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# Rheological behavior of cereal straw suspensions

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# **RHEOLOGICAL BEHAVIOR OF CEREAL STRAW SUSPENSIONS**

By

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Federal University of Technology, Owerri, Nigeria 2002

A thesis

presented to Ryerson University

in partial fulfillment of the  
requirements for the degree of  
Master of Applied Science  
in the Program of  
Chemical Engineering

Toronto, Ontario, Canada, 2010

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Sandra Ukaigwe



# **Abstract**

## Rheological Behavior of Cereal Straw Suspensions

Sandra Ukaigwe, Master of Applied Science, Department of Chemical Engineering, Ryerson University, Toronto, Canada. 2010

The rheological properties (yield stress and viscosity) of cereal straw suspensions are especially important in bioethanol production as they determine the mixing behaviour of the suspension during enzymatic hydrolysis.

Yield stress measurements are generally difficult to perform in straw suspensions due to sedimentation, which commonly occur in the suspensions and because of the difficulty encountered in loading the suspension into the measuring equipment. The process of placing the suspension in the measuring instrument causes a disturbance likely to induce the yielding of the suspension before the actual measurements are taken. Moreover cereal suspensions at high straw concentration (10-40 wt%) are soft solids and pourability is particularly difficult with solids.

Rheological behavior of straw suspensions made from wheat, Oats and malt barley of fiber sizes 0.15 mm-4.20 mm (mesh sizes 20 to 100) and concentrations 5.0-15.0 wt% were studied. The suspensions were initially prepared by dispersing milled and sieved straws in distilled water at room temperature, followed by vortexing to aid the dispersion process; this was later modified to include a 30-minute de-aeration of the suspensions using vacuum and 2-minute mixing using a general purpose mixer at about 162 rpm. However, none these procedures produced a homogenous suspension. The viscosity of the dispersion medium was modified by the addition of Xanthan gum. This produced homogenous suspensions which remained suspended for about 20 minutes. The rheological properties of these suspensions were measured on a Bohlin rheometer in the controlled stress mode using a vane and cup measuring instrument, and the suspension yield stress determined by extrapolation and by regression of Herschel-Bulkley, Casson and Bingham models. Yield

stress obtained from extrapolation ranged from 2-19 Pa, while model results ranged from 0.96- 8.15 Pa, for 5.0 wt% Oats straw suspensions with Xanthan gum strengths of 0.1-0.5 wt%. Extrapolation results for 7.5 wt% Oats straw suspensions with Xanthan gum strengths of 0.1-0.5 wt% ranged from 20-36 Pa while model results were in the range of 4.38-18.76 Pa. Wheat and malt barley straw suspensions evaluated using Herschel-Bulkley model at similar Oats straw suspension conditions of 5.0 wt% fiber concentration with 0.3 wt% Xanthan gum strength produced statistically equivalent yields stress to Oats straw suspensions in the range of 2.31-4.04 Pa for fibers of mesh size 40-100.

Extrapolation to 0.0 wt% Xanthan gum solution produced negatives yield stress values for 5.0 wt% Oats straw suspensions with 0.1-0.5 wt% Xanthan gum. However for 7.5 wt% Oats straw suspensions, extrapolated yield stress values were in the range of 3.8-18 Pa for suspensions made from fibers of mesh size 40-100.

Cereal straw suspensions are non-Newtonian fluids with yield stresses that are highly straw concentration dependent.

## **Acknowledgements**

I would like to express my deepest and heartfelt gratitude to my indefatigable supervisor Dr. Ginette Turcotte for giving me the opportunity to work on this project. Dr. Turcotte was always there to listen and give advice even when it was not convenient for her. She showed me different ways to approach research problems and the need to persevere. Her unremitting motivation remains indelible in my life.

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I would also like to express my sincere thanks to all the friends I have made at Ryerson University, Erlita Mastan, Ruston Bedasie, Basma Matti and the others too numerous to mention, you all made the work easier for me. I appreciate you all.

## **Dedication**

Dedicated to my husband, Alford Kenechukwu Ukaigwe, who gave his all beyond measure to make this dream a reality, I am eternally grateful.

And to my princess and prince, Akwaugo and Jideofor Ukaigwe, who endured my long absence from home in pursuit of knowledge, God bless you both.

