their molecular structure. A voluminous review of the general literature was made by Bondi (1967). Associations of structure with equilibrium properties (including density, heat capacity, temperature, and pressure) and transport phenomena (relaxation of dipoles) of a wide variety of fluids were discussed, and relationships were derived from fundamental considerations of molecular transport by using "semiempirical correlation schemes" with temperature and pressure. Such a theory could possibly

predict ideal calibration materials, in terms of the desirable Newtonian and handling properties mentioned above.

Mathlouthi and Kasprzyk (1984) reviewed theoretical and empirical relationships of sugar-water solution concentration, temperature, and viscosity. Despite this being a relatively simple system compared with many fluids of practical interest, the authors wrote: "Viscosity of sugar solutions is not easy to put into equations if we take into account the fact that the sucrose molecule is capable of hydration, sugar-sugar association or the promotion of 'water-structure'." Forty-six equations relating viscosity to various parameters were discussed. Most were derived from polymer science studies. Most empirical relations used in the sugar industry were found to be adaptations of theoretical predictions.

Any predictions from theory must be confirmed. It seems apparent, therefore, that empirical observations should figure prominently in any scheme to supplement current oil-based calibration fluids with materials more suitable for large-volume applications. For all gases and most low molecular weight homogenous fluids, the shear stress is a linear function of the shear rate, passing through the origin at $\dot{\gamma} = 0$ (Boger et al., 1985). This class of materials conforms to the Newtonian model very well.

Solutions and melts of flexible macromolecules, as well as many suspensions, typically decrease in apparent viscosity with increasing rate of shear. The decrease is usually

ascribed to the breakdown of a structure at the collodial or molecular level. An example of this change in structure is the behavior of macromolecules, which can become more aligned and therefore less entangled and resistant to shear with increasing rate of shear.

3.6.2. Survey of Literature Materials

Few fluids have been cited in the literature as having been actually used or proposed as calibration materials for viscometry. Besides the water standard, petroleum oils, butene polymers, and silicone already discussed, only two other groups of fluids have been seriously considered as Newtonian calibration fluids. The groups can be classified as pure compounds and solutions.

3.6.2.1. Pure Compounds

Hardy (1962) noted that the use of pure chemicals as reference standards had been proposed in the scientific community. The rationale held that suitable pure compounds could be characterized by a standards laboratory, then confidently used in other laboratories after appropriate routine purification. Unfortunately, according to Hardy, the techniques for both purification and checking purity of many potential calibration fluids were too specialized for most laboratories.

By 1984, however, this situation had changed. Various organic solvents became available with remarkable purities (part per billion levels in some cases) to serve the burgeoning application of spectroscopy and chromatography

analyses. Bauer and Meerlender (1984) studied low viscosity fluids (less than that of water) with the aim of improving the reproducibility (several percent) of measurements of the same fluid on different viscometers. They recommended that several commercially available hydrocarbons and halogenated hydrocarbons be used as viscosity standards. The fluids were commonly available with purity sufficient to characterize viscosity to within 0.4%.

Few pure compounds that exist as fluids at 25°C have viscosities above 0.1 Pa s (Weast, 1971). Glycerin's viscosity is 0.954 Pa s but is hygroscopic (Stecher, 1960) and therefore unstable for critical uses. Glycerin was, however, used as one of a series of Newtonian fluids in a study of heat transfer in a food canning process (Anantheswaran and Rao, 1985). Glycerin is available in the U.S. in 570 pound drums for about \$1 per pound at a purity of 99.7% (Simpson, 1989). Approximate bulk costs of other fluids per pound in the U.S. are: polybutenes, \$2 (Collins, 1987); silicone oils, \$8 to \$25 (Pucinich, 1989); 67% sucrose syrup, \$0.46; corn syrups, \$0.11 to \$0.20 (Simpson, 1989).

Purification and analysis of purity is a critical factor limiting the use of high-viscosity pure compounds as calibration materials for viscometry. Another problem with use of pure compounds is the need to have several fluids of various viscosities available, since many applications require that a range of conditions be evaluated. Ease of use, cost, and safety are also important considerations con-

tributing to the disuse of this class of materials as calibration fluids for viscometry.

3.6.2.2. Solutions

A true solution is a homogeneous molecular dispersion of two or more substances. In a solution, the individual components are subdivided into particles of molecular size, and can only be separated by physical processes. A solution contains two phases, in which one or more *solute*(s) are dispersed in a liquid *solvent* of some kind, where the solvent is that component which retains its original physical state after the solute(s) are added (Quagliano and Vallarino, 1969). While most viscosity reference materials are true solutions, they consist of two or more *fluid* components. For purposes of this discussion, let us consider solutions to be solid solutes dissolved in liquid solvents.

3.6.2.2.1. Sucrose

The only solution proposed as a calibration material is sucrose-water. Andrade (1947) stated that "The capillary tube viscometer is extensively used for ordinary laboratory measurements of viscosity, being calibrated by the use of a standard liquid such as water or sucrose solution." Bates (1942) reviewed the use of sucrose solutions to calibrate viscometers in the sugar industry. Sucrose solutions were recommended because of a perceived need to reduce errors when using relative viscometers by "employing for calibration purposes liquids with physical properties not very different from the liquids to be investigated." Subsequent

discussion by Bates leads one to surmise there were no other calibration fluids besides water available at that time. In fact, NBS began supplying hydrocarbon oils for viscometer calibration in 1938 (Hardy, 1962).

Bates (1942) discussed several problems with using sucrose solutions. Sucrose purity was a potential factor, but NBS did (or now does) furnish crystalline sucrose standards. Preparation of the solution was recommended one the same day as use, but filtering (to eliminate dust) of the prepared solution could change concentration. Use of the solution required special care to avoid condensation and evaporation, including a recommendation to work in a temperature range of 15°C to 25°C.

Table 1 shows the dependency of solution viscosity on sucrose concentration (Bates, 1942). At moderate concentrations, the viscosity of sucrose solutions are well under 0.1 Pa s. Only the most concetrated solutions have viscosities of about 1 Pa s.

Another aspect of the data shown in Table 1 is the effect of sucrose solution concentration on viscosity. The table shows that a slight inaccuracy in the knowledge of sucrose concentration at point of use can lead to a large error in the assumed viscosity of the calibration material. For example, the viscosity of a 73% sucrose solution is only 72% of the viscosity of a 74% sucrose solution. Most "liquid sugar" syrups sold to the food industry in the U.S. are 67% sucrose (Hoynak and Bollenback, 1966). Thus it

Table 1. Selected sucrose-water solution viscosities at 20°C.

% Sucrose	η (Pas)
60	0.0589
61	0.0697
62	0.0830
63	0.0998
64	0.1210
65	0.1482
70	0.4850
71	0.6408
72	0.8609
73	1.178
74	1.643
75	2.344

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seems reasonable that preparing and using sucrose solutions of viscosity above 0.4 Pa s involves considerable inconvenience and potential error.

3.6.2.2.2. Polymers

An almost infinite variety of polymer materials exists. Pure polymers that exist in the fluid state are, with apparently few exceptions, soluble only in organic solvents. They are therefore unsuitable for large-volume viscometer calibration uses in the food industry, whatever merits their other characteristics may have.

One class of polymers attractive to rheologists are those at least partially soluble in water. Some examples commonly used in the food industry include many polysaccharides such as xanthan, modified celluloses and starches, pectin, various gums, alginates, and gelatin. These materials are commonly used to form gels or provide texture to a variety of liquid and semi-liquid products (Sanderson, 1981).

Most of these water-associative polymers form solutions that are shear-thinning, with a few being shear-thickening (Szczesniak and Farkas, 1962). Simply stated, these polymers are non-Newtonian for one or both of the following reasons. First, they are very large and entangled in solution. The molecular network aligns and deforms in the direction of shear, and this effect increases with rising shear rates. Second, individual molecules of many of these polymers associate with other molecules in solution via

hydrogen bonds, ionic attractions, or vanderWaals forces. Some of these associative forces are weak enough to be overcome by shear, even at low rates.

Consider the specific example of the widely used gum from the microorganism Xanthomonas campestris (Bewersdorff and Singh, 1988). Xanthan gum may be considered to be an anionic polyelectrolyte repeating polymer of pentasaccharide The primary structure in solution is formed by the units. charged trisaccharide side chain folded around a cellulose backbone, yielding a rod-like structure stabilized by intramolecular non-covalent bonding. The secondary structure undergoes a helix-coil transition depending on conditions of salinity and temperature. In solutions of low ionic strength, the xanthan molecule is a highly extended chain resulting from intra-chain electrostatic repulsions. Adding small amounts of electrolytes to the xanthan gum solution causes the gum to contract and assume a configuration of rigid, worm-like coils, which associate with each other at higher ionic strengths.

One way to obtain Newtonian behavior from water-soluble polymers would be to choose those polymers that exhibit little of the above behavior. Specifically, a polymer candidate for a Newtonian fluid would be relatively small, and not form secondary associations with its other polymer neighbors in solution. Many corn syrups are solutions of such polymers, along with smaller saccharides.

3.6.2.2.3. Corn Syrups

Corn syrups, known in the United Kingdom as "glucose syrups," have been defined (U.S. Govt., 1977) as:

a clarified, concentrated, aqueous solution of the products obtained by the partial hydrolysis of corn starch. Depending on the degree of hydrolysis of the starch, glucose syrups may contain dextrose, maltose, or higher oligosaccharides.

The corn industry places a lower limit of 20 DE ("dextrose equivalent," a measure of chemical conversion of starch to simpler sugars, using a scale from 0 (no conversion) to 100 (complete conversion) on its definition of corn syrups. This limit differentiates corn syrup from lower conversion products typically referred to as maltodextrins (Junk and Pancoast, 1973).

Corn syrups of very high or complete conversion are available that are virtually pure solutions of monosaccharides. Theoretically, these should behave identically to sucrose with respect to shear independency. As the degree of conversion decreases, syrups have increasingly higher concentrations of increasingly larger polysaccharides, thus giving increasing viscosity. In fact, the variety of corn syrups available on the world market is quite remarkable. Table 2 illustrates the range available from one manufacturer's line of corn syrups, and some of their properties (A.E. Staley Mfg. Co., 1987).

One concern expressed above is the potential of a calibration material to gain or lose moisture during use. Corn syrups do have a tendency to take up or lose moisture to the

Table 2. Composition and physical properties of A.E. Staley Co. corn syrups.

SYRUP TYPE: Staley number

DATA	200	300) 1	300	7300		7350	230	0 4	4300	4400	5500	100
Deg. of Conver'n	v.lo	v la	W	reg.	reg	•	med.	mec	i.	high	high	v.high	v.high
DE, %	26	3	35	43	4	2	50) !	54	63	6 3		
Dextrose, %		5	13	1	9	9	1	0	27	37	37	41	50
Fructose, %		0	(0	0	0)	0	0	0	0	55	42
Maltose, %		8	10	1	4	34	4	2	22	29	29	90	3
Maltotriose, %		11	1	1	13	2	4	22	1	5	9	90	0
Higher Sacchar.,	% [′]	76	66	5	4	33	2	6	36	25	25	4	3-5
Total Solids, %	77.5)	80	80.3	80	.4	80.7	7	81	81.6	83.6	77	71
Moisture, %	22.5	2	20	19.7	19.	6	19.3	: 1	19	18.4	16.4	33	29
рН	4.7	4.'	7	4.7	4.	7	4.7	4	.7	4.7	4.7	3.5	5 4

surrounding atmosphere. This behavior, called hygroscopicity, is controlled by the syrup's equilibrium relative humidity (ERH), the relative humidity at which moisture is neither gained or lost. High DE syrups attract moisture because they have a low ERH, while low DE syrups have a high ERH and so will tend to lose moisture to their surroundings (Dziedzic and Kearsley, 1984). Ideally, the viscosity of any material proposed as a calibration fluid should be relatively unaffected by absorption or loss of moisture during calibrating operations.

Several workers have made rheological measurements of corn or similiar syrups. Rao and Cooley (1984) used corn syrups diluted with water to various viscosities to determine shear rates in viscometers employing complex geometries such as mixer paddles. The corn syrups were found to be Newtonian when measured with a coaxial cylinder viscometer (Haake Rotovisco). Castell-Perez, et al. (1986) used corn syrups to evaluate a mixer viscometer system, finding the syrups to be Newtonian using a Brookfield coaxial cylinder viscometer. Prilutski et al. (1983) showed that the behavior of the Boger fluid (Boger, 1977/8), a solution of polyacrylamide in corn syrup, was a logical consequence of dissolving a small amount of a high molecular weight polymer in a highly viscous Newtonian fluid. The fluid has a constant viscosity provided by the syrup, yet is highly elastic, the behavior being a sum of the solvent and polymer contributions. Cutler et al. (1983) used syrups similar to

those from corn (maple, rosehip, honey, and "pancake" syrup) as Newtonian fluids to study sensory viscosity perception. A cone-plate viscometer (Rheometrics) was used to characterize the viscosity of the syrups, finding them to be Newtonian. Finally, Steffe et al. (1983) found, in a review of the literature, that corn syrups and most fruit juices are Newtonian.

Chapter 4

MATERIALS

ASTM viscosity calibration oils were obtained from Cannon Instrument Co, State College, PA. Oils used (nominal viscosity, Pa s at 25°C) included S60 (0.1), S600 (1.4), S8000 (21) and S30000 (77).

Corn syrup samples were donated by A.E. Staley Co., Decatur, IL. Samples (nominal viscosity, Pa s at 25 °C) included Isosweet 100 (0.17), Isosweet 5500 (0.80), Staley 4300 (17), Staley 3260 (20), Neto 7350 (47), Sweetose 4400 (87), Staley 1300 (87), and Staley 300 (170). The nominal chemical composition and physical properties for these fluids are listed in Table 2.

All samples were used as received.

Chapter 5

METHODS

With the literature suggesting that corn syrups are Newtonian, the work focused on evaluating the Newtonian behavior of syrups of a wide range of viscosities. Additionally, repetitive analyses were made on the same sample of syrup over a period of days to determine if the syrups changed viscosity as a result of normal laboratory handling. 5.1. Temperature Considerations

The target temperature for all analyses was 25° C. The Carrimed CS500 rheometer's temperature control was \pm 0.1°C. The Haake RV-12 rheometer's temperature control was difficult and time-consuming to adjust, so that a few analyses were conducted at average temperatures as low as 24.0°C and as high as 25.6°C. Most analyses were conducted between 24.8°C and 25.2°C; the temperature within each analysis varied less than \pm 0.1°C.

5.2. Determining the Degree of Newtonian Behavior

Corn syrups were compared with Cannon oil standards (assumed to be Newtonian) for fundamental behavior indicative of Newtonian fluids: linearity of shear stress vs. shear rate, insignificant G', and insignificant time and shear dependency.

5.2.1. Linearity of Shear Stress vs. Shear Rate in Steady Shear

5.2.1.1. Haake Coaxial Cylinders

Analyses were performed with a Haake RV12 rheometer (Fisons Instruments, Saddle Brook, NJ) with M-150 and M-500 measuring heads. A Haake F3-K controlled temperature bath supplied oil to a "temperature vessel" which surrounds only the vertical side of the inserted sample cup. The sample cups, designated MV (inner radius = 0.0210 m) and SV (radius = 0.01155 m), include a hole in the bottom through which a temperature probe was inserted, positioned a few millimeters away from the bottom of the inner rotor during analysis. Rotors (the inner, rotating cylinder, also known as "bob") used included the SVI (0.010147 m radius, 0.061468 m height), the SVII (0.010084 m radius, 0.019329 m height), the MVA (0.018402 m radius, 0.05936 m height), and the MVB (0.020053 m radius, 0.061341 m height). The bottom and top surfaces of these rotors were recessed at least 0.015 m. The MVA and MVB rotors were fabricated at the Kellogg Company and were similar to the MVI and MVII rotors sold by Fisons Instruments.