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# Nomenclature

ABIP	Agricultural Bioproduct Innovation Program
AFEX	Ammonia Fiber Expansion
ASAE	American Society of Agricultural Engineers
Bh	Bingham
CALA	Canadian Agricultural Loan Program
Cs	Casson
GHG	Green house gases
GHGMP	Greenhouse gas mitigation program for Canadian Agriculture
HB	Herschel-Bulkley
LVDT	Linear variable differential transformer
n	Flow behavior index
k	Consistency index (Pa.s <sup>n</sup> for HB model) and (Pa.s for Casson and Bingham models)
$\tau$	Shear stress (pa)
$\tau_0$	Yield stress (Pa)
$\dot{\gamma}$	Shear rate (s <sup>-1</sup> )



# Chapter 1

## Introduction

Global increase in demand for energy has risen considerably in the last century as a result of world population growth, industrialization, a decline in universal oil production (Campbell and Laherrere, 1998) which is expected to reduce current global oil production level from the present 25 bbl to about 5 bbl in the next four decades and rising oil prices. Presently fossil fuel is the main source of energy supply globally and following the aforementioned challenges, it is expected that soon oil will become so scarce and expensive that it will force a change in humanity's way of life. Globally, most economic is dependent on oil. Therefore the effect of scarcity might be critical. Hence there is a need to identify and implement ways to save energy and provide alternative sources of energy supply.

Global interest in energy sources has currently shifted to renewable materials to reduce dependence on fossil fuel, and the potentials of lignocellulose biomass such as straws, wood, grasses, pulp, etc, which contain a significant amount of carbohydrates like hemicellulose and cellulose to produce biofuel is well recognized (Kim and Dale, 2004).

Even though the use of renewable energy is not new, more than 150 years ago, wood supplied up to 90% of the world's energy needs, but as the use of fossil fuel expanded, the world became less reliant on lignocellulose biomass as an energy source. Today, the world is looking again at renewable sources to find new ways to use them to help meet its energy needs and combat the harsh effects of the use of fossil fuel on the environment.

However, a major drawback in the use of bioethanol as an alternative energy source is the economics of the production process, the cost of production of bioethanol is still rather

high compared to fossil fuel partly due to the difficulty in mixing encountered during enzymatic hydrolysis, resulting from the high straw concentration required to make the process economically feasible (Malik and Sridhar, 2009; Knutsen and Liberator, 2009; Jorgensen et al., 2007) the other being the cost of enzymes. Managing the rheological properties of high solids mixture is a major challenge particularly when these properties changes as the process progresses which occur during enzymatic hydrolysis. Therefore an understanding of how the system deforms and flows that is the straw suspension rheology before and during enzymatic hydrolysis will provide useful insight into this processing challenge. Once the flow behaviour has been established, more can be understood about the way components of the system interact and a direct assessment of processability of the straw suspensions can be obtained.

Studying the rheological behaviour of straw suspensions also has its other challenges, because making a straw suspension which remained homogenous long enough for its rheological properties to be measured is hard to accomplish regardless of suspension preparation conditions. Therefore the viscosity of the dispersion medium for the straw suspensions preparation applied in this study was modified using Xanthan gum, then the rheological properties of the suspensions obtained by extrapolation.

The thesis is divided as such:

- Chapter 2 gives a brief review of the literature, to present the fundamentals in lignocellulose straws, lignocellulose straw suspensions, Xanthan gum properties, rheology of straw suspensions and yield stress determination.
- Chapter 3 presents comprehensive description of the material used, sources of material, experimental procedures and equipments used in this work.
- Chapter 4 discusses qualitative evaluation of straw suspensions that remained homogeneous long enough for their yield stress to be measured and the quantitative determination of the rheological property of straw suspensions.
- In Chapter 5, conclusion and recommendations for future work is presented.

# Chapter 2

## Literature Review

Bioethanol is produced from renewable resources; plants, organic waste, etc. (Sun and Cheng, 2002; Kumar et al., 2009) and can be used as an alternative to fossil fuels. Theoretically, bioethanol can be produced from any (biological) carbon source but the most common, easily accessible and readily available source is lignocellulose biomass (Hahn-Hagerdal et al. 2006; Gray and Zhou, 2006), a by-product of cereal crops. Various other plants like cassava, sugar cane and plant-derived materials like, soybean hulls, bagasse, corncobs, etc., can also be used for bioethanol production (Yan and Lin, 2009), but conflict with land use for food and food production has greatly impeded their use. Global bioethanol production is booming (Balat and Balat, 2009), as higher oil prices and technological breakthroughs in biofuel production (Tolan, 2002) have made it a profitable business (Yan and Lin, 2009; Henrich et al., 2009; Laser et al., 2009). Other factors which have contributed to the increased interest in the development and use of bioethanol include its potential to reduce green house gas emissions (GHG), increase energy security and support of rural economy (Yan and Lin, 2009), especially when the feedstock is based on cereal crops.