The rotational velocity of the inner rotor during an analysis was programmed using the Haake PG140 controller. Two different types of rotational velocity programs were used: continuous and step-ramp. The first approach (recommended by Haake) consists of continuously increasing the rotational velocity of the bob from the initial resting state to the maximum velocity desired. The step-ramp method quickly increases ("steps") rotational velocity to a desired value, then holds it there for a length of time to establish

equilibrium. The velocity is then stepped to the next desired value, and held again. The various steps span the desired shear rate range.

The choice of sample fixtures (rotor and cup) and rotational velocities was dictated by the maximum torque generated by turning the rotor against the various viscosity fluids tested. The maximum torque capability of the measuring heads limited the shear rates available to under 500 s⁻¹ for the lowest viscosity materials. Table 3 shows the rotors used, their dimensions, and the ratio, R, of the rotor to cup radii.

The Haake RV12 was connected to an IBM-PC for data capture and subsequent analysis. A Data Translations, Inc. (Marlborough, MA) DT2801 board installed in the IBM-PC converted the rheometer's analog signals of rotational velocity, torque, and temperature to digital form, and stored them to a disk at 2 second intervals.

Viscosity results were calculated from the digitized data using Lotus 123 (Lotus Development Corp, Cambridge, MA). The Lotus worksheet calculated shear rate from rotational velocity using a generalized method that does not assume a fluid model *a priori* (Krieger, 1968). Step-ramp

Table 3. Haake concentric cylinder dimensions.

Rotor	Radius (m)	Height (m)	R		
MVA	0.01840	0.05936	0.876		
MVB	0.02005	0.06134	0.955		
SV1	0.01015	0.06147	0.879		
SV2	0.01008	0.01933	0.873		

experiments used step intervals of 30 seconds duration, and were calculated using the average of the last 16 seconds of each step. Continuous-ramp experiments used all points of data.

5.2.1.2. Carrimed Cone and Plate

The Carrimed Controlled Stress Rheometer CS500 (Carrimed, Ltd., Dorking, England) was used with cone and plate geometry. Various cone angles and diameters were used: 1'-4cm, 1'-2cm, 2'-2cm, and 2'-6cm. The Carrimed was supplied with an optional "solvent trap," a device designed to eliminate sample drying at the edge of the cone-plate gap.

Figure 3 shows a diagram of the cone and plate with the solvent trap in place. An appropriate solvent (water was used for corn syrup samples) was placed in the well surrounding the cone's shaft, and the solvent trap was lowered in place. The solvent formed a barrier to air circulation between the air gap inside the trap and outside. This solvent trap was not used during any experiments with the Cannon oils, but was used for most corn syrup experiments.

The Carrimed was programmed to increase torque in a continuous program (analogous to that of the Haake instrument) and measure the resulting rotational velocity. Achieving a fixed maximum shear rate was therefore a trial and error process. All replicate experiments used identical torque programs.



Figure 3. Carrimed cone and plate geometry with solvent trap.

TX). The software both controlled the Carrimed instrument and calculated experimental data. Shear rate and shear stress were calculated for each of the approximately 200 data points available for a typical experiment of two minutes duration. A straight line with non-zero intercept was fit to the data using the method of least-squares, and a correlation coefficient, r^2 , was calculated. The correlation coefficient and magnitude of the non-zero intercept were used as indicators of the degree of Newtonian behavior. 5.2.2. Dynamic Oscillatory Shear Experiments

The Carrimed CS500 was also used for dynamic oscillatory tests. The reason for using this testing mode was to check for elastic behavior. Fluids are known to exist that are very elastic, yet whose steady shear viscosity does not change with shear rate (Boger, 1977/78).

The Carrimed instrument had an oscillation frequency range of 0.01 to 10 Hz, while its torque range stretched to 50 N m. Two types of experiments were conducted: torque sweeps at constant frequency, and frequency sweeps at constant torque. The amplitude of oscillation was automatically limited to 10 milliradians via software control. Torque sweeps used a frequency of 0.5 Hz (in the logarithmic middle of the available range), while the frequency sweeps were conducted from 0.05 to 4.332 Hz, the widest efficient range available on the CS500.

5.2.3. Time-Dependency

A truly Newtonian fluid not only has a viscosity which is constant with varying shear rate, but also with repeated sampling over time (non-time-dependent). The tendency of test fluids to change with continuing or sequential analysis was therefore studied. Additionally, an ideal calibration material should have a long shelf-life, i.e., should maintain constant properties for useful periods after manufacture. Viscometric analyses of the same fluid were therefore performed on different days.

5.2.3.1. Multiple Analyses of Same Sample Load

Most steady shear analyses were performed with an up--ramp (increasing rate of shear) immediately followed by a down-ramp. A single shear stress - shear rate plot of both ramps should show identical results with no thixotropic loop present.

A second approach taken was to simply perform a series of identical analyses on a sample without removal from the rheometer. A few analyses were conducted after leaving the sample in the rheometer for a period of one to several days, allowing for the possibility of structural recovery in the sample.

5.2.3.2. Separate Analyses Conducted Days or Months

Apart on the Same Sample

Samples were repeatedly analyzed over a period of months to determine shelf stability. Noting that the current ASTM calibration oils have a shelf-life of one year in a sealed

jar, comparisons were made between the differences among successive oil analysis results, and the corresponding differences differences among corn syrup analyses.

Chapter 6

RESULTS AND DISCUSSION

6.1. Haake Sensor Windup

The RV-12 measuring head uses a spring to measure the torque exerted on the fluid by the cylinder rotating against the fluid being tested. The measuring spring requires an angular displacement to register torque. In an experiment covering a range of rotational speeds, the torque-measuring spring will deflect to differing degrees, resulting in the "windup effect" (Whorlow, 1980; Steffe, 1987).

The windup effect is shown in Figure 4, a plot of torque vs. rotational speed for two typical continuous-ramp Haake experiments. Each experiment was conducted by increasing the sensor's rotational speed at a constant rate of increase from an initial resting state to the maximum speed, then back down again. These two parts of a single experiment are called the "up-ramp" and the "down-ramp." A perfectly Newtonian fluid, measured using a perfectly stiff torque sensing device, should show identical traces for both the up and down portions of each experiment.

The graph shows, however, that the down-ramp trace is above that of the up-ramp. A time-dependent fluid, one which would be expected to break down over the course of this experiment, would be expected to give a down-ramp below that of the up-ramp. It was established above (Section 3.5.4.2.), however, that the Cannon oils are Newtonian,



Figure 4. Haake "windup" effect.
certainly true for this experiment conducted at shear rates below 300 s⁻¹.

The anomalous behavior shown in Figure 4 may be explained by either (or both) of two mechanisms. First, consider the windup effect mentioned above. The sensor, being constantly rotated faster on the up-ramp, never comes to equilibrium until the point when the rotational speed begins its descent during the down-ramp portion. Then, the torque sensing spring is always wound too tightly during the down--ramp. The result is that the up-ramp results are too low, while the down-ramp results are too high.

A second possible source of the effect of the response lag could be the inertia of the fluid and rotating sensor, but the magnitude of such error should be small. Sample and/or rotor densities or sizes (and thus masses) would need to be varied to experimentally test such a hypothesis, because the two effects cannot otherwise be separated. It seems easier to use the rotor rotation programming technique below, which will compensate for both error sources.

The continuous increase of sensor rotational speed is the manufacturer's recommended method for conducting "absolute viscosity" measurements over a range of shear rates. One way to eliminate the windup effect is to take data only once the torque spring has achieved equilibrium by conducting a step-ramp experiment. Use of this technique has been reported (Rao et al., 1975). Figure 5 shows this behavior for the Haake RV-12 sensor during an experiment that



Figure 5. Haake step-ramp program and sensor lag, Cannon S30000 oil.

included both an up-ramp and a subsequent down-ramp analysis of Cannon S30000 oil using the SVII geometry. The lag of torque response behind the rpm program is small but does illustrate the error due to the twisting of the measuring spring.

6.2. Degree of Newtonian Behavior

6.2.1. Steady Shear

6.2.1.1. Haake Coaxial Cylinders

One measure of the Newtonian behavior of a fluid is the linearity of a shear stress - shear rate plot. Table 4 compares a Cannon calibration oil, S60, with a Staley corn syrup, Isosweet 100. Analyses were conducted on the Haake using the MVB coaxial cylinders, continuous or step-ramps to a maximum rpm of 200 or 250 for the oil or syrup, respectively. Only the up-ramp (increasing rotational velocity) data are included. Syrup analyses employed a cover for the top of the sample holder to reduce drying during the analyses.

The table shows that the Staley corn syrups have correlation coefficients approximately equal to that of the accepted Newtonian standards.

Another way way of examining the same analytical results is via a plot of apparent viscosity $\eta_a vs. \dot{\gamma}$, where $\eta_a = \sigma/\dot{\gamma}$. A perfectly Newtonian material, in an ideal viscometer, should yield a $\eta_a vs. \dot{\gamma}$ plot that is a straight line horizontal to the x axis. Figure 6 illustrates this type of plot comparing single analyses of syrup and oil

Table 4. Linearity of shear stress - shear rate analysis results as expressed by correlation coefficient, r^2 , for low viscosity fluids, concentric cylinders.

	NEWT	ONIAN		BINGHAM	
MATERIAL		r ²	η, Pa s	σ _y , Pa	r ²
Continuou	s ramp	data:			
C. S60	592	0.999	0.111	-0.892	0.999
**	596	0.999	0.0996	-0.584	0.999
**	596	0.999	0.0974	-0.688	0.999
I.S. 100	478	0.999	0.181	-0.611	0.999
**	478	0.999	0.180	-0.283	0.999
Step ramp	data:				
C. S60	596	0.999	0.0980	-0.288	0.999
I.S. 100	478	0.999	0.179	-0.029	0.999

taken from Table 4. The corn syrup behaves very similarly to the oil. Both fluids show an abrupt increase in viscosity at low shear rates due to the windup effect. Because the spring lags behind the rotation program of the inner rotor, the reported rotational velocity is greater than it actually is. The fluid therefore "appears" to be less viscous than it really is during this early portion of the experiment.

Another manifestation of this effect is that the opposite shape of the curve occurs in down-ramp experiments (not shown). Both fluids show relatively constant viscosity at the higher shear rates, as expected for a Newtonian fluid.

Similar comparisons for medium and high viscosity fluids follow. Table 5 has both medium and high viscosity data included. Analyses were performed using the SVII coaxial cylinder system, with step-ramps of 50 to 100 maximum rpm. The corn syrup data is as linear as that of the calibration oils.

6.2.1.2. Carrimed Cone and Plate

The cone and plate geometry has several advantages over coaxial cylinders. Implemented in the Carrimed CS500 controlled-stress rheometer, the geometry is very easy to load. One simply places a measured amount of liquid on the plate surface, then raises the plate to a close, pre-determined proximity with the cone. An excess of fluid, easily visually inspected, is carefully wiped or scraped away, leaving an optimal sample load between the moving cone and the fixed plate.



Figure 6. Linearity of low viscosity fluids, concentric cylinders.

Table 5.	Linearity of shear stress - shear rate analysis
	results as expressed by correlation coefficient,
	r^2 , for medium and high viscosity fluids, concen-
	tric cylinders.

		NEWTON	IAN	BINGHAM		
MAT	ERIAL	η, Pa s	r ²	η, Pa s 	σ _y , Pa	r ²
c.	S600	1.33	0.999	1.36	-1.77	0.999
s.	IS5500	0.829	0.999	0.840	-1.39	0.999
	**	0.812	0.999	0.836	-2.59	0.999
c.	S30000	73.8	0.997	72.1	43.3	0.999
	**	70.2	0.998	68.8	37.6	0.998
	**	76.8	0.999	77.1	-6.38	0.999
s.	N7350	51.9	0.997	50.0	45.8	0.999
	**	47.2	0.997	45.2	46.6	0.999
	**	53.3	0.998	52.0	31.9	0.999
s.	S4400	87.0	0.999	85.8	19.7	0.999
s.	1300	82.7	0.999	81.4	21.0	0.999
	**	87.2	0.999	86.1	17.3	0.999

Another major advantage is that, for any given angular velocity of the spinning cone, the shear rate, and consequently the shear stress, experienced by the fluid in the gap is the same throughout the gap (Whorlow, 1980) as long as the cone angle θ is less than 5°. The calculation of shear rate is then simply

$\dot{\mathbf{y}} = \boldsymbol{\omega} / \boldsymbol{\theta}$

and the construction of the shear stress-shear rate curve is straightforward and linear across a wide range of shear rates.

The uniform shear rate advantage, together with the CS500's constant stress operating-measuring principle (as opposed to the Haake's torsion spring), should result in well-behaved flow curves. Figure 7 shows a η_a vs. $\dot{\gamma}$ curve for relatively low viscosity fluids. The Staley IsoSweet 100 corn syrup's flow curve has a shape very similar to that of the somewhat more viscous Cannon S600 calibration oil.

Similarly, Figure 8 compares flow curves for high viscosity fluids. The curves, again, have similar shapes, suggesting that the corn syrups are as Newtonian as the accepted ASTM oils when measured in this way. The large amount of scatter seen in this figure is probably due to a slightly warped or misaligned cone and plate fixture. The high initial results seen in both figures is most likely due to fluid and instrument inertia, as no torque measuring spring is used in the CS500. A potential lag in response from applied torque and measured angular displacement,



Figure 7. Flow curves of lower viscosity fluids, cone and plate.



Figure 8. Flow curves of higher viscosity fluids, cone and plate.

caused by the finite digital sampling frequency of the data collection electronics, should be negligible.

Finally, consider Table 6, a comparison of linearity of flow curves of oils and syrups generated in the Carrimed's cone and plate geometry. The correlation coefficients, r^2 , for syrups compare very favorably with those of the oils. Once again, the syrups show evidence of Newtonian behavior similar to that of the currently accepted calibration materials.

6.2.2. Dynamic Oscillation

As discussed in Section 2.1.2., dynamic oscillatory experiments can be used to check for a fluid's solid-like behavior in a way that steady shear analyses cannot. The dynamic viscosity, η' , should maintain the same value across a range of frequencies, and have the same value as the steady shear viscosity. At the same time, the value of tan (δ) should be much greater than 1, since the fluid properties should predominate over the solid properties. Varying oscillation frequency is an experimental analog to varying shear rate in steady shear. Finally, η' should have the same value as η (steady shear viscosity).

The Carrimed oscillation results, while somewhat erratic, show the behavior expected of a pure liquid. An example is shown in Table 7, which contains the results of simple 0.05 to 4.332 Hz frequency sweeps of Cannon S8000 oil using an amplitude of 0.01 radians. One can see that the η' results were reasonably consistent, and compared reasonably to

Table 6. Linearity of shear stress - shear rate analysis results as expressed by correlation coeffecient, r^2 , cone and plate.

MATERIAL	η, Pa s	\mathbf{r}^{2}
Staley I.S. 100	0.195	0.999
**	0.161	0.999
Cannon S600	1.25	0.999
	1.12	0.999
11	1.29	0.999
**	1.29	0.999
Staley S. 4300	17.3	0.999
Staley 3260	19.9	0.999
**	19.4	0.999
**	17.4	0.999
Cannon S8000	18.7	0.999
11	17.6	0.999
Cannon S30000	77.8	0.999
**	78.3	0.999
17	74.9	0.999
Staley 4400	101	0.999

the fluid's calibration certificate: an average of the results was 8.9% higher than expected. At the same time, tan (δ) values were very high, being somewhat erratic.

Table 8 is a comparison of Carrimed oscillation results of standard oil and a syrup of similar viscosity. Note that while the data is again somewhat erratic (probably due to the CS500's limited computer digital feedback control rate, significant instrument and fluid inertia, mechanical resonances, and slight sensor misalignment) the syrup did show increasing G' values with increasing frequency, whereas the oil did not exhibit this behavior. One may conclude that while the dynamic viscosity was constant over the range studied, the syrup had a significant elastic component. One possible cause of this behavior was the drying of the syrup at the edge of the cone and plate sample cell. Drying could occur despite use of the solvent trap accessory, since a brief interval was inescapably required to position the solvent trap after loading the syrup between the cone and plate. The dried syrup would show significant elasticity; no analogous structure would form when testing an oil.

6.3. Time and Shear-Dependency

6.3.1. Up-Ramps vs. Down-Ramps

All Carrimed steady shear analyses and most Haake analyses were performed by increasing rotational velocity from zero to a maximum, then decreasing rotational velocity from the maximum to zero. These two parts of an analysis should yield identical results if the fluid does not change

Table 7. Carrimed dynamic oscillation results for Cannon S8000 oil at a constant amplitude of 0.01 radians.

Frequency, Hz	tan (δ), rad/s	η', Pas
0.0500	-229	22.9
0.0661	-79	23.8
0.0873	2480	23.3
0.115	110	23.1
0.153	720	23.4
0.202	51	23.3
0.264	170	23.1
0.352	61	22.8
0.465	151	22.9
0.615	124	22.7
0.813	132	22.9
1.07	4480	22.6
1.42	207	22.7
1.88	127	22.5
2.48	79	22.5
3.28	173	22.4
4.33	272	22.3

Table 8. Carrimed dynamic oscillation results for Cannon S8000 oil and Staley 3260 syrup.

	Cannon	<u>\$8000 oil</u>	Staley 32	aley 3260 syrup	
Freq. (Hz)	G', Pa	η′, Pas	G', Pa	η′, Pa s	
0.0500	0.106	22.6	0.236	26.0	
0.0661	-0.121	23.0	0.281	25.7	
0.0873	-0.154	23.0	0.483	25.2	
0.115	0.0221	22.7	0.551	24.6	
0.153	-0.647	22.5	0.700	24.8	
0.202	-0.796	21.9	1.12	24.4	
0.266	0.0104	22.3	1.46	24.2	
0.352	-0.364	22.3	2.39	24.2	
0.465	-0.122	21.9	2.50	23.6	
0.615	0.0329	22.1	3.99	23.7	
0.813	0.954	22.3	4.52	23.9	
1.07	0.0482	21.9	6.65	23.4	
1.42	0.664	22.3	10.6	23.2	
1.88	-1.12	22.1	14.6	22.9	
2.48	-4.63	21.8	16.6	22.6	
3.28	-9.25	20.8	30.8	21.4	
4.33	-25.4	19.5	45.6	20.6	
5.73	5.37	0.0	46.7	20.2	
7.57	15.8	0.780	92.5	19.7	
10.0	49.1	1.53	40.0	19.7	

with time or shear history. A thixotropic loop is typically seen in fluids that break down during the first part of the analysis. A hypothetical example of a thixotropic loop for a shear-thinning material is shown in Figure 9. A proper thixotropic loop is completely reversible, whereas a nonreversible decrease in viscosity is called rheomalaxis (Whorlow, 1980).

The Carrimed in steady shear mode was used to check for thixotropy. The Haake was not used due to its "wind-up" property which prevented accurate comparison of up- and down-ramps. Typical results for medium and high fluids are shown in two plots, Figure 10 and Figure 11, respectively. No significant thixotropic loop is evident from the graphs; the somewhat jagged curves are probably due to a slight warp or misalignment in the Carrimed's fixtures.

Results for the low viscosity Staley Isosweet 100 syrup were unusual. Figure 12 compares the syrup with a Cannon S60 standard oil. While the oil shows essentially no difference between the up and down curves, the syrup shows a down loop that first drops below the up loop at the higher shear rates, then crosses so that the down loop is above the up loop at the lower shear rates. This anomalous behavior is probably due to drying of the syrup at the edge of the cone and plate. The lowest viscosity fluids were analyzed without the benefit of a solvent trap. Drying certainly would also have happened with the higher viscosity syrups had a solvent trap not been used during those analyses.



Figure 9. Theoretical thixotropic loop.



Figure 10. Flow curves of medium viscosity fluids, cone and plate.



Figure 11. Flow curves of high viscosity fluids, cone and plate.



Figure 12. Flow curves with thixotropic loop of low viscosity fluids, cone and plate.

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6.3.2. Repeated Measures on Same Sample Load

The tendency of a fluid to degrade with time and with shear over time was tested by analyzing the same sample of fluid repeatedly. The sample was simply left in the test geometry between test runs. A comparison of Haake analysis results for several fluids is found in Table 9. The table includes the Newtonian viscosity of each of several test runs performed on several fluids, as well as the percent difference by which subsequent results vary from the first result. All data reported are from the up-ramp part of the analysis only.

The data show that the standard calibration oils tended to decrease in viscosity with repeated analysis. The simplest explanation for this behavior is slight viscous heating during each analysis, a phenomenon in which some of the energy applied to cause flow was converted to heat, raised the temperature and thereby slightly lowered the viscosity for subsequent analyses. For example, data taken from the Cannon S8000 oil's bottle label shows that an increase from 25.00°C to 26.00°C would result in a viscosity drop of 7.8%. The Haake's removable outer coaxial cylinder was enclosed in an aluminum container through which recirculating oil was pumped, but the heat transfer was less than perfect. Moreover, the walls of the narrow-diameter SV cup were approximately 10 mm of solid stainless steel, reducing even more the ability of the circulating fluid to maintain constant sample temperature. The Haake rheometer is typical of

Table 9. Results of analyses repeated on the same load of various oils and syrups, concentric cylinders.

Fluid	run no.	η (Pas)	% Difference
S60 oil	1	0.0977	
	2	0.0973	-0.4
	3	0.0977	0
I.S. 100 syrup	1	0.175	
• -	2	0.177	0.7
	3	0.177	1.1
S8000 oil	1	20.6	
	2	19.6	-4.7
	3	19.3	-6.3
Neto 7350 syrup	1	51.9	
	2	51.8	-0.1
	3	51.8	-0.1
S300000 oil	1	76.8	
	2	75.9	-1.2
	3	75.9	-1.2
1300 syrup	1	82.7	
	2	83.7	1.2
	3	84.6	2.4

many coaxial cylinder instruments, and rather complicated corrections for this effect have been published (Whorlow, 1980). Corrections for cone and plate geometries are even more involved than those for coaxial cylinders because the thickness of the sample fluid varies with radius.

Table 9 shows that corn syrups behaved differently than the standard oils. Whereas the oils' viscosity decreased slightly with repeated analysis, the syrups' viscosity increased slightly, except the Neto 7350 syrup, which was essentially unchanged. The syrups probably increased due to drying at the edge of the coaxial cylinders. This drying occurred despite use of a cover plate, positioned 5-10 mm above the top of rotating cylinder. The cover plate had a hole slightly larger than the rotor's shaft, and certainly allowed some contact of the sample with circulating ambient air. The increase seen was small, but did point out the sensitivity of corn syrups to drying during analysis. It is also possible that the syrups could absorb water both during transfer to the sample fixture and during testing. Perhaps the edge drying and moisture gain effects canceled each other out for the Neto 7350 syrup. Only a controlled study would differentiate these effects.

6.3.3. Repeated Measures on Different Sample Loads

An important requirement for viscosity calibration fluids is that they remain stable over a reasonable period of time. Several fluids were therefore analyzed on different days using the Haake with coaxial cylinders. To

accomplish this, samples were re-loaded each day. Multiple loads were run on some days to avoid confounding the effect of sample load with that of different days. Multiple runs (analyses) were run for most sample loads. Up-ramp viscosity results, including averages and the results of statistical comparisons, are shown in Table 10. Student's t test (for comparison of a single pair) or Dunnett's t test (for multiple comparisons within a single fluid type) were used to compare subsequent day's analyses with those obtained initially for a given type of fluid. The probability of a Type I error was 0.05 (Gill, 1978).

The table shows that the standard oils were generally more different from initial results on subsequent days than were the syrups. Only the Neto 7350 syrup was not significantly different on a following day. The Staley 1300 syrup smelled slightly fermented when analyzed the second time; all samples were stored at ambient temperature, approximatelv 22°C. The addition of a suitable preservative, such as potassium sorbate, could extend the shelf-life of the syrup, while not materially changing the syrup's rheological properties. Certainly, the present study is not a definitive evaluation of the reproducibility of Haake viscosity analy-However, one can see that the syrups, when not spoilses. ed, were no less reproducible than the standard oils during the period studied.

Table	10.	Result	s of	analyse	s repe	ated	on	diffe	rent	sample
		loads	of	various	oils	and	sy	rups,	cond	centric
		cylind	ers.							

Fluid	Days After Test	Run no.	Up Ramp η (Pa s)	Avg η (Pas)	% Diff.	Sig. Diff.?
S60 oil	0	1	0.109			
	126	1	0.0977			
		2	0.0973			
		3	0.0977	0.0976	-10.0	yes
	146	1	0.0952			
		2	0.0951			
		3	0.0960			
		4	0.0959	0.0956	-11.9	yes
I.S. 100	0	1	0.173			
syrup		2	0.175	0.175		
		3	0.177			
	0.0	4	0.177	0.177		
	20	1	0.179			
		2	0.178	0.179		
		3	0.178	• • •		
	•	4	0.179	0.179	-1.3	yes
\$30000 011	0	1	73.8			
		2	72.8	50 0		
		3	72.1	72.9		
		4	70.Z			
		S C	69.6	C 0 7		
	0.5	0	09.1	09.1		
	90	1	75 0			
		2	75.9	76 0	6 0	
	138	3 1	79 1	10.2	0.9	yes
	150	2	77 1	77 7	0 1	WOO
Neto 7350	0	1	51 0		5.1	yes
avrun	v	2	51.8			
Sjiup		3	51.8	52.8		
		4	47.2	02.0		
		5	46.4	46.8		
	185	1	53.3	10.0		
	200	2	53.7			
		3	51.5			
		4	54.7	53.3	0.9	no
1300 syrup	0	1	82.7	#	- • •	
v 1		2	83.7			
		3	84.6	83.7		
	185	1	53.7		-35.8	yes

6.4. Sample Stability in Handling

The Cannon fluids proved to be very stable during the typical manipulations required for laboratory experimentation over a period of months. Since solvent vapors can potentially dilute stored oil (Manning, 1987), care was taken to clean viscometer fixtures and sample handling equipment well away from sample bottles.

The most important stability concern when handling corn syrups was drying on exposure to air. A slight skin was noticeable at the fluid's surface in the sample container when spooning or pipetting most samples, being more conspicuous for the more viscous fluids. Stirring the sample before removing a specimen for analysis seemed to alleviate any negative effects of the skin in the container itself.

Sample drying during analysis is a common problem in viscometry, as has been alluded to several times in the above discussions with regard to corn syrups. Of the instruments used in this research, the Carrimed's cone and plate geometry was by far the most susceptible to sample drying.

Figure 13 shows a comparison of steady shear flow analyses performed on the Carrimed for Sweetose 4300 syrup. The loop on the lower right results from an up- and down--ramp test using the solvent trap attachment for the cone and plate fixture. The syrup shows a slight thixotropic loop, as the down-ramp portion is below that of the up-ramp. The upper loop is the same syrup (different sample load)



Figure 13. Flow curves of Staley Sweetose 4300 corn syrup, effect of solvent trap on cone and plate results.

using the same cone, but without the solvent trap. The up-ramp's curve turns up, almost certainly due to drying during the 30 second analysis period. Confirming this conclusion, the down-ramp's curve is well <u>above</u> the up-ramp, showing such a large degree of drying that the viscosity (the slope of a line tangent to the curve at any point of interest) continues to increase as the torque is continuously decreased.

The large effect of the solvent trap discussed above was opposite in both trend and degree to that expected for a fluid that is not sensitive to air. One would expect a small amount of drag from the solvent held in the solvent trap's well (see Figure 3). A test of the solvent trap's potential effect was made by first performing three successive up-down ramp analyses on one sample load of Cannon S8000. The solvent trap was then positioned without disturbing the sample between the cone and plate, and water was added to the trap's well. A second set of three analyses was then conducted. The mean plus or minus one standard deviation for the "without trap" and "with trap" results (six results per trap status) were 22.02 ± 0.47 and $21.49 \pm$ 0.43, respectively. These means are not significantly different in a t test at p = 0.05. The trend in the data is unexpected, and may be due to slight sample loss or warming of the sample.

The stability of corn syrup viscosity over extended periods of corn syrups was not systematically studied. Some

of the high fructose syrups require storage above ambient to minimize crystallization and "color development." A.E. Staley Co. recommended that Isosweet 100 be stored at 35°C to 40.5°C. Samples stored at 22°C did form crystals, but these were dissolved by heating at 37°C overnight. The data presented in Table 10 suggest that most syrups should have stable viscosities for several months.

Chapter 7

CONCLUSIONS

Corn syrups were shown to have potential for use as Newtonian calibration fluids in some applications where the established standard oils are not suitable. Specifically, these applications include food industry pilot and plant calibration operations that require large volumes of test fluids and subsequent water-based cleanup. Examples of potential calibration uses are tube viscometers, pumping systems, process viscometers, mixers, manifolds, filters and screens, heat exchangers, and extruders.

The syrups were shown, under the conditions tested, to have viscosities as constant with varying shear rate as those of standard ASTM calibration oils. Some syrups showed significant elasticity that may be due to their tendency to dry upon exposure to air. Appropriate precautions in handling and analysis were able to reduce this effect to insignificant levels for many practical food industry purposes. The stability of corn syrup viscosity was apparently several months but probably well under one year.

Those wishing to use syrups as calibration fluids should carefully characterize not only the material with respect to its application, but also the application itself. Properties of the fluid that must be determined include steady shear viscosity and temperature sensitivity, elasticity, sensitivity to air drying, and shelf-life. The appli-

cation should be characterized as to needed viscosity and temperature range, fluid exposure to air, and the length of time needed to conduct the calibration.

Chapter 8

SUGGESTIONS FOR FURTHER STUDY

Several areas of study should be pursued by those wishing to use corn syrups as calibration fluids. First, a systematic study, using control charts, should be made of the shelf-life of the chosen fluid. This study would be made using a laboratory viscometer of reasonably small volume so that a Cannon standard oil of similar viscosity could be included for comparison. Second, a demonstration of use of the syrup in a tube viscometer or other calibration pumping apparatus would: a) provide experience in handling the syrups; b) allow development of techniques for minimizing drying and other deleterious effects; and, c) help understand the specific relationship between the syrup's tendency to dry and its rheological behavior in the laboratory and in the pumping apparatus. Finally, an inquiry should be made into the effect, if any, of the syrup's elasticity on the chosen application.

The author's professional experience with developing control samples for rheological analyses suggests the following: anyone considering using calibration fluids should have at least some understanding of statistical process control and control sample charting. Personal experience with developing control sample programs for rheological analyses suggests that simple one-point calibration checks of equipment can be severely misleading as to the accuracy and

precision of results obtained with such equipment. In fact, appropriate control charting frequently demands that routine calibrations <u>not</u> be carried out (Anderson, 1989).

Another important use of statistics in calibration work is the design of the experiments and subsequent analysis of results obtained. Careful random sampling will minimize systematic bias, maximize productivity, and thus lead most directly to correct conclusions about the magnitude and sources of variation in the system being studied. Proper control charting, ideally in consultation with an experienced statistician, is the only simple way to achieve an accurate estimate of the reliability of a potential calibration fluid and the equipment with which it is used.

BIBLIOGRAPHY

BIBLIOGRAPHY

- A.E. Staley Mfg. Co. 1987. Analyses of Staley corn syrups. Technical Data Sheet 110 384011, Sweetener Business Group, A.E. Staley Mfg. Co., Decatur, IL.
- American Society for Testing Materials. 1973. Standard method of basic calibration of master viscometers and viscosity oil standards. D 2162-64. ASTM Committee D-2, Philadelphia, PA.
- American Society for Testing Materials. 1987. Standard method of basic calibration of master viscometers and viscosity oil standards. D 2162-79. ASTM Committee D-2, Philadelphia, PA.
- American Society for Testing Materials. 1983. Standard test method for kinematic viscosity of transparent and opaque liquids (and the calculation of dynamic viscosity). D 445-83. ASTM Committee D-2, Philadelphia, PA.
- Anantheswaran, R.C., and Rao, M.A. 1985. Heat transfer to model newtonian liquid foods in cans during end-over-end rotation. J. Food Engr. 4:1.
- Anderson, S. 1989. private communication. Statistician, Kellogg Co., Battle Creek, MI.
- Andrade, E.N. da C. 1947. Viscosity and plasticity. Cambridge University Press, Cambridge, England.
- Bates, F.J. 1942. Polarimetry, saccharimetry and the sugars. Circ. NBS C440. U.S. Govt. Printing Office, Washington, DC.
- Bauer, H., and Meerlander, G. 1984. Precise viscosity measurements of newtonian liquids with $v < 1 \text{ mm}^2/\text{s}$ for the selection of suitable standards. Rheol. Acta 23:514.
- Bewersdorff, H.W., and Singh, R.P. 1988. Rheological and drag reduction characteristics of xanthan gum solutions. Rheol. Acta 27:617.