Cereals (wheat, Oats, malt barley, rye, etc.) are grasses grown for their edible, nutrient-rich, starchy seeds. They are produced worldwide because they can grow in many geographical areas and so huge amounts of fibrous by-product (lignocellulose straws) are available in most countries. It is estimated that about half the yield of cereal crops are straws (Montane et al., 2008; Mielenz, 2001), made up of mostly cell walls, which contain fermentable sugars

that could be converted into bioethanol. Therefore an inexhaustible amount of feedstock is available worldwide for the development and sustenance of the biofuel industry.

In Canada, cereal crops are produced extensively round the year. They are the bedrock of the Canadian crop economy. Important cereal crops produced in Canada include wheat, malt barley, Oats, rye, corn, triticale and grain millets. Canada produces about 5 % of the world wheat, 9.9 % of the world malt barley, 14 % of the world Oats and 1.4 % of the world corn (Ernest, 1999). Estimably, Canada has approximately 561 million dry tonnes of these materials which might be available for bioethanol production (Mabeel and Saddler, 2006) and this quantity of bioethanol can provide up to 50 % of Canada's transportation fuel demand.

With these abundant cereal crops, which is a huge source of raw material for bioethanol production and the urgent need to diversifying the energy sector with cleaner, renewable fuels such as bioethanol, the Canadian government is investing huge resources into the research and development of the bioethanol industry through programs like Agricultural Bioproduct Innovation Program (ABIP), Canadian Agricultural Loans Act (CALA), and Greenhouse Gas Mitigation Program for Canadian Agriculture (GHGMP).

## **2.1 Types of Lignocellulose Straws**

Although there are many types of lignocellulose plant material from which straws are obtained, this project was only involved with three types: Oats, wheat and malt barley.

Wheat straw is an agricultural residue made up of dried leaves, stalks and stems of the wheat plant, obtained from the harvest of wheat, which can serve as a low cost feedstock for conversion into bioethanol fuel. It contains about 58 – 78 wt% total sugar depending on the variety and species, with the remaining being extractable organic compounds (Himmel et al., 2007; Kim and Dale 2004). The total sugar in wheat straw is comparable to those of corn stover which is the main bioethanol feedstock in North America in the making of bioethanol. Currently, wheat straws and other agricultural residues are usually plowed back into the soil, composted, burned or disposed in landfills; therefore the use of wheat

straw as feedstock for bioethanol production would not result in large impact on the agricultural system and would likely have good sustainability.

Oats straw is a by-product from the harvest of Oats, consisting of the dried leaves, stalks and stems of the Oats plant (*Avena sativa*) with chemical composition of 34-47 wt% carbohydrate, 32-48 wt% fiber and small percentages of ash, depending on the species.

Oats straw like most agricultural residues has a huge potential as a bioethanol feedstock. With global production of 24.2 Tg, the utilization of Oats straws as a feedstock could produce about 225 ML of bioethanol globally, replacing 161 ML of gasoline (Kim and Dale 2004), when ethanol is used as an E85 fuel. Canada could produce 0.74 GL bioethanol equivalent to 5.3 million barrel gasoline (Kim and Dale 2004).

Malt barley straw is also an agricultural residue made up of dried leaves, stalks and stems which is mainly used as algaecide. Currently, it has a global annual production record of about 124 Tg, with Europe producing 62 %, Asia 15 % and North America producing 14 % (Himmel et al., 2007; Kim and Dale, 2004). Hence about 18GL of global bioethanol could be available, with Canada producing about 17 % of it equivalent to 2.20GL of gasoline.

The annual availability of Canadian agricultural residues from lignocellulose crops production has been estimated at between 2.7 and 18 million dry tonnes per annum with bioethanol potential of over 65 GL yr<sup>-1</sup>, with wheat straw having the second highest potential of approximately 30.8 GL yr<sup>-1</sup> while Oats straw and malt barley straw both contribute substantial amounts. This represents between 0.7 % - 11.9 % total Canadian gasoline consumption (Mabeel and Saddler, 2006; Gronowska et al., 2004; Mabeel et al., 2006). Thus utilizing lignocellulose biomass would move Canada towards greater transportation fuel independence, increase the stability and security of the energy sector by reducing the impact of localized disruptions in supply. However the utilization of lignocellulose straws as feedstock is still largely dependent on the rheological behaviour of the fibers during enzymatic hydrolysis, and to understand this process, studying the rheological behaviour of suspensions made from lignocellulose fiber becomes essential.