- Bingham, E.C., and Jackson, R.F. 1919. Standard substances for the calibration of viscometers. Nat. Bur. Std. (U.S.) Bull. 14:59.
- Boger, D.V. 1977/78. A highly elastic constant-viscosity fluid. J. Non-Newt. Fluid Mech. 3:87.
- Boger, D.V., Denn, M.M., and Binnington, R.J. 1985. Characterization and flow of rheologically-complex liquids. p 2.3. Society of Rheology, Inc., New York
- Bondi, A. 1967. Viscosity and molecular structure. In: "Rheology: Theory and Applications," F.R. Eirich, ed. Academic Press, New York. p1.
- Cali, J.P, Mears, T.W., Michaelis, R.E., Reed, W.P, Seward, R.W., Stanley, C.L., Yolken, H.T., and Ku, H.H. 1975. The role of standard reference materials in measurement systems. U.S. Natl. Bur. Stand. Monograph 148. Washington, D.C.
- Cannon Instrument Company 1988. Catalog and price list. State College, PA.
- Cannon, M.R. 1944. Viscosity measurement, master viscometers. industrial and engineering chemistry. Analytical Edition, IENAA. 16:708.
- Castell-Perez, M.E., Steffe, J.F., and Morgan, R.G. 1986. Adaptation of a Brookfield (HBTD) viscometer for mixer viscometry studies. J. Texture Studies 18:359.
- Cheng, D.C-H., Hunt, J.A., and Madhvi, P. 1985. Status report on process control viscomters: current applications and future needs. Warren Spring Laboratory, Stevenage, England.
- Collins, E.A. 1987. private communication. Rheology consultant to Mitech Corporation, Willoughby, OH.
- Cutler, A.N., Morris, E.R., and Taylor, L.J. 1983. Oral perception of viscosity in fluid foods and model systems. J. Texture Studies 14:377.
- Delancy, M. 1988. private communication. Manager of Technical Support, Haake Division of Fisons Instruments, Saddle Brook, NJ.
- Dziedzic, S.Z., and Kearsley, M.W. 1984. Physico-chemical properties of glucose syrups. In: "Glucose Syrups: Science and Technology," S.Z. Dziedzic and M.W. Kearsley, eds., Elsevier Academic Press, London.
- Gill, J.L. 1978. "Design and Analysis of Experiments in the Animal and Medical Sciences." The Iowa State University Press, Ames.
- Hardy, R.C. 1962. "NBS Viscometer Calibrating Liquids and Capillary Tube Viscometers." Natl. Bur. Stand. (U.S.) Monograph 55.
- Hoynak, P.X., and Bollenback, G.N. 1966. "This is Liquid Sugar." Refined Syrups and Sugars, Inc. Yonkers, NY.
- IOS (International Organization for Standardization). 1977. Technical Report 3666.
- Jones, T.E.R, Davies, J.M., and Thomas, A. 1987. Fluid inertia effects on a controlled stress rheometer in its oscillation mode. In: "Carrimed CS500 Operations Manual," Carrimed, Ltd., Dorking, England.
- Junk, W., and Pancoast, H. 1973. "Handbook of Sugars." AVI Publishing Co., Westport, CT.
- Kawata, M., Kurase, K., and Yoshida, K. 1969. Realization of a viscosity standard. Proc. Fifth Int. Congress on Rheology, Vol I, S. Onogi, ed. p 453.
- Kreiger, I.M. 1968. Shear rate in the couette viscometer. J. Rheol. 12:5.
- Mailiarov, G.A. 1959. Absolute viscosity of water at a temperature of 20°C. Trudy Vses. Nauchn-Issled, Inst. Metrl. 37(97):125.
- Manning, R.E. 1987. private communication. Principal Scientist, Cannon Instruments, State College, PA.
- Marsh, K.N., ed. 1980. Recommended reference materials for realization of physicochemical properties: section viscosity. Pur. and Appl. Chem. 52:2393.
- Marvin, R.S. 1971. The accuracy of measurements of viscosity of liquids. J. Res. Nat. Bur. Stds. 75A:535.
- Marvin, R.S. 1972. Calibration of viscometers. In: "Precision Measurement and Calibration", R.L. Bloss and M. Orloski, Eds., Nat. Bur. Std. (U.S.) Spec. Publ. 300, 8:557.
- Mathlouthi, M., and Kasprzyk, P. 1984. Viscosity of sugar solutions. Sugar Tech. Rev. 11:209.
- Miller, J.C., and Miller, J.N. 1984. "Statistics for Analytical Chemistry." Halsted Press, New York.

- Penn, R.W., and Kearsley, E.A. 1971. An absolute determination of viscosity using channel flow. J. Res. Nat. Bur. Stand. (U.S.), 75A(6):553.
- Porter, R.S., and Johnson, J.F. 1960. Bulk and solution flow properties of polybutenes. ACS Div. Polymer Chem. 1, No. 1.
- Prentice, J.H. 1984. "Measurements in the Rheology of Foodstuffs." Applied Science Publishers, London.
- Prilutski, G., Gupta, R.K., Sridhar, T., and Ryan, M.E. 1983. Model viscoelastic fluids. J. Non-Newt. Fluid Mech. 12:233.
- Pucinich, S. 1989. private communication. Sales agent, Silicon Division, General Electric Corporation, Waterford, NY.
- Quagliano, J.V., and Vallarino, L.M. 1969. "Chemistry," 3rd ed. Prentice-Hall, Englewood Cliffs, NJ.
- Rao, M.A., and Cooley, H.J. 1984. Determination of effective shear rates in rotational viscometers with complex geometries. J. Texture Studies 15:327.
- Rao, V.N.M, Hamann, D.D., and Humphries, E.G. 1975. Flow behavior of sweet potatoe puree and its relation to mouthfeel quality. J. Texture Studies 6:197.
- Roscoe, R., and Bainbridge, W. 1958. Viscosity determination by the oscillating vessel method. Proc. Physical Society 72(4):585.
- Sanderson, G.R. 1981. Polysaccharides in food. Food Technol. 35(7):50.
- Simpson, B. 1989. private communication. Purchasing Agent, Kellogg Company, Battle Creek, MI.
- Skoog, D.A., and West, M.W. 1971. Principles of instrumental analysis. Holt, Rinehart and Winston, New York.
- Stecher, P.G. 1960. "The Merck Index of Chemicals and Drugs," 7th Edition. Merck and Co., Rahway, NJ.
- Steffe, J.F., Mohamed, I.O., and Ford, E.W. 1983. Rheological properties of fluid foods. ASAE 83-6512.
- Steffe, J.F. 1987. private communication. Professor of Food Engineering, Michigan State University, East Lansing, MI.

- Swindells, J.F., Coe, J.R., and Godfrey, T.B. 1952. Absolute viscosity of water at 20°C. J. Res. Nat. Bur. Std. 48(1):1.
- Szczesniak, A.S., and Farkas, E. 1962. Objective characterization of the mouthfeel of gum solutions. J. Food Sci. 27:381.
- Tung, M.A. 1987. private communication. Chairman, Food Science Department, Technical University of Nova Scotia, Halifax, NS.
- Ubbelohde, L. 1936. The suspended lever viscometer. J. Inst Petroleum Technologists 22:37.
- United States Government 1977. Legal definition of glucose syrup. Federal Register 42:14479.
- Uriano, G.A, and Gravatt, C.C. 1977. The role of reference materials and reference methods in chemical analysis. CRC Crit. Rev. in Anal. Chem. 6(4):361.
- Walker, B. 1989. private communication. Brookfield Engineering Laboratories, Stoughton, MA.
- Weast, R.C. 1971. "Handbook of Chemistry and Physics." The Chemical Rubber Co., Cleveland.
- Wernimont, G.T. 1985. "Use of Statistics to Develop and Evaluate Analytical Methods." Association of Official Analytical Chemists, Arlington, VA (USA).
- White, H.S., and Kearsley, E.A. 1971. An absolute determination of viscosity using a torsional pendulum. J. Res. Nat. Bur. Stand. (U.S.), 75A(6):541.
- Whorlow, R.W. 1980. "Rheological Techniques." Ellis Horwood Limited, Chichester; Wiley, New York.

APPENDICES

APPENDIX I

APPENDIX I. ORIGINAL HAAKE CONCENTRIC CYLINDERS DATA

The original "raw," unprocessed data from an individual Haake analysis consisted of several hundred data points, collected every 2 s, for the typical 10 minute analysis time. Each point in an analysis consisted of time of analysis (s), rotor rotational measurement (rpm), and torque measurement (% full scale). This raw data was then converted to shear stress and shear rate data, either for each point (for continuous-ramp analyses) or for an average of the last 8 points in each 15-point step (for step-ramp analyses). The shear stress and shear rate data was then fit to several rheological models: Herschel-Bulkley, Bingham, and Newtonian.

Since the volume of "raw" and "converted" data, for Haake and both Carrimed analysis modes, stretched to several hundred pages, only summaries are presented for all analyses. After the data summary, sample sets of raw and converted data sets are included as examples.

In the table, a position occupied by the < sign means that the entry in that position is the same as for the previous analysis.

The Haake was calibrated by removing the sensor head from its holding bracket, laying it on its side, and hanging a series of balance calibration weights from a rotor at-

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tached to the head. The weights were suspended from the rotor with thin nylon line, to generate a known torque. The resulting percent full scale torque readings taken from the RV-12 were linearly regressed against the torques. The resulting linear coefficients of slope (units: [N m] / [% full scale torque reading]) and intercept (units: N m) were subsequently used to calculate measured torque directly from observed percent full scale torque readings during fluid analysis.

The total number of Haake analyses conducted was 70. The original Haake data is contained in Table 11. Table 11. Original Haake data.

Analysis number:	1	2	3	4	5
Parameter:					
Sample: oil or syrup	oil	<	<	<	<
Sample: i.d. number	S30000	<	<	<	<
Sample: lot number	87101	<	<	<	<
Sample: load status	30 days	<	<	fresh	<
Replicate number	1	2	3	1	2
Avg. temperature, 'C		26.0		25.4	<
Haake sensor head	M500	<	<	<	<
Haake rotor/cup	SVII	<	<	<	<
Sensor calib. slope					
$x = 10^4$, N m/% F.S. rdg.	4.728	<	<	4.683	<
Sensor calib. intent.		·	-		-
$x = 10^4$. N m	7.218	<	<	-0.890	<
Step or Cont. ramp	C	č	č	<	č
analyzis time (min)	5	, i i i i i i i i i i i i i i i i i i i	č	č	ì
may rotor speed rom	64			60	
Bosults:	04			00	
$\frac{1}{1}$	57 G	/		54 0	53 0
Up-nomp 0 Do o	61 097	61 777	62 016	72 760	79 769
p^{-1} amp η , ras	01.907	01.111	02.010	13.100	0 000
I. Down-momm m Do o	0.991	0.330	62 049	0.991 74 040	0.990
100 m ramp η , ras	02.040	02.000	03.040	14.044	13.003
r-	0.995	0.997	0.996	0.996	0.998
Analysis number:	6	7	8	9	10
Analysis number: Parameter:	6	7	8	9	10
Analysis number: Parameter: Sample: oil or syrup	6 oil	7 <	8 <	9 <	10 <
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number	6 oil <	7 < <	8 < <	9 < <	10 < S60
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number	6 oil < <	7 < < <	8 < <	9 < < <	10 \$60 87302
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status	6 < < <	7 < < fresh	8 < < <	9 < < <	10 < \$60 87302 fresh
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number	6 < < 3	7 < < fresh 1	8 < < < 2	9 < < < 3	10 < S60 87302 fresh 1
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature. 'C	6 < < 3 25.4	7 < < fresh 1 25.6	8 < < 2 25.6	9 < < < 3 25.6	10 < S60 87302 fresh 1 23.9
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup	6 < < 3 25.4 <	7 < < fresh 1 25.6 <	8 < < 2 25.6 <	9 < < < 3 25.6 <	10 < S60 87302 fresh 1 23.9 MVB
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head	6 < < 3 25.4 < <	7 < < fresh 1 25.6 < <	8 < < 2 25.6 < <	9 < < 3 25.6 < <	10 < S60 87302 fresh 1 23.9 MVB M150
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope	6 oil < < 3 25.4 < <	7 < < fresh 1 25.6 < <	8 < < 2 25.6 < <	9 < < < 3 25.6 < <	10 < S60 87302 fresh 1 23.9 MVB M150
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ . N m/% F.S. rdg	6 oil < < 3 25.4 < <	7 < < fresh 1 25.6 < < <	8 < < 2 25.6 < < <	9 < < < 3 25.6 < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg.	6 oil < < 3 25.4 < <	7 < < fresh 1 25.6 < <	8 < < 2 25.6 < < <	9 < < < 3 25.6 < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m	6 oil < < 3 25.4 < <	7 < < fresh 1 25.6 < < < <	8 < < 2 25.6 < < < <	9 < < < 3 25.6 < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m	6 oil < < 3 25.4 < < <	7 < < fresh 1 25.6 < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 < < < 3 25.6 < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m <u>Step or Cont. ramp</u> analysis time (min)	6 oil < < 3 25.4 < < <	7 < < fresh 1 25.6 < < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 < < 3 25.6 < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 <
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m <u>Step or Cont. ramp</u> analysis time (min) max_rotor speed	6 oil < < 3 25.4 < < < < < <	7 < < fresh 1 25.6 < < < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 < < < 3 25.6 < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < < 250
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m <u>Step or Cont. ramp</u> analysis time (min) max. rotor speed, rpm	6 oil < < 3 25.4 < < < < < < <	7 < < < fresh 1 25.6 < < < < < < < < < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 < < < 3 25.6 < < < < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < < 250
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg. Sensor calib. intcpt. x 10 ⁴ , N m <u>Step or Cont. ramp</u> analysis time (min) max. rotor speed, rpm Results: maximum & c ⁻¹	6 oil < < 3 25.4 < < < < < < < <	7 < < < fresh 1 25.6 < < < < < < < < < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 < < 3 25.6 < < < < < < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < 250 592 4
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m <u>Step or Cont. ramp</u> analysis time (min) max. rotor speed, rpm Results: maximum ý, s ⁻¹	6 oil < < 3 25.4 < < < < < < < < < < < < < < <	7 < < fresh 1 25.6 < < < < < < < < < < < < <	8 < < 2 25.6 < < < < < < < 53.9 60.526	9 < < 3 25.6 < < < < < < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < 250 592.4 0 100
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m Step or Cont. ramp analysis time (min) max. rotor speed, rpm Results: maximum ý, s ⁻¹ Up-ramp η, Pa s	6 oil < < 3 25.4 < < < < < < < < < < < < < < < < < < <	7 < < fresh 1 25.6 < < < < < < < < < < < < <	8 < < 2 25.6 < < < < < < < 53.9 69.636	9 < < < 3 25.6 < < < < < < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < 250 592.4 0.109 0.000
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m Step or Cont. ramp analysis time (min) max. rotor speed, rpm Results: maximum ý, s ⁻¹ Up-ramp ¶, Pa s r ²	6 oil < < 3 25.4 < < < < < < < < < < < < <	7 < < fresh 1 25.6 < < < < < < < < < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 < < < 3 25.6 < < < < < < < < < < < < <	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < 250 592.4 0.109 0.999 0.999
Analysis number: Parameter: Sample: oil or syrup Sample: i.d. number Sample: lot number Sample: load status Replicate number Avg. temperature, 'C Haake rotor/cup Haake sensor head Sensor calib. slope x 10 ⁴ , N m/% F.S. rdg Sensor calib. intcpt. x 10 ⁴ , N m <u>Step or Cont. ramp</u> analysis time (min) max. rotor speed, rpm Results: maximum ý, s ⁻¹ Up-ramp η, Pa s r ² Down-ramp η, Pa s	6 oil < < 3 25.4 < < < < < < < < < < < < <	7 < < < fresh 1 25.6 < < < < < < < < < < < < <	8 < < 2 25.6 < < < < < < < < < < < < <	9 	10 < S60 87302 fresh 1 23.9 MVB M150 1.431 -0.778 < 250 592.4 0.109 0.999 0.111

Analysis number:	11	12	13	14	15
Parameter:					
Sample: oil or syrup	oil	<	<	<	<
Sample: i.d. number	S30000	<	<	S8000	<
Sample: lot number	87101	<	<	86104	<
Sample: load status	fresh	<	<	fresh	<
Replicate number	1	2	3	1	2
Avg. temperature, 'C	24.0	25.0	25.0	25.0	25.1
Haake sensor head	M500	<	<	<	<
Haake rotor/cup	SVII	<	<	<	<
Sensor calib. slope					
$x 10^4$. N m/% F.S. rdg.	4.893	<	<	<	<
Sensor calib. intcpt.					
$\times 10^4$ N m	-1.080	<	<	<	<
Step or Cont. ramp	S	<	<	<	<
analysis time (min)	5	<	<	<	<
max, rotor speed, rpm	55		<	150	200
Results:	00	•	•	100	200
maximum $\dot{\mathbf{v}}$, s ⁻¹	49.5	49.5	49.5	136.1	185.6
Up-ramp 1. Pa s	76.833	76.833	75.911	20.574	19,603
r ²	0.999	0.999	0.999	0.997	0.987
Down-ramp 1. Pa s	79.667	79.667	77.151	20.836	19.404
r^2	0.996	0.997	0.999	0.997	0.995
-	0.000	01001	0.000	0.001	0.000
Analysis number:	16	17	18	19	20
Parameter:					
Sample: oil or syrup	<	<	<	<	oil
Sample: i.d. number	<	<	<	<	S600
Sample: lot number	<	<	<	<	87202
Sample: load status	<	<	<	<	fresh
Replicate number	3	4	5	6	1
Avg. temperature, 'C	25.1	25.0	25.0	25.0	25.1
Haake rotor/cup	<	<	<	<	MVA
Haake sensor head	<	<	<	<	M500
Sensor calib. slope					
$\times 10^4$, N m/% F.S. rdg.	<	<	<	<	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	<	<	<	<	<
Step or Cont. ramp	<	<	<	<	<
analysis time (min)	<	<	<	<	<
max. rotor speed, rpm	<	<	50	<	258
Results:					
maximum ÿ, s ⁻¹	185.9	185.6	44.2	44.2	233.8
Up-ramp ¶, Pa s	19.271	19.026	20.296	20.194	1.385
r ² 0.987	0.989	0.999	0.999	0.999	0.999
Down-ramp 7, Pa s	19.147	18.945	20.665	20.851	1.417
r ²	0.995	0.995	0.999	0.999	0.998

Analysis number:	21	22	23	24	25
Parameter:					
Sample: oil or syrup	oil	<	<	<	<
Sample: i.d. number	S600	<	<	<	<
Sample: lot number	87202	<	<	<	<
Sample: load status	per 20	<	fresh	<	<
Replicate number	2	3	1	2	3
Avg. temperature, 'C	25.1	25.0	24.9	25.0	25.0
Haake sensor head	M500	<	<	<	<
Haake rotor/cup	MVA	<	MVB	<	<
Sensor calib. slope					
$x 10^4$, N m/% F.S. rdg	. 4.893	<	<	<	<
Sensor calib. intcpt.					
$x 10^4$, N m	-1.080	<	<	<	<
Step or Cont. ramp	С	<	<	<	<
analysis time (min)	5	<	<	<	<
max. rotor speed. rpm	250	<	90	<	<
Results:					
maximum ý. s ⁻¹	228.8	229.3	214.4	214.3	214.6
U_{D} -ramp 1. Pa s	1.376	1.375	1.379	1.365	1.356
r ²	0.999	0,999	0.999	0.999	0.999
- Down-ramp 11. Pa s	1.412	1.411	1.439	1.415	1.407
r^2	0.999	0.999	0.999	0.999	0.999
Analysis number:	26	27	28	29	30
Parameter:					
Sample: oil or syrup	<	<	<	syrup	<
Sample: i.d. number	S60	<	<	15100	<
Sample: lot number	87302	<	<	7K1X2	<
Sample: load status	fresh	<	<	fresh	fresh
Replicate number	1	2	3	1	1
Avg. temperature, 'C	25.0	25.1	25.1	25.0	25.2
Haake rotor/cup	MVB	<	<	<	<
Haake sensor head	M150	<	<	<	<
Sensor calib. slope					
$x 10^4$, N m/% F.S. rdg	. 1.397	<	<	<	<
Sensor calib. intcpt.					
x 10 ⁴ N m	-0.085	<	<	<	<
Step or Cont. ramp	С	<	<	<	<
analysis time (min)	5	<	<	<	<
max. rotor speed. rpm	250	<	<	200	<
Results:		-	-		-
maximum ý. s ⁻¹	596.4	596.6	596.6	478.4	478.0
Up-ramp 1. Pa s	0.0977	0.097	0.0977	0.173	0.175
r ²	0.999	0,999	0,999	0.999	0.999
Down-ramp 11. Pa s	0.101	0.101	0.101	0.180	0,184
r^2	0.999	0.999	0.999	0.999	0.999
-					

Analysis number:	31	32	33	34	35
Parameter:					
Sample: oil or syrup	syrup	<	oil	<	<
Sample: i.d. number	IS100	<	S60	<	<
Sample: lot number	7K1X2	<	87302	<	<
Sample: load status	per 30	<	fresh	<	<
Replicate number	2	3	1	2	1
Avg. temperature, 'C	25.1	25.1	25.0	25.0	25.0
Haake sensor head	M150	<	<	<	<
Haake rotor/cup	MVB	<	<	<	<
Sensor calib. slope					
$x 10^4$, N m/% F.S. rdg.	1.397	<	1.387	<	<
Sensor calib. intcpt.					
$x 10^4$, N m	-0.085	<	-0.418	<	<
Step or Cont. ramp	С	<	<	<	S
analysis time (min)	5	<	<	<	10
max. rotor speed. rpm	200	<	250	<	<
Results:					
maximum $\dot{\mathbf{y}}$, s ⁻¹	478.3	477.6	596.1	597.1	596.3
Up-ramp 1. Pa s	0.177	0.177	0.095	0.095	0.096
r ²	0.999	0.999	0,999	0.999	0.999
- Down-ramp 1. Pa s	0.183	0.184	0.098	0.098	
r^2	0.999	0.999	0.999	0.999	
-					
Analysis number:	36	37	38	39	40
Parameter:					
Sample: oil or syrup	<	syrup	<	<	<
Sample: i.d. number	<	IS100	<	<	<
Sample: lot number	<	7K1X2	<	<	<
Sample: load status	<	fresh	<	fresh	<
Replicate number	2	1	2	1	2
Avg. temperature, 'C	25.0	25.1	25.0	25.0	25.0
Haake rotor/cup	<	<	<	<	<
Haake sensor head	<	<	<	<	<
Sensor calib. slope					
$x 10^4$, N m/% F.S. rdg.	<	<	<	<	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	<	<	<	<	<
<u>Step or Cont. ramp</u>	<	<	<	С	<
analysis time (min)	<	<	<	<	<
max. rotor speed, rpm	<	200	<	<	<
Results:					
maximum ý, s ⁻¹	596.8	478.1	478.3	478.2	478.4
Up-ramp ¶, Pa s	0.096	0.179	0.178	0.178	0.179
r ²	0.999	0.998	0.994	0.999	0.999
Down-ramp ¶, Pa s					
r ²					

Analysis number:	41	42	43	44	45
Parameter:					
Sample: oil or syrup	syrup	oil	<	<	syrup
Sample: i.d. number	IS5500	S600	<	<	IS5500
Sample: lot number	K720169	87202	<	<	K70169
Sample: load status	fresh	fresh	<	<	fresh
Replicate number	1	1	2	3	1
Avg. temperature, 'C	25.0	25.2	25.1	25.0	25.0
Haake sensor head	M150	M500	<	<	<
Haake rotor/cup	MVB	MVB	<	<	<
Sensor calib. slope					
$x 10^4$, N m/% F.S. rdg.	1.387	4.920	<	<	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	-0.418	-2.602	<	<	<
Step or Cont. ramp	S	<	<	<	<
analysis time (min)	10	8.5	<	<	10
max. rotor speed. rpm	50	95	<	<	150
Results:					
maximum v. s ⁻¹	119.5	226.5	1.334	226.7	359.3
Up-ramp 1. Pa s	0.791	1,335	1.334	1.369	0.829
r ²	0.999	0.999	0.999	0.999	0.999
			4.0	4.0	5.0
Analysis number:	46	47	48	49	50
Parameter:					
Sample: oil or syrup	<	<	<	<	<
Sample: i.d. number	<	<	<	7350	<
Sample: lot number	<	<	<	7K11X105	<
Sample: load status	<	fresh	<	fresh	<
Replicate number	2	1	2	1	2
Avg. temperature, C	25.1	25.0	25.0	25.0	25.0
Haake rotor/cup	<	<	<	SVII	<
Haake sensor head	<	<	<	<	<
Sensor calib. slope					
x 10 ⁴ , N m/% F.S. rdg.	. <	<	<	4.893	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	<	<	<	0.437	<
<u>S</u> tep or <u>C</u> ont. ramp	<	<	<	<	<
analysis time (min)	<	<	<	<	<
max. rotor speed, rpm	<	<	<	85	<
Results:					
maximum γ, s ⁻¹	359.3	322.7	359.3	76.6	76.8
Up-ramp ¶, Pa s	0.825	0.812	0.815	51.87	51.80
r ²	0.999	0.999	0.999	0.997	0.997

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Analysis number:	51	52	53	54	55
Parameter:					
Sample: oil or syrup	syrup	oil	<	syrup	<
Sample: i.d. number	7350	S30000	<	7350	<
Sample: lot number	7K11X105	87101	<	7K11X105	<
Sample: load status	per 49	fresh	<	fresh	<
Replicate number	3	1	2	1	2
Avg. temperature, 'C	25.1	25.0	25.0	25.0	25.0
Haake sensor head	M500	<	<	<	<
Haake rotor/cup	SVII	<	<	<	<
Sensor calib. slope					
x 10 ⁴ , N m/% F.S. rdg	. 4.893	<	<	<	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	0.437	<	<	<	<
<u>S</u> tep or <u>C</u> ont. ramp	S	<	<	<	<
analysis time (min)	10	<	<	<	<
max. rotor speed, rpm	85	60	<	85	<
Results:					
maximum γ, s ⁻¹	76.6	54.5	54.4	76.0	76.2
Up-ramp 7, Pa s	51.84	78.05	77.44	47.18	46.40
r ²	0.997	0.997	0.998	0.997	0.998
Analysis number:	56	57	58	5 9	60
Parameter:					
Sample: oil or syrup	<	<	<	<	<
Sample: i.d. number	1300	<	<	<	<
Sample: lot number	7L11Z60	<	<	<	<
Sample: load status	fresh	<	<	fresh	<
Replicate number	1	2	3	1	2
Avg. temperature, 'C	25.1	25.0	25.0	24.8	24.9
Haake rotor/cup	<	<	<	<	<
Haake sensor head	<	<	<	<	<
Sensor calib. slope					
$x 10^4$, N m/% F.S. rdg	. <	<	<	4.757	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	<	<	<	-1.236	<
<u>S</u> tep or <u>C</u> ont. ramp	<	<	<	<	<
analysis time (min)	<	<	<	<	<
max. rotor speed, rpm	50	<	<	<	<
Results:					
maximum γ, s ⁻¹	44.9	45.0	45.0	45.3	45.1
Up-ramp ¶, Pa s	82.67	83.70	84.64	87.17	86.63
r ²	0.999	0.999	0.999	0.999	0.999

100

Analysis number:	61	62	63	64	65
Parameter:	GUNUD				
Sample: oll of syrup	AAOO		300		630000
Sample: 1.d. number	7 1202212		71 4 2 2 4		87101
Sample: lot number	1029A312		1L4A24 freah		67101 freeh
Sample: load status	resn 1	х о	1 resn	х о	1 resn
Replicate number		2	1	2	25 0
Avg. temperature, C	25.0	25.0	24.9	24.9	25.0
Haake sensor head	MSUU	<	< c	<	< CUT
Haake rotor/cup	SVII	<	<	<	SVI
Sensor calib. slope			_		
$x 10^{-}$, N m/% F.S. rdg	3. 4.757	<	<	<	<
Sensor calib. intept.					
x 10 ⁻ , N m	-1.236	<	<	<	<
<u>S</u> tep or <u>C</u> ont. ramp	S	<	<	<	<
analysis time (min)	10	<	<	<	<
max. rotor speed, rpm	50	<	27	<	18
Results:					
maximum ÿ, s ⁻¹	45.2	45.3	22.5	22.6	16.1
Up-ramp ¶, Pa s	86.96	88.21	171.54	127.49	78.65
r ²	0.999	0.998	0.999	0.999	0.999
Analysis number:	66	67	68	69	70
Parameter:					
Sample: oil or syrup	syrup	<	<	<	<
Sample: i.d. number	7350	<	<	<	1300
Sample: lot number	7K11X105	<	<	<	7L11Z6
Sample: load status	fresh	<	fresh	<	fresh
Replicate number	1	2	1	2	1
Avg. temperature, C	25.0	25.0	25.1	25.0	25.0
Haake rotor/cup	<	<	<	<	<
Haake sensor head	SVII	<	<	<	<
Sensor calib. slope					
x 10 ⁴ , N m/% F.S. rdg	s. <	<	<	<	<
Sensor calib. intcpt.					
x 10 ⁴ , N m	<	<	<	<	<
<u>S</u> tep or <u>C</u> ont. ramp	<	<	<	<	<
analysi s time (min)	<	<	<	<	<
max. rotor speed, rpm	85	<	<	<	<
Results:					
maximum ÿ, s ⁻¹	76.2	76.5	76.5	76.9	79.0
Up-ramp ¶, Pa s	53.34	53.73	51.52	54.74	53.72
n ²	0.998	0.998	0.997	0.997	0.992

APPENDIX II

APPENDIX II. ORIGINAL CARRIMED STEADY SHEAR DATA

The original "raw," unprocessed data from Carrimed analyses were written in IBM-PC computer files, one file per individual analysis. The files were written in ASCII text, in a proprietary format. The files contained sample identification, analysis conditions (temperature, fixtures, analysis mode, etc.), programed torques and the measured angular velocities or amplitudes. An option in the Carrimed control and analysis software was used to compute, from the raw data file, shear stress - shear rate values at each sample point (typically 2-3 per second, over an analysis time period of several minutes). The program then fit a variety of shear models to the data set, allowing the user to control which points from the data set to include in the least-squares regression computations. The regression coefficients reported in the data summary below were generated using this ap-The shear stress - shear rate curves used in the proach. figures above showing Carrimed data were calculated and printed to a computer disk using a Lotus 123 program. The figures are identical to those generated by a similar utility in the Carrimed software program.

54 Carrimed steady shear analyses results are summarized below in Table 12. The units of sensor calibration slope are (N m) / (% full scale reading).