## 2.2 Structure of Lignocellulose Straws

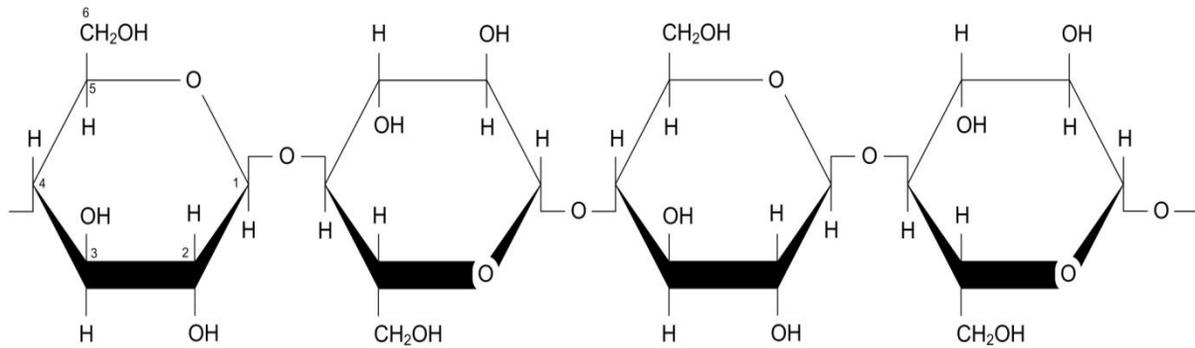
Lignocellulosic straws consist mainly of cellulose, hemicellulose, lignin and minor amounts of free sugars, starch, proteins and extractable organic compounds. The highly crystalline cellulose, which provides stiffness to the plant, is surrounded by a matrix composed of hemicellulose and lignin (Rowel, 2000).

Cellulose, the most abundant polysaccharide on earth (Mielenz, 2001) is a linear polymer of D-glucose units linked by  $\beta$ -1,4-glucosidic bond, with  $-\text{CH}_2\text{OH}$  groups alternating above and below the plane of the cellulose molecule thus producing long, unbranched chains (Figure 2.1). The beta linkage which differentiates it from starch connects the first carbon ( $\text{C}_1$ ) of one glucose to the fourth carbon ( $\text{C}_4$ ) of the next glucose. Cellulose has a strong tendency to form intra and intermolecular hydrogen bonds between OH groups within the same cellulose chain and surrounding cellulose chains, the chains tend to arrange in parallel and form a crystalline super molecular structure. Bundles of linear cellulose chains in the longitudinal direction form micro-fibrils which are laid down in a matrix in the cell wall structure.

Due to its fibrous structure and strong hydrogen bonds cellulose has a high tensile strength and is insoluble in most solvents (Corredor, 2006). Orientation of the  $\beta$ -1,4-glucosidic bond also makes the polymer rigid and protects the interior of the plant cells, thereby inhibiting the flexing of the molecules which must occur during hydrolysis.

The breakdown of cellulose by the enzyme cellulase into cellobiose repeating unit ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) and finally into glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) during hydrolysis reaction is the basis of enzymatic hydrolysis used in the production of bioethanol, enzymatic hydrolysis is not only difficult but also enzyme specific thereby leading to high bioethanol production cost.

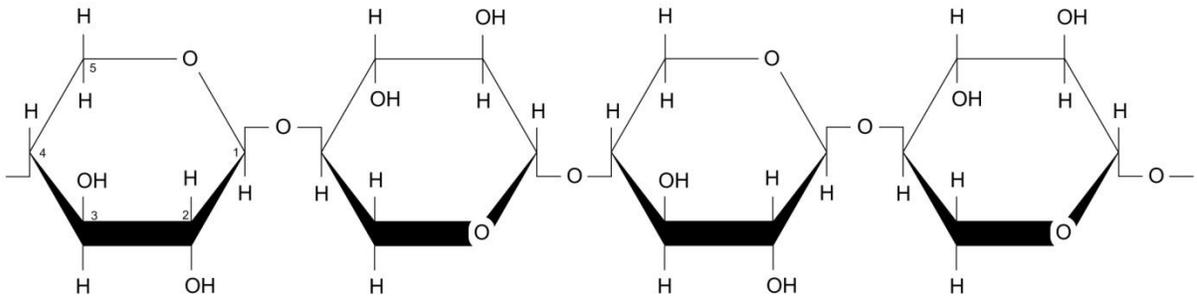
Cellulose typically account for more than 40 % of the lignocellulose (Ramirez, 2005) in most lignocellulose materials.



**Figure 2.1 Cellulose structure**

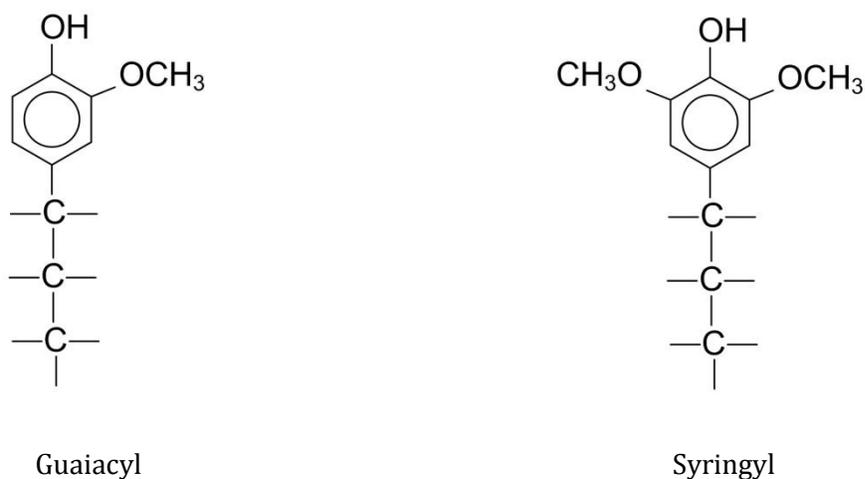
Hemicellulose is a polysaccharide of five different polymers containing highly branched chains of the sugars D-xylose, D-glucose, D-galactose, L-arabinose, D-mannose, and D-glucouronic acid. These sugars are part of the supporting matrix for the cellulose microfibrils and partially responsible for the moisture absorption of lignocellulosic fibres. (Baltazar-y-Jimenez and Bismarck, 2007).

Hemicellulose is usually classified according to the main sugar in their backbone, e.g., xylans, mannans, and glucans, with xylans and mannans being the most common. Hemicellulose is relatively easier to hydrolyze than cellulose due to their branched, amorphous nature. Most hemicellulose contains mostly xylan, a soluble heteropolymer that also provide additional structural support to the plant cell wall and acts as a barrier to cellulose essentially blocking cellulase action. Structurally, xylan provides the matrix in which the crystalline cellulose micro-fibrils are embedded. It is in this role that xylan becomes a barrier to efficient cellulose function and thus needs to be removed for effective biomass hydrolysis. Hemicellulose accounts for about 20 wt% of the lignocellulose (Ramirez, 2005) in most lignocellulose materials.



**Figure 2.2 Xylan structure**

Lignin is an amorphous but very complex polymer of phenyl-propane units with hydrophobic character (Rowel et al, 2005) present in all lignocellulosic biomass. It is a three-dimensional polyphenolic network built up of dimethoxylated (syringyl), monomethoxylated (guaiacyl) (Figure 2.3) and non-methoxylated (*p*-hydroxyphenyl) phenylpropanoid units, derived from the corresponding *p*-hydroxycinnamyl alcohols, which give rise to a variety of sub-units including different ether and C-C bonds. Lignin is essentially a bonding agent in the cellulose-hemicellulose matrix which also provides thermal, chemical and biological resistances (Bismark et al., 2005). Lignin effectively protects plants against microbial attack and only a few organisms, including rot-fungi and some bacteria, can degrade it. Lignin restricts cellulose hydrolysis by shielding cellulose surfaces or by adsorbing and inactivating enzymes. The close union between lignin and hemicellulose restricts swelling of the fibers, hence affecting enzyme accessibility to cellulose (Corredor, 2008).



**Figure 2.3 Building units of lignin**

Despite the potentials of lignocellulosic straw as feedstock for bioethanol, its use is still greatly impeded due to the natural resistance of plant cell walls to microbial and enzymatic deconstruction (Himmel et al., 2007) a condition known as “biomass recalcitrance” that is largely responsible for the high cost of lignocellulose conversion. Thus lignocellulose straws are usually pretreated to overcome this condition and make them amenable to hydrolysis.

### 2.3 Lignocellulose Straw Pretreatment

Pretreatment is a necessary process in the utilization of lignocellulosic materials to obtain high degree of fermentable sugars. It alters the structure of cellulosic biomass, to make cellulose more accessible to enzymes that convert carbohydrate polymers into fermentable sugars. The goal of pretreatment is to break the lignin seal, solubilize hemicellulose, reduce crystallinity of the cellulose and increase the surface area and pore volume of the fibers (Patel et al., 2009). Pretreatment techniques can be grouped into four categories: physical, physico-chemical, chemical, and biological.