102

Analysis number: 1 2 3 4 5 Parameter: ____ _ _ _ _ _ _ _ _ _ _ ____ _ _ _ _ _ < Sample: oil or syrup oil < < Sample: i.d. number S8000 < < < < < < < Sample: lot number 86104 < < < fresh Sample: load status fresh fresh fresh 3 Replicate number 1 2 $\begin{array}{ccc}
 3 & 1 \\
 25.0 & 24.5
 \end{array}$ 1 2 25.0 Temperature, [°]C 25.0 < 1-0 < < < < Cone angle, deg-min < 4 < < < Cone diameter, cm < Cone-plate gap, µm 26.1 < < < N < < < < Solvent trap? 5000 1000 < < < Maximum torque, µN m < Analysis time (min) 4 < < < Results: maximum $\dot{\gamma}$, s⁻¹ 3.1 3.0 2.9 4.0 4.1 19.63 Up-ramp ¶, Pa s 18.80 19.51 22.03 21.27 \mathbf{r}^2 0.9999 0.9999 0.9999 0.9999 0.9999 Down-ramp ¶, Pa s 19.07 20.10 20.01 22.35 21.53 r² 0.9999 0.9999 0.9999 0.9999 0.9999 7 Analysis number: 6 8 9 10 Parameter: ____ ____ _ _ _ _ _ ____ _ _ _ _ _ Sample: oil or syrup < < < < < Sample: i.d. number < < S60 < < < Sample: lot number < < 86301 < < Sample: load status fresh fresh fresh fresh 3 Replicate number 1 < < < Temperature, °C < 25.0 24.9 24.5 < Cone angle, deg-min < < 2-0 1-0 < 2 Cone diameter, cm < < 4 < Cone-plate gap, µm < 52.2 < 26.1 < < Solvent trap? < < < < Maximum torque, µN m 1000 50000 40000 1000 < < 4 < < < Analysis time (min) Results: maximum ý, s⁻¹ 0.9 1300 1100 42 42 Up-ramp ¶, Pa s 17.65 20.64 19.44 1.411 1.406 r^2 0.9999 0.9932 0.9972 0.9999 0.9999

20.74

0.9999

17.36

0.9972

1.418

0.9999 0.9999

1.413

Down-ramp ¶, Pa s

r²

Table 12. Original Carrimed steady shear data.

Analysis number:	11	12	13	14	15
Parameter:					
Sample: oil or syrup	oil	syrup	<	<	<
Sample: i.d. number	S600	IS100	<	4300	<
Sample: lot number	86301	7A27X221	<	7C13XLT7	<
Sample: load status	per 10	fresh	fresh	fresh	3rd
Replicate number	2	1	1	1	1
Temperature, °C	25.0	<	<	<	<
Cone angle, deg-min	1-0	<	<	<	<
Cone diameter, cm	4	<	<	<	<
Cone-plate gap, µm	26.1	<	<	<	<
Solvent trap?	N	<	<	<	<
Maximum torque, µN m	1000	250	5000	<	50000
Analysis time (min)	4	<	<	<	<
Results:					
maximum $\dot{\gamma}$, s ⁻¹	44	77	1828	8.5	102
Up-ramp ¶, Pa s	1.339	0.195	0.1608		29.00
r ²	0.9999	0.9997	0.9999		0.9989
Down-ramp ¶, Pa s	1.344	0.186	0.163	22.53	
r ²	0.9999	0.9997	0.9999	0.9976	
Analysis number:	16	17	18	19	20
Parameter:					
Sample: oil or syrup	oil	<	<	<	<
Sample: i.d. number	S600	<	<	<	S8000
Sample: lot number	86301	<	<	<	86104
Sample: load status	fresh	fresh	fresh	fresh	fresh
Replicate number	1	2	1	2	1
Temperature, °C	<	<	<	<	<
Cone angle, deg-min	<	<	<	<	<
Cone diameter, cm	<	<	<	<	<
Cone-plate gap, µm	<	<	<	<	<
Solvent trap?	<	<	<	<	<
Maximum torque, µN m	1000	<	40000	<	1000
Analysis time (min)	<	<	<	<	<

47

0.9999

1.254

1.257

0.9999

48

1.234

1.236

0.9999

0.9999

2200

1.122

0.9991

0.9996

1.108

2200

1.072

1.088 18.67

0.9989 0.9999

0.9999 0.9999

3

19.05

Table 12 (cont'd.).

Results: maximum $\dot{\gamma}$, s⁻¹ Up-ramp η , Pa s

Down-ramp η , Pa s

 r^2

r²

Analysis number:	21	22	23	24	25
Parameter:					
Sample: oll or syrup	011			syrup	
Sample: 1.d. number	06104			3200	
Sample: locd status	90104 Don 20	fmach		212-214	
Sample: 10ad Status	per 20	1 resn	1	1 resn	``````````````````````````````````````
Tempenature 'C	25 0	1	1	1	2
Cone angle dog-min	25.0				
Cone diameter cm	1-0				
Cone-plate dap um	26 1				Ì
Solvent tran?	20.1 N			v	
Maximum torque, uN m	50000	1000	50000	1000	50000
Analysis time (min)	4	1000	20000 K	1000	00000 <
Regulte.	-		•	Ň	Ň
$maximum \dot{v} = e^{-1}$	175	3	175	3.0	186
UD-ramp 1. Pa s	17.60	18.70	17.98	19.95	16.01
r ²	0.9996	0.9999	0.9997	0.9999	0.9996
Down-ramp 1. Pa s	17.50	19.14	17.89	20.27	16.24
r ²	0.9999	0,9999	0.9999	0.9999	0.9998
•					
Analysis number:	26	27	28	29	30
Parameter:					
Sample: oil or syrup	<	<	<	oil	<
Sample: i.d. number	<	<	<	S600	<
Sample: lot number	<	<	<	86301	<
Sample: load status	2nd	<	2nd	fresh	<
Replicate number	1	2	1	1	2
Temperature, °C	<	<	<	<	<
Cone angle, deg-min	<	<	<	<	<
Cone diameter, cm	<	<	<	<	<
Cone-plate gap, µ	<	<	<	<	<
Solvent trap?	<	<	<	N	<
Maximum torque, µN m	1500	50000	1000	<	<
Analysis time (min)	<	<	<	<	<
Results:					
maximu m ý, s ⁻¹	3	170	2.5	45	45
Up-ramp ¶, Pa s	19.41	17.38	19.79	1.292	1.294
r ²	0.9998	0.9998	0.9997	0.9999	0.9999
Down-ramp ¶, Pa s	19.91	17.44	19.79	1.295	1.296
	0 0007	<u> </u>	0 0000	0 0000	0 0000

Analysis number:	31	32	33	34	35
Farameter:					
Sample: id number	5600	58000	5600	560	AAOO
Sample: lot number	86301	86104	86301	87302	7.1298
Sample: load status	$\frac{00001}{29}$	freeh	fresh	2nd	FRESH
Benlicate number	per 23	1	1	1	1
Temperature °C	25 0	24 5	Ĩ	24 5	1
Cone angle deg-min	1-0	24.0	$\hat{0}$	24.5	1-0
Cone diameter, cm	4	~	~ ~ ~	č	· · ·
Cone-plate gap um	26 1	[×]	100		26 1
Solvent tran?	20.1 N		100		v
Maximum torque uN m	40000	50000	1000	100	50000
Analysis time (min)	40000	50000	1000	100	50000
Reculte.	7				
$\frac{1}{1}$	1900	140	59	85	31
lin-remp 1. De e	1.234	21.04	1 345	0 094	92.80
r ²	0 9997	0 0000	0 0000	0.004	0 9997
Down-ramp 10 Pag	1.221	20 94	1.352	0.094	94 34
r^2	0.9999	0.9999	0.9999	0.9995	0.9998
1	0.0000	0.0000	0.0000	0.0000	0.0000
Analysis number:	36	37	38	39	40
Parameter:					
Sample: oil or syrup	<	oil	<	<	<
Sample: i.d. number	<	S8000	<	<	<
Sample: lot number	<	86104	<	<	<
Sample: load status	fresh	fresh	fresh	fresh	<
Replicate number	1	<	<	2	3
Temperature, 'C	<	<	<	<	<
Cone angle, deg-min	<	<	<	<	<
Cone diameter, cm	<	<	<	<	<
Cone-plate gap, µ	<	<	<	<	<
Solvent trap?	<	<	<	<	<
Maximum torque, µN m	<	1000	<	<	<
Analysis time (min)	<	<	<	<	<
Results:					
maximum ý, s ⁻¹	35	3	2.8	3.0	3.0
Up-ramp η, Pa s	94.07	21.23	21.83	21.72	21.86
r ²	0.9999	0.9999	0.9999	0.9998	0.9998
Down-ramp ¶, Pa s	94.05	21.68	22.25	21.72	21.86
r ²	0.9998	0.9999	0.9999	0.9999	0.9998

42 45 Analysis number: 41 43 44 Parameter: _ _ _ _ ----_ _ . oil Sample: oil or syrup < < < syrup \$8000 < < 4400 Sample: i.d. number < 86104 < < < 7A25Z Sample: lot number per 39 < < < Sample: load status fresh 2 3 Replicate number 1 4 1 Temperature, [°]C 24.5 < < < < Cone angle, deg-min 1-0 < < < < < < < < Cone diameter, cm 4 Cone-plate gap, µ 26.1 < < < < Y < < < Solvent trap? N Maximum torque, µN m 1000 < < < 50000 Analysis time (min) < < < 4 < Results: maximum γ, s⁻¹ 3.0 3.0 3.0 3.0 29 Up-ramp ¶, Pa s 21.70 21.11 21.19 21.25 100.7 r² 0.9998 0.9998 0.9998 0.9998 0.999922.03 21.97 Down-ramp ¶, Pa s ___ 21.87 101.0 r^2 0.9999 0.9998 _ _ _ 0.9998 0.9998 Analysis number: 46 47 48 49 50 Parameter: ____ _ _ _ _ _ _ _ _ ____ _ _ _ _ oil or syrup Sample: oil < < < < Sample: i.d. number S30000 < < < < Sample: lot number 87101 < < < < load status < Sample: fresh fresh fresh < Replicate number 1 < < < < Temperature, °C 25.0 < < < < Cone angle, deg-min 1-0 < < < < < < Cone diameter, cm 2 < < < Cone-plate gap, µm 28.8 < < < < Solvent trap? Ν < < < Maximum torque, µN m 41888 419 41888 419 41888 Analysis time (min) < < < < < Results: maximum ý, s 260 2.8 280 2.8 280 Up-ramp ¶, Pa s 77.82 78.32 74.85 67.07 65.40 r^2 0.9997 0.9999 0.9998 0.9999 0.9998

77.10

0.9999

79.75

0.9999

74.47

0.9999

68.77

0.9998 0.9999

64.97

Table 12 (cont'd.).

Down-ramp η , Pa s

 r^2

Analysis number:	51	52	53	54	55
Parameter:					
Sample: oil or syrup	oil	<	<	<	
Sample: i.d. number	S30000	<	<	<	
Sample: lot number	87101	<	<	<	
Sample: load status	fresh	<	fresh	<	
Replicate number	1	<	<	<	
Temperature, °C	25.0	<	<	<	
Cone angle, deg-min	1-0	<	<	<	
Cone diameter, cm	1	<	<	<	
Cone-plate gap, µm	28.8	<	<	<	
Solvent trap?	N	<	<	<	
Maximum torque, µN m	419	41888	419	41888	
Analysis time (min)	4	<	<	<	
Results:					
maximum ý, s ⁻¹	2.8	280	2.8	280	
Up-ramp ¶, Pa s	75.90	75.51	83.90	83.90	
r ²	0.9991	0.9999	0.9999	0.9999	
Down-ramp ¶, Pa s	78.42	75.14	83.92	85.92	
r^2	0.9999	0.9999	0.9999	0.9999	

APPENDIX III. ORIGINAL CARRIMED OSCILLATORY SHEAR DATA

The original "raw" data from the oscillation experiments conducted on the Carrimed were of the same form as the steady shear data reported in Appendix II. The only real difference is that, instead of shear stress and shear rate data compiled for each data point, input torque, frequency, resulting (or controlled) angular amplitude, and the dynamic moduli are reported. No regression is fit to the results.

The analysis results are reported in Table 13, below.

Analys Sample type Sample I.D. Sample lot Sample load Replicate n	is no.: 1 : : status: o.:	oil S8000 86104 2nd 1	Cone angle, Cone diamet Cone-plate Solvent tra Temperature	deg-min.: er, cm: gap, µm: p?; , C:	2-1 6 56.2 N 24.9
Result Torque, µN m	s: Frequency, Hz	G', Pa	tan (δ)	Amplitude, radians	η′, Pas
50.0 403.6 757.1 1111 1464 1818 2171 2525 2879 3232 3586 3939 4293 4646 5000	0.30	$\begin{array}{c} 6.969\\ 2.896\\ 1.257\\ 1.807\\ -1.49\\ -0.727\\ -0.276\\ 1.136\\ -0.910\\ 0.2907\\ -0.186\\ 1.031\\ -0.680\\ -0.364\\ -0.460\\ \end{array}$	5.115 13.93 31.13 22.46 -27.6 -56.7 -144 35.36 -45.0 140.5 -222 39.20 -60.1 -111 -88.4	$\begin{array}{c} 8.57E-4\\ 6.21E-3\\ 0.0120\\ 0.1702\\ 0.0222\\ 0.2745\\ 0.0339\\ 0.3911\\ 0.0438\\ 0.0493\\ 0.0540\\ 0.0654\\ 0.0654\\ 0.0654\\ 0.0715\\ 0.0765\end{array}$	$18.91 \\ 21.41 \\ 20.75 \\ 21.53 \\ 21.76 \\ 21.86 \\ 21.15 \\ 21.31 \\ 21.70 \\ 21.67 \\ 21.92 \\ 21.44 \\ 21.67 \\ 21.58 \\ 21.5$
Analys Sample type Sample I.D. Sample lot: Sample load Replicate n	is no.: 2 : : status: o.:	per 1 " per 1 2	Cone angle, Cone diamet Cone-plate Solvent tra Temperature	deg-min.: per er, cm: gap, μm: p?; , C:	1
Result Torque, µN m	s: Frequency, Hz	G', Pa	tan (δ)	Amplitude, radians	η′, Pas
	$\begin{array}{c} 0.010\\ 0.0141\\ 0.1995\\ 0.0282\\ 0.0398\\ 0.0562\\ 0.0794\\ 0.1122\\ 0.1585\\ 0.2239\\ 0.3162\\ 0.4467\\ 0.6310\\ 0.8913\\ 1.259\\ 1.778\\ 2.512\\ 3.548\\ 5.012\\ 7.079\\ 10.00\\ \end{array}$	$\begin{array}{c} -5.36E-4\\ -1.65E-3\\ 5.61E-4\\ 3.11E-3\\ 4.61E-3\\ -2.86E-3\\ 0.0111\\ 0.2626\\ 0.0666\\ 0.1407\\ 0.0806\\ 0.3813\\ -0.269\\ 1.316\\ 1.750\\ -5.17\\ 1.714\\ -16.2\\ -40.6\\ -117\\ -271\end{array}$	$\begin{array}{c} -2470\\ -1140\\ 4771\\ 1224\\ 1163\\ -2640\\ 966\\ 568\\ 316.5\\ 209.9\\ 523.5\\ 155.4\\ -313\\ 87.98\\ 92.05\\ -46.0\\ 189.2\\ -27.5\\ -15.2\\ -7.04\\ -4.16\end{array}$	$\begin{array}{c} 0.705\\ 0.498\\ 0.349\\ 0.245\\ 0.174\\ 0.123\\ 0.0873\\ 0.0626\\ 0.0443\\ 0.0316\\ 0.0221\\ 0.0157\\ 0.0111\\ 8.07E-3\\ 5.80E-3\\ 3.92E-3\\ 2.88E-3\\ 2.09E-3\\ 2.88E-3\\ 2.09E-3\\ 0.0015\\ 0.0015\\ 0.00111\\ 7.82E-4 \end{array}$	$\begin{array}{c} 21.09\\ 21.13\\ 21.34\\ 21.49\\ 21.43\\ 21.43\\ 21.43\\ 21.44\\ 21.15\\ 21.18\\ 21.00\\ 21.23\\ 21.12\\ 21.30\\ 20.67\\ 20.36\\ 21.31\\ 20.55\\ 20.02\\ 19.63\\ 18.55\\ 17.95\end{array}$

Table 13. Original Carrimed oscillatory data.

Analysis no.: 3 Sample type: Sample I.D.: Sample lot: Sample load status: Replicate:		oil S8000 86301 per 1 1	Cone angle, deg-min.: Cone diameter, cm: Cone-plate gap, µm: Solvent trap?; Temperature, C:		2-1 6 56.2 N 24.9
Result Torque, µN m	s: Frequency, Hz	Gʻ, Pa	tan (8)	Amplitude, radians	η', Pas
	$\begin{array}{c} 0.100\\ 0.1259\\ 0.1585\\ 0.1995\\ 0.2512\\ 0.3162\\ 0.3981\\ 0.5012\\ 0.6310\\ 0.7943\\ 1.000\\ 1.259\\ 1.585\\ 1.995\\ 2.512\\ 3.612\\ 3.981\\ 5.012\\ 6.310\\ 7.943\\ 10.00\\ \end{array}$	$\begin{array}{c} 0.02001\\ 0.01173\\ 0.02698\\ 0.02964\\ 0.05329\\ 0.09529\\ 0.03978\\ 0.1851\\ 0.3333\\ 0.7878\\ 0.9017\\ -0.182\\ 2.403\\ 4.651\\ 8.095\\ 14.15\\ 31.59\\ 40.89\\ 43.35\\ 71.03\\ 31.85\end{array}$	$\begin{array}{c} 655.3\\ 1393\\ 766.2\\ 884.4\\ 620.9\\ 440.1\\ 1325\\ 360.2\\ 251.4\\ 134.4\\ 147.5\\ -926\\ 87.06\\ 56.91\\ 40.80\\ 28.87\\ 15.75\\ 14.82\\ 17.26\\ 11.60\\ 1.197\\ \end{array}$	$\begin{array}{c} 0.712\\ 0.571\\ 0.452\\ 0.356\\ 0.282\\ 0.223\\ 0.177\\ 0.140\\ 0.111\\ 0.0882\\ 0.0702\\ 0.0554\\ 0.0446\\ 0.0353\\ 0.0283\\ 0.0229\\ 0.0188\\ 0.0154\\ 0.0154\\ 0.0125\\ 0.0113\\ 0.0980\\ \end{array}$	$\begin{array}{c} 20.87\\ 20.65\\ 20.76\\ 20.91\\ 20.96\\ 21.11\\ 21.07\\ 21.17\\ 21.14\\ 21.21\\ 21.17\\ 21.30\\ 21.01\\ 21.11\\ 20.93\\ 20.56\\ 19.88\\ 19.24\\ 18.87\\ 16.50\\ 0.6070\\ \end{array}$
Analysis no.: 4 Sample type: Sample I.D.: Sample lot: Sample load status: Replicate:		syrup 4300 7C12XLT7 fresh 1	Cone angle, deg-min.: Cone diameter, cm: Cone-plate gap, µm: Solvent trap?; Temperature, C:		1-0 4 26.1 N 25.0
Result Torque, µN m	s: Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	ή, Pas
$\begin{array}{c} \textbf{5.000} \\ \textbf{361.8} \\ \textbf{718.6} \\ \textbf{1075} \\ \textbf{1432} \\ \textbf{1789} \\ \textbf{2146} \\ \textbf{2503} \\ \textbf{2859} \\ \textbf{3216} \\ \textbf{3573} \\ \textbf{3930} \\ \textbf{4286} \\ \textbf{4643} \\ \textbf{5000} \end{array}$	0.5000	$\begin{array}{c} -15.3\\ -0.476\\ -0.347\\ 0.07319\\ 0.4188\\ 0.1869\\ 0.6047\\ -0.108\\ 0.399\\ 0.08189\\ 0.01012\\ 0.3467\\ 0.2712\\ -0.0168\\ 0.2185\end{array}$	$\begin{array}{c} 2.855 \\ -185 \\ -260 \\ 1240 \\ 218.1 \\ 486.6 \\ 153.1 \\ -856 \\ 232.0 \\ 1134 \\ 9198 \\ 271.1 \\ 342.6 \\ -5610 \\ 429.0 \end{array}$	$\begin{array}{c} 1.12E-4\\ 4.29E-3\\ 8.30E-3\\ 0.0124\\ 0.0163\\ 0.0205\\ 0.0242\\ 0.0281\\ 0.0321\\ 0.0361\\ 0.0400\\ 0.0435\\ 0.0481\\ 0.0513\\ 0.0556\end{array}$	-13.9 27.96 28.72 28.88 29.08 28.95 29.47 29.53 29.49 29.56 29.56 29.56 29.92 29.57 29.99 29.85

Analysis Sample type: Sample I.D.: Sample lot: Sample load s Replicate:	alysis no.: 5 type: syrup [.D.: 4300 lot: 7C13XLT7 load status: per 5 te: 1		Cone angle, deg-min.: Cone diameter, cm: Cone-plate gap, µm: Solvent trap?; Temperature, C:		1-0 4 26.1 N 25.0
Results: Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η', Pas
$\begin{array}{c} 222.4\\ 303.6\\ 416.0\\ 592.0\\ 792.6\\ 1096\\ 1534\\ 2156\\ 2978\\ 4105\\ 5786\\ 7737\\ 10710\\ 13400\\ 4328 \end{array}$	$\begin{array}{c} 0.05000\\ 0.06947\\ 0.09653\\ 0.1341\\ 0.1864\\ 0.2590\\ 0.3598\\ 0.5000\\ 0.6947\\ 0.9653\\ 1.341\\ 1.864\\ 2.590\\ 3.598\\ 5.000 \end{array}$	$\begin{array}{c} 5.288\\ 1.934\\ 9.876\\ 18.89\\ 23.97\\ -78.2\\ -40.3\\ 35.04\\ 101.9\\ 202.9\\ 167.0\\ 474.7\\ -5.06\\ 4208\\ -8.59E-3 \end{array}$	$\begin{array}{c} 206.6\\ 774.0\\ 215.7\\ 151.0\\ 164.5\\ -70.6\\ -192\\ 305.8\\ 145.0\\ 102.6\\ 166.7\\ 81.20\\ -10200\\ 15.47\\ -44500 \end{array}$	$\begin{array}{c} 0.0204\\ 0.0203\\ 0.0195\\ 0.0208\\ 0.0201\\ 0.0198\\ 0.0201\\ 0.02016\\ 0.02016\\ 0.02016\\ 0.0201\\ 0.0208\\ 0.0201\\ 0.0207\\ 0.0206\\ 0.1158\\ \end{array}$	$\begin{array}{r} 3477\\ 3429\\ 3512\\ 3384\\ 3367\\ 3392\\ 3431\\ 3411\\ 3384\\ 3433\\ 3292\\ 3174\\ 2880\\ 12.17\end{array}$
Analysis Sample type: Sample I.D.: Sample lot: Sample load s Replicate:	s no.: 6 status:	syrup 3260 212-214 fresh 1	Cone angle, de Cone diameter Cone-plate gas Solvent trap? Temperature,	eg-min.: , cm: p, μm: [;] C:	per 5 "
Results: Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η', Pas
$168.5 \\ 204.2 \\ 253.4 \\ 318.6 \\ 431.3 \\ 550.4 \\ 715.3 \\ 911.4 \\ 1182 \\ 1556 \\ 2045 \\ 2673 \\ 3495 \\ 4539 \\ 6020 \\ 7383 \\ 9380 \\ 11750 \\ 14750 \\ 19650 \\ 19650 \\ 19650 \\ 1000 \\ 1$	$\begin{array}{c} \textbf{0.05000}\\ \textbf{0.06608}\\ \textbf{0.08733}\\ \textbf{0.1154}\\ \textbf{0.1525}\\ \textbf{0.2016}\\ \textbf{0.2664}\\ \textbf{0.3521}\\ \textbf{0.4654}\\ \textbf{0.6151}\\ \textbf{0.8129}\\ \textbf{1.074}\\ \textbf{1.420}\\ \textbf{1.877}\\ \textbf{2.480}\\ \textbf{3.278}\\ \textbf{4.332}\\ \textbf{5.725}\\ \textbf{7.566}\\ \textbf{10.00} \end{array}$	$\begin{array}{c} 0.09889\\ 0.1373\\ 0.1680\\ -0.144\\ 0.2197\\ -0.106\\ 0.4289\\ 0.4680\\ 1.648\\ 1.944\\ 2.345\\ 3.952\\ 5.777\\ 7.334\\ 7.350\\ 14.28\\ 26.30\\ 41.90\\ 46.91\\ 53.96\end{array}$	$\begin{array}{r} 85.96\\78.18\\80.08\\-118\\98.74\\-265\\83.74\\99.56\\37.19\\41.45\\44.91\\34.85\\30.96\\32.35\\41.25\\27.21\\18.51\\14.81\\16.37\\18.40\end{array}$	$\begin{array}{c} 0.0206\\ 0.0198\\ 0.0196\\ 0.0207\\ 0.0203\\ 0.0208\\ 0.0204\\ 0.0201\\ 0.0201\\ 0.0201\\ 0.0202\\ 0.0202\\ 0.0202\\ 0.0202\\ 0.0202\\ 0.0204\\ 0.0199\\ 0.0207\\ 0.0198\\ 0.0201\\ 0.0197\\ 0.0200\\ 0.0205\end{array}$	$\begin{array}{c} 27.06\\ 25.85\\ 24.51\\ 23.43\\ 22.63\\ 22.25\\ 21.45\\ 21.06\\ 20.96\\ 20.85\\ 20.62\\ 20.40\\ 20.05\\ 20.12\\ 19.45\\ 18.86\\ 17.88\\ 17.25\\ 16.15\\ 15.81\end{array}$

Analysi Sample type: Sample I.D.: Sample lot: Sample load Replicate:	s no.: 7	syrup 3260 212-214 fresh 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	eg-min.: , cm: p, µm: [;] C:	1-0 4 26.1 Y 25.0
Results Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η', Pas
$\begin{array}{c} 150.0\\ 207.0\\ 270.7\\ 351.7\\ 452.8\\ 603.4\\ 784.8\\ 1029\\ 1359\\ 1755\\ 2328\\ 3092\\ 4012\\ 5249\\ 6485\\ 8576\\ 11170\\ 13330\\ 18400\\ 22510 \end{array}$	$\begin{array}{c} 0.05000\\ 0.06608\\ 0.08733\\ 0.1154\\ 0.1525\\ 0.2016\\ 0.2664\\ 0.3521\\ 0.4654\\ 0.6151\\ 0.8129\\ 1.074\\ 1.420\\ 1.877\\ 2.480\\ 3.278\\ 4.332\\ 5.725\\ 7.566\\ 10.00 \end{array}$	$\begin{array}{c} 0.2357\\ 0.2807\\ 0.4825\\ 0.5513\\ 0.6996\\ 1.123\\ 1.463\\ 2.391\\ 2.496\\ 3.985\\ 4.521\\ 6.648\\ 10.59\\ 14.46\\ 16.57\\ 30.77\\ 45.64\\ 46.74\\ 92.47\\ 40.00\\ \end{array}$	$\begin{array}{c} 34.60\\ 38.00\\ 28.71\\ 32.35\\ 33.97\\ 27.52\\ 27.20\\ 22.37\\ 27.70\\ 23.72\\ 26.94\\ 23.11\\ 19.52\\ 18.64\\ 21.25\\ 14.29\\ 12.27\\ 15.52\\ 10.14\\ 30.95 \end{array}$	$\begin{array}{c} 0.0192\\ 0.0202\\ 0.0204\\ 0.0205\\ 0.0198\\ 0.0203\\ 0.0202\\ 0.0200\\ 0.0205\\ 0.0205\\ 0.0205\\ 0.0199\\ 0.0199\\ 0.0204\\ 0.0202\\ 0.0203\\ 0.0202\\ 0.0203\\ 0.0203\\ 0.0203\\ 0.0208\\ 0.0192\\ 0.0204\\ 0.0189\\ \end{array}$	$\begin{array}{c} 25.96\\ 25.69\\ 25.24\\ 24.59\\ 24.80\\ 24.40\\ 24.20\\ 24.18\\ 23.64\\ 23.72\\ 23.85\\ 23.41\\ 23.17\\ 22.87\\ 22.59\\ 21.36\\ 20.58\\ 20.16\\ 19.72\\ 19.70\\ \end{array}$
A Sample type: Sample I.D.: Sample lot: Sample load Replicate:	nalysis no. status:	: 8 oil S8000 86104 2nd 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	eg-min.: , cm: p, µm: 	1-0 4 26.1 N 24.5
Results Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η', Pas
$\begin{array}{c} 69.30\\ 89.92\\ 121.1\\ 159.8\\ 209.3\\ 274.4\\ 351.6\\ 474.0\\ 626.1\\ 811.6\\ 1086\\ 1444\\ 1873\\ 2519\\ 3175\\ 4142\\ 5124\\ 6816\\ 5115\\ 1447\\ \end{array}$	$\begin{array}{c} 0.05000\\ 0.06608\\ 0.08733\\ 0.1154\\ 0.1525\\ 0.2016\\ 0.2664\\ 0.3521\\ 0.4654\\ 0.6151\\ 0.8129\\ 1.074\\ 1.420\\ 1.877\\ 2.480\\ 3.278\\ 4.332\\ 5.725\\ 7.566\\ 10.00 \end{array}$	$\begin{array}{c} 0.1057\\ -0.121\\0154\\ 0.02212\\ -0.647\\796\\ 0.01045\\ -0.364\\ -0.122\\ 0.0329\\ 0.9537\\ 0.04824\\ 0.6641\\ -1.12\\ -4.63\\ -9.25\\ -25.4\\ 5.368\\ 15.79\\ 49.07 \end{array}$	$\begin{array}{r}$	$\begin{array}{c} 0.0102\\ 9.82E-3\\ 0.0100\\ 0.0101\\ 0.0101\\ 0.0103\\ 9.80E-3\\ 0.0100\\ 0.0102\\ 9.88E-3\\ 9.94E-3\\ 0.0102\\ 9.83E-3\\ 0.0102\\ 9.83E-3\\ 0.0101\\ 9.72E-3\\ 0.0101\\ 9.72E-3\\ 0.0101\\ 0.0100\\ 0.156\\ 0.0653\\ 0.0106\\ \end{array}$	$\begin{array}{c} 22.56\\ 22.98\\ 22.95\\ 22.74\\ 22.55\\ 21.86\\ 22.32\\ 22.30\\ 21.88\\ 22.15\\ 22.28\\ 21.87\\ 22.25\\ 22.12\\ 21.80\\ 20.78\\ 19.48\\ 0.07157\\ 0.779\\ 1.529\end{array}$