Milling is a physical pretreatment technique that can be used to alter the size of lignocellulose straws, thereby increasing the surface area and possibly pore sizes of the

fiber, while reducing the degree of crystallinity of fibers making them more amenable to hydrolysis. (Taherzadeh and Karimi, 2008) showed that without any other pretreatment, corn stover fiber of 53-75  $\mu\text{m}$  produced 1.5 times more glucose than corn stover fiber of 425-710  $\mu\text{m}$ , and that following crystallinity reduction by high ball milling that produced straws of about 60  $\mu\text{m}$ , saccharification of more than 50 % of straw cellulose with minimal glucose degradation becomes possible at mild acid hydrolytic condition. However, size reduction is usually more efficient if combined with other pretreatment.

Physico-chemical pretreatment combines both chemical and physical pretreatment processes and includes, steam explosion, ammonia fiber expansion (AFEX),  $\text{CO}_2$  explosion, liquid hot water pretreatment, etc., chemical pretreatment include alkaline hydrolysis, acid hydrolysis, organolysis process etc., while biological pretreatment basically involve the use of microorganism to degrade the part of the lignocellulose material before hydrolysis.

## 2.4 Lignocellulose Fiber Suspensions

Lignocellulose fiber suspensions are made by dispersing milled lignocellulose straws in water and agitating the mixture. The suspensions are typically two-phase mixtures and non-homogenous as sedimentation and floatation regularly occur with these suspensions.

Fiber suspension is a heterogeneous system of incompressible fluid and dispersed fibers. At low concentrations, <5.0 wt%, the fibers in the suspension are far apart and have negligible interaction. But as solids concentration increase, so do hydrodynamic interactions between fibers and the surrounding fluid as well as interaction between fibers. Hence the fibers come together to form floccules, which are held together by weak interparticle cohesive forces and therefore easy to break apart. At a high solids concentration, >5.0 wt%, the fibers interact to form a fiber network structure that possesses the properties of a solid, like strength and elasticity (Babkin, 2002). Wet fibers are highly compressible and easily stick together making them difficult to shear and mix uniformly.

Most researchers use pretreated corn stover in their study of the rheological behaviour of lignocellulose straw suspensions, with a few exceptions; this is shown in Table 2.1. However the homogeneity of these suspensions was always omitted in their publications.

In this study, both pretreated and untreated Oats, wheat and malt barley suspensions made homogenous with the aid of Xanthan gum was used.

**Table 2.1 Research history on rheology of lignocellulose straw suspensions**

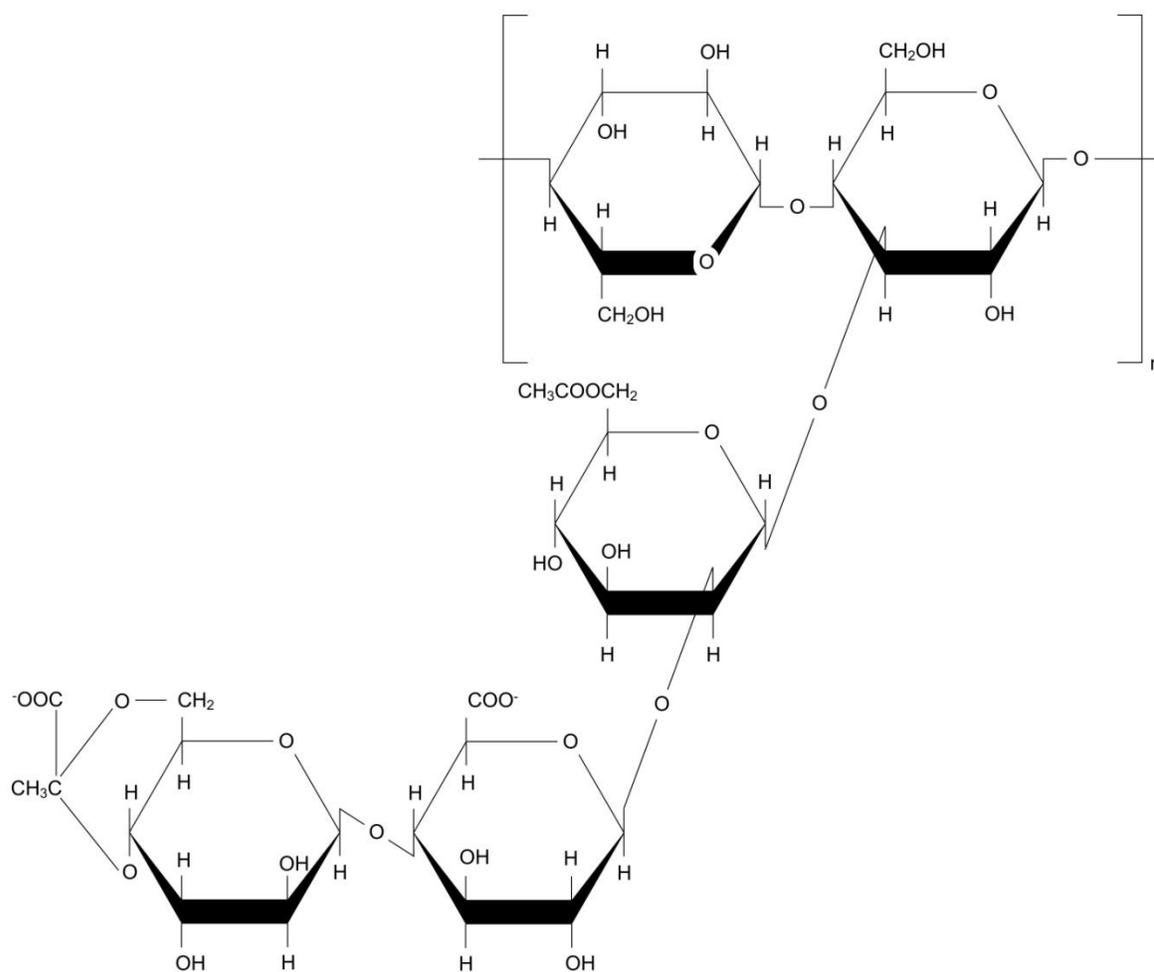
<b>Author</b>	<b>Topic</b>	<b>Date</b>
J.S Knutsen and M. W. Liberator	Rheology of High Solid Biomass Slurries for Biorefinery Application	2009
Viamajala et al	Rheology of Cornstover Slurries at High Solid Concentration – Effect of Saccharification and Particle Size	2009
J.J Stickel and J.S knutsen	Rheology Measurements of a Biomass Slurry: An Inter-laboratory Study	2009
Rizwan Bashir	Yield stress of concentrated wheat straw suspension	2008
R.K Dasari and R.E Berson	The Effect of Particle Size on Hydrolysis Reaction Rate and Rheological Properties of Cellulosic Slurries	2007
N.V Pimenova and T.R Hanley	Effect of Corn stover Concentration on Rheological Characteristics	2004
N.V Pimenova and T.R Hanley	Measurement of Rheological Properties of Corn stover Suspension	2003

## 2.5 Xanthan Gum

Xanthan gum is a complex microbial exo-polysaccharide industrially produced from glucose via fermentation by the plant-pathogenic bacterium, *Xanthomonas campestris* pv. *campestris*. It has the chemical formula  $C_{35}H_{49}O_{29}$ , and molecular weight of approximately 2 million. It has a  $\beta$ -D-glucose backbone like cellulose, but every second glucose unit is attached by the side to a trisaccharide consisting of mannose, glucuronic acid, and mannose (Figure 2.4). The mannose closest to the backbone has an acetic acid ester on carbon 6, and the terminal mannose carries pyruvic acid between carbons 6 and 4 (Rosalam and England, 2006).

Xanthan gum is widely used in a broad range of industries, such as in foods, toiletries, oil recovery, cosmetics, as water-based paints, etc. It is also used as a stabiliser for emulsions and suspensions (Rosalam and England, 2006). The wide applications of Xanthan gum may be due to its ability to form high viscosity solution at low shear forces, its high stability at many process conditions, and its resistance to mechanical degradation and biodegradability (Malik and Sridhar, 1992).

The rheological properties of Xanthan gum both in dilute and concentrated solutions have also being extensively studied and it shows that the behaviour of Xanthan gum solution changes with change in the solution concentration (Malik and Sridhar, 1992).



**Figure 2.4 Structure unit of Xanthan gum**

## 2.6 Rheology

The study of the deformation and flow of matter, mainly liquids and soft solids, with complex flow behaviour is called rheology. Materials with complex flow behaviour include muds, sludges, suspensions, polymers, many foods, bodily fluids, and other biological materials. The shear rate of these substances when subjected to a shear stress cannot be defined by a single value of viscosity at a fixed temperature even for materials that are relatively temperature independent like fiber suspensions (Viamajala et al., 2009; Knutsen and Liberator, 2009). Their viscosities also depend on shear duration and structure of the substance. Their responses to shearing effects are typically non-Newtonian (Viamajala et al., 2009). Rheology is thus concerned with establishing predictions for mechanical behaviour *i.e.*, relationship between the stress applied to that material and the deformation that the material exhibits, based on its micro- structure.