Analysi Sample type: Sample I.D.: Sample lot: Sample load Replicate no	s no.: 9 status:	oil S8000 86104 fresh 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	eg-min.: , cm: p, µm: ⁱ C:	0-0 4 1000 N 24.5
Results Torque, µN m	Frequency, Hz	G', Pa	tan (δ)	Amplitude, radians	η', Pas
18.27 23.95 32.48 55.65 74.46 98.22 128.6 167.4 222.7 291.6 389.5 507.1 674.5 883.5 1170 1546 1954 2521	$\begin{array}{c} 0.05000\\ 0.06608\\ 0.08733\\ 0.1154\\ 0.1525\\ 0.2016\\ 0.2664\\ 0.3521\\ 0.4654\\ 0.6151\\ 0.8129\\ 1.074\\ 1.420\\ 1.877\\ 2.480\\ 3.278\\ 4.332\\ 5.725\\ 7.566\\ 10.000\\ 0$	$\begin{array}{c} -3.15E-3\\ -0.125\\ 5.167E-3\\ 0.1522\\ 0.03113\\ 0.5831\\ 0.2278\\ 0.8212\\ 0.4442\\ 0.7095\\ 0.8865\\ 0.03045\\ 0.9774\\ 2.087\\ 4.437\\ 2.658\\ 2.231\\ -35.9\\ -96.2\\ -400\end{array}$	-2290 -79.0 2475 110.0 720.0 50.71 169.9 61.36 151.0 123.7 132.3 4479 207.5 127.1 79.06 173.5 272.1 -20.6 -9.15 -2000	0.0101 9.65E-3 0.0102 0.0101 9.88E-3 0.0100 0.0101 0.0102 9.93E-3 0.0101 9.94E-3 0.0101 9.98E-3 0.0101 9.98E-3 0.0101 9.98E-3 0.0100 9.97E-3 0.0100 0.0102 0.0102 0.0100 0.0102	$\begin{array}{c} 22.95\\ 23.79\\ 23.31\\ 23.39\\ 23.34\\ 23.12\\ 22.77\\ 22.93\\ 22.71\\ 22.95\\ 22.59\\ 22.59\\ 22.50\\ 22.51\\ 22.51\\ 22.40\\ 22.31\\ 20.58\\ 18.50\end{array}$
Analysi Sample type: Sample I.D.: Sample lot n Sample load Replicate no	s no.: 10 o.: status:	per 9 \$600 86301 2nd 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	eg-min.: , cm: p, µm: ; C:	per 9 100 per 9 per 9
Results Torque, µN m	: Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η', Pas
$\begin{array}{r} 8.728\\11.08\\15.71\\20.85\\29.27\\38.40\\52.48\\70.72\\93.15\\124.6\\166.9\\221.4\\291.3\\383.6\\502.7\\672.6\\899.3\\1273\\1666\end{array}$	$\begin{array}{c} 0.0500\\ 0.06608\\ 0.08733\\ 0.1154\\ 0.1525\\ 0.2016\\ 0.2664\\ 0.3521\\ 0.4654\\ 0.6151\\ 0.8129\\ 1.074\\ 1.420\\ 1.877\\ 2.480\\ 3.278\\ 4.332\\ 5.725\\ 7.556\end{array}$	$\begin{array}{c} 3.229E-3\\ 4.586E-3\\ 0.01467\\ -6.84E-3\\ 0.01558\\ -9.56E-3\\ -1.97E-3\\ 3.873E-3\\ -0.0350\\ 5.767E-3\\ 0.03904\\ 0.08232\\ 3.588E-3\\ 0.06201\\ 0.07257\\ 0.02054\\ 0.2365\\ 1.235\\ 1.425\end{array}$	$\begin{array}{c} 103.3\\ 96.09\\ 42.80\\ -124\\ 74.20\\ -165\\ -1080\\ 724.0\\ -107\\ 870.4\\ 170.6\\ 106.3\\ 3203\\ 242.1\\ 275.2\\ 1285\\ 147.8\\ 38.21\\ 42.42\end{array}$	0.0104 0.0100 9.95E-3 9.82E-3 0.0101 9.67E-3 9.81E-3 0.0100 9.88E-3 9.86E-3 9.96E-3 0.0100 0.0100 0.0100 0.0101 9.88E-3 9.88E-3 9.88E-3 9.88E-3 9.83E-3 9.83E-3 0.0101 9.60E-3	$\begin{array}{c} 1.062\\ 1.061\\ 1.144\\ 1.165\\ 1.206\\ 1.247\\ 1.272\\ 1.267\\ 1.281\\ 1.296\\ 1.288\\ 1.273\\ 1.281\\ 1.282\\ 1.281\\ 1.282\\ 1.281\\ 1.302\end{array}$

Analysi Sample type: Sample I.D.: Sample lot: Sample load Replicate no	s no.: 11 status:	oil S600 86301 per 10 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	leg-min.: , cm: p, μm: [;] C:	0-0 4 100 N 24.5
Results Torque, µN m	Frequency,	Gʻ, Pa	tan (δ)	Amplitude, radians	η', Pas
10.00 109.0 208.0 307.0 406.0 505.0	0.05000	5.877E-3 1.232E-3 7.815E-3 7.776E-4 4.766E-4 6.525E-3	55.25 328.9 519.7 520.6 846.6 611.9	$\begin{array}{c} 0.0122 \\ 0.107 \\ 0.204 \\ 0.302 \\ 0.400 \\ 0.503 \end{array}$	1.0331.2891.2931.2881.2881.2841.273
Analysi Sample type: Sample I.D.: Sample lot n Sample load Replicate no	s no.: 12 o.: status: o.:	per 11 " 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	leg-min.: ^c , cm: ^c p, µm: [;] C:	per 11 "
Results Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η′, Pas
$\begin{array}{c} 1.000\\ 50.95\\ 100.9\\ 150.8\\ 200.8\\ 250.7\\ 300.7\\ 350.6\\ 400.6\\ 450.5\\ 550.5\\ 550.4\\ 600.4\\ 650.3\\ 700.3\\ 750.2\\ 800.2\\ 850.1\\ 900.1\\ 900.1\\ 950.0\\ 1000 \end{array}$		$\begin{array}{c} 0.7547\\ 0.0936\\ 0.1070\\ 0.0461\\ 0.0923\\ -0.078\\ 0.0628\\ 0.0132\\ 0.0480\\ 0.0488\\ 0.0413\\ 0.0359\\ 0.0602\\ 0.0488\\ 0.0413\\ 0.0359\\ 0.0602\\ 0.0599\\ 0.0230\\ 0.0260\\ 0.0468\\ 0.0287\\ 0.0411\\ 0.0477\\ 0.0510\\ \end{array}$	$\begin{array}{c} 2.212\\ 83.24\\ 72.39\\ 172.4\\ 86.19\\ -102\\ 126.4\\ 599.6\\ 165.4\\ 162.6\\ 192.2\\ 240.6\\ 131.8\\ 133.0\\ 345.8\\ 304.3\\ 169.8\\ 277.9\\ 193.4\\ 166.9\\ 156.3\\ \end{array}$	$\begin{array}{c} 2.37E-4\\ 2.60E-3\\ 5.18E-3\\ 7.53E-3\\ 0.0100\\ 0.0125\\ 0.0150\\ 0.0175\\ 0.0200\\ 0.0226\\ 0.0251\\ 0.0276\\ 0.0276\\ 0.0301\\ 0.0324\\ 0.0350\\ 0.0376\\ 0.0400\\ 0.0423\\ 0.0449\\ 0.0474\\ 0.0498\end{array}$	$\begin{array}{c} 0.2657\\ 1.240\\ 1.233\\ 1.266\\ 1.267\\ 1.262\\ 1.265\\ 1.265\\ 1.265\\ 1.265\\ 1.265\\ 1.262\\ 1.262\\ 1.262\\ 1.262\\ 1.269\\ 1.265\\ 1.269\\ 1.266\\ 1.269\\ 1.266\\ 1.266\\ 1.266\\ 1.270\\ \end{array}$

Analysis no.:13Sample type:oilSample I.D.:S60Sample lot:86301Sample load status:freshReplicate no.:1	Cone angle, deg-min.: Cone diameter, cm: Cone-plate gap, µm: Solvent trap?; Temperature, C:	0-0 4 100 N 24.5
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Result	ts:				
Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η′, Pas
$\begin{array}{r} 1.000\\ 5.950\\ 10.950\\ 15.85\\ 20.80\\ 25.75\\ 30.70\\ 35.65\\ 40.60\\ 45.55\\ 50.50\\ 55.45\\ 60.40\\ 65.35\\ 70.30\\ 75.25\\ 80.20\\ 85.15\\ 90.10\\ 95.05\\ 100.0\end{array}$	0.5000	$\begin{array}{c} 0.1466\\ 0.07885\\ 0.06055\\ 0.03904\\ 0.03156\\ 0.02141\\ 0.01732\\ 0.01288\\ 0.01199\\ 7.699E-3\\ 7.843E-3\\ 4.269E-3\\ 4.269E-3\\ 3.952E-3\\ 3.952E-3\\ 3.952E-3\\ 3.952E-3\\ 1.100E-3\\ 4.911E-4\\ 1.973E-3\\ -4.96E-4\\ -8.22E-4\\ \end{array}$	$\begin{array}{r} 1.087\\ 2.826\\ 4.305\\ 7.299\\ 9.067\\ 13.49\\ 17.08\\ 23.34\\ 24.91\\ 39.09\\ 38.48\\ 70.67\\ 70.40\\ 76.57\\ 100.7\\ 276.1\\ 617.3\\ 153.4\\ -612\\ -715\\ -370\end{array}$	$\begin{array}{c} 2.49E-3\\ 0.0102\\ 0.0159\\ 0.0209\\ 0.0270\\ 0.0328\\ 0.0382\\ 0.0435\\ 0.0435\\ 0.0497\\ 0.0552\\ 0.0610\\ 0.0667\\ 0.0725\\ 0.0610\\ 0.0667\\ 0.0784\\ 0.0842\\ 0.0897\\ 0.0957\\ 0.102\\ 0.107\\ 0.113\\ 0.119\end{array}$	$\begin{array}{c} \hline 0.05075\\ 0.07093\\ 0.08297\\ 0.09069\\ 0.09110\\ 0.09196\\ 0.09571\\ 0.09576\\ 0.09579\\ 0.09566\\ 0.09579\\ 0.09607\\ 0.096032\\ 0.09631\\ 0.09632\\ 0.09649\\ 0.09665\\ 0.09665\\ 0.09657\\ 0.00657\\ 0.$

Analysis no.: 14 Sample type: Sample I.D.: Sample lot: Sample load status: Replicate no.:		per 13 "Cone angle, de Cone diameter Cone-plate ga fresh Solvent trap? 2 Temperature,		leg-min.: ;, cm: .p, μm: ; C:	per 13 " "
Results Torque, µN m	: Frequency, Hz	Gʻ, Pa	tan (8)	Amplitude, radians	η', Pas
$\begin{array}{c} 1.000\\ 1.460\\ 1.460\\ 2.921\\ 4.177\\ 6.895\\ 11.63\\ 22.38\\ 41.73\\ 83.41\\ 168.9\\ 352.4\\ 728.0\\ 1476 \end{array}$	$\begin{array}{c} 0.05000\\ 0.07300\\ 0.1066\\ 0.1556\\ 0.2272\\ 0.3317\\ 0.4843\\ 0.7071\\ 1.032\\ 1.507\\ 2.201\\ 3.213\\ 4.691\\ 6.849\\ 10.00 \end{array}$	$\begin{array}{c} 1.449E-3\\ 2.290E-3\\ 5.046E-3\\ 0.01077\\ 0.01470\\ 0.02972\\ 0.04796\\ 0.05760\\ 0.02861\\ -0.0254\\ -0.270\\ -0.428\\ -1.23\\ -1.58\\ -1.51\end{array}$	$10.53 \\ 13.16 \\ 7.679 \\ 5.235 \\ 6.914 \\ 5.602 \\ 5.584 \\ 7.416 \\ 23.62 \\ -41.1 \\ -5.71 \\ -5.48 \\ -2.34 \\ -3.04 \\ -1.61 \\ \end{bmatrix}$	$\begin{array}{c} 0.0261\\ 0.0193\\ 0.0150\\ 0.0103\\ 0.0113\\ 9.81E-3\\ 9.78E-3\\ 9.61E-3\\ 9.61E-3\\ 0.0101\\ 9.99E-3\\ 9.91E-3\\ 0.0101\\ 0.0102\\ 0.0103\\ 0.0102\\ 0.0102\\ 0.0102\\ \end{array}$	$\begin{array}{c} 0.04857\\ 0.06572\\ 0.05786\\ 0.05765\\ 0.07119\\ 0.07987\\ 0.08801\\ 0.09615\\ 0.1042\\ 0.1100\\ 0.1115\\ 0.1163\\ 0.09747\\ 0.1117\\ 0.03875\end{array}$

Analysi Sample type: Sample I.D.: Sample lot: Sample load Replicate no	status:	syrup 4400 7J29X312 2nd 1	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	leg-min.: , cm: 	1-0 4 100 Y 24.5
Results Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η΄, Pas
$\begin{array}{c} 100.0\\ 595.0\\ 1090\\ 1585\\ 2080\\ 2575\\ 3070\\ 3565\\ 4060\\ 4555\\ 5050\\ 5545\\ 6040\\ 6535\\ 7030\\ 7525\\ 8020\\ 8515\\ 9010\\ 9505\\ 10000\\ \end{array}$	0.5000	$\begin{array}{c} -1.46\\ 3.022\\ 4.014\\ 4.876\\ 6.103\\ 2.487\\ 2.574\\ 2.574\\ 2.661\\ 2.384\\ 1.662\\ 2.170\\ 2.244\\ 1.346\\ -0.308\\ 0.4287\\ 1.586\\ 0.9273\\ 2.160\\ 1.555\\ 1.310\\ 0.6989\end{array}$	$\begin{array}{r} -47.7\\ 61.07\\ 54.84\\ 47.11\\ 40.11\\ 103.4\\ 98.55\\ 96.77\\ 109.9\\ 158.3\\ 121.7\\ 119.1\\ 200.7\\ -874\\ 625.5\\ 171.4\\ 292.6\\ 125.4\\ 174.9\\ 208.7\\ 388.2 \end{array}$	$\begin{array}{c} 1.49E-3\\ 3.36E-3\\ 5.16E-3\\ 7.19E-3\\ 8.85E-3\\ 0.0104\\ 0.0126\\ 0.0144\\ 0.0161\\ 0.0180\\ 0.0199\\ 0.0216\\ 0.0233\\ 0.0253\\ 0.0273\\ 0.0288\\ 0.0308\\ 0.0328\\ 0.03621\\ 0.03621\\ 0.0384\\ \end{array}$	$\begin{array}{c} 22.24\\ 58.74\\ 70.07\\ 73.11\\ 77.91\\ 81.87\\ 80.76\\ 83.44\\ 83.77\\ 84.09\\ 85.44\\ 83.77\\ 84.09\\ 85.95\\ 85.64\\ 85.36\\ 86.51\\ 86.36\\ 86.55\\ 87.04\\ 86.38\\ 86.38\\ \end{array}$
Analysi Sample type: Sample I.D.: Sample lot: Sample load Replicate no	s no.: 16 status:	per 15 " 2	Cone angle, d Cone diameter Cone-plate ga Solvent trap? Temperature,	leg-min.: ^c , cm: ^c p, μm: ⁱ C:	per 15 "
Results Torque, µN m	Frequency, Hz	Gʻ, Pa	tan (δ)	Amplitude, radians	η′, Pas
$\begin{array}{r} 68.76\\ 66.18\\ 403.9\\ 490.1\\ 878.1\\ 1391\\ 2145\\ 3234\\ 5150\\ 7450\\ 10560\\ 368.8\\ 1556\\ 411.7\\ 846.4 \end{array}$	$\begin{array}{c} \textbf{0.05000}\\ \textbf{0.07300}\\ \textbf{0.1066}\\ \textbf{0.1556}\\ \textbf{0.2272}\\ \textbf{0.3317}\\ \textbf{0.4843}\\ \textbf{0.7071}\\ \textbf{1.032}\\ \textbf{1.507}\\ \textbf{2.201}\\ \textbf{3.213}\\ \textbf{4.691}\\ \textbf{6.849}\\ \textbf{10.00} \end{array}$	$\begin{array}{c} -0.175\\ 0.1138\\ 0.4355\\ 0.2787\\ -1.46\\ 0.5666\\ 4.309\\ 5.868\\ -0.134\\ 10.03\\ 84.54\\ 11.04\\ 19.43\\ 58.90\\ 110.1\end{array}$	$\begin{array}{r} -26.9\\ 63.01\\ 74.58\\ 184.3\\ -62.2\\ 256.2\\ 53.53\\ 59.68\\ -3950\\ 78.92\\ 13.08\\ 1.753\\ 1.245\\ 0.7443\\ 0.7758\end{array}$	$\begin{array}{c} 0.0152\\ 9.61E-3\\ 0.013\\ 9.94E-3\\ 0.0101\\ 9.98E-3\\ 9.68E-3\\ 9.62E-3\\ 0.0101\\ 9.80E-3\\ 9.93E-3\\ 0.0194\\ 0.0592\\ 9.55E-3\\ 9.50E-3\\ 9.50E-3\\ \end{array}$	$\begin{array}{c} 15.02\\ 15.63\\ 48.50\\ 52.51\\ 63.70\\ 69.66\\ 75.80\\ 78.82\\ 81.94\\ 83.56\\ 79.97\\ 0.9588\\ 0.8210\\ 1.019\\ 1.360\end{array}$