Lignocellulose fiber suspensions have complex rheological properties (Viamajala et al., 2009; Barnes and Walters, 1985), especially at solids concentration greater than 5 wt% which is desirable in biofuel production for optimum ethanol yield (Knutsen and Liberator, 2009; Jorgensen, 2007). Their rheological properties are important in the mixing operation encountered in ethanol production, as they determine equipment design or selection thereby controlling process power consumption and overall process economics. The group of Fan observed a 4 % increase in solids content of paper sludge resulted in a fivefold increase in mixing power consumption. Study by Wyman, also proved that, bioethanol processing costs were functions of solid concentration. Hence the importance of rheological properties in bioethanol production cannot be over emphasized. The rheological properties of lignocellulose fiber suspensions, which control their flow behaviour, are yield stress and viscosity.

## 2.7 Yield Stress

Yield stress of a material is the maximum stress below which no flow occurs. The accurate measurement of this point however requires that the strain reaches a zero value after the removal of the applied stress. Yield stress can be studied using constant shear stress or shear rate, the magnitude of the result depends on the time allowed for the sample being measured to attain

steady state, hence yield stress becomes a function of applied shear stress, shear rate and time. The importance of yield stress in fluids is well recognized industrially; examples include leveling and sagging of paints, start up power requirement in pumping through pipe lines, existence of dead zones in mixing equipments etc.

The fibers in lignocellulose fiber suspensions interact with each other by entanglement that can lead to formation of fiber networks or floccules which can result in complex slurries or suspensions that do not flow instantaneously especially at fiber concentration above 5 wt% for untreated biomass (Viamajala et al., 2009; Zhu et al., 2005) and above 20 wt% for pretreated biomass (Knutsen and Liberator, 2009). Therefore lignocellulose fiber suspensions possess yield stress.

The conventional technique used for the determination of yield stress involves the extrapolation of the flow curve *i.e* the shear stress – shear rate curve to where shear rate equals zero. The shear stress – shear rate data can also be fitted to a model (Cheng, 1986; Nguyen and Boger, 1992; Steffe, 1996; Pimenova and Hanley, 2004). The disadvantages of this method are that the yield stress value obtained is not measured but calculated. Hence it is also influenced by the sensitivity of the measuring instrument and the rheological model used (Cheng, 1986; Nguyen and Boger, 1992; and Steffe, 1996). The flow curve method has been used by several researchers to determine the yield stress of pretreated corn stover suspension, a lignocellulose fiber suspension (Knutsen and Liberator, 2009; Sticke and Knutsen, 2009; Dasari and Berson, 2007; Zhu et al., 2005; Pimenova and Hanley, 2004).

Step stress test is essentially a multiple creep test; it entails applying a small stress to a sample and holding it for pre-defined time, then measuring the strain response. The stress is increased gradually until a measurable flow is obtained. This is a more accurate method of obtaining a material's yield stress as it measures the "exact" point at which the material begins to yield, and therefore produces a more accurate result than the flow curve method but it is time consuming as the measurement time is much longer than the measurement time used in flow curve experiment. The step stress test is usually carried out in the controlled rate mode.

The ramp stress test involves applying a gradual stress on a sample and monitoring the instantaneous viscosity until the material starts to flow. The disadvantage of this method is

that there is no check to ensure the viscosity is being recorded at steady state, and if the test conditions are altered, (ramp rate or shear range), data obtained become incomparable to previous results. This method is however suitable for quality control measurements. Ramp stress test, is a controlled stress test.

The flow curve method was used work to determine the yield stress of lignocellulose fiber suspensions.

## 2.8 Rheological Models

Several rheological models are available for the determination of the rheological behaviour of industrial fluids. Newtonian and non-Newtonian fluids are both commonly encountered industrially. Some Non-Newtonian fluids are characterized by a yield stress. One of the many models which describe these fluids is the Herschel-Bulkley model, given by Equation (2.1).

$$\tau = k\dot{\gamma}^n + \tau_o \quad (2.1)$$

Where  $k$  is the consistency index in unit of Pa.s<sup>n</sup>,  $n$  (-) is the flow behaviour index,  $\tau$  (Pa) is the shear stress,  $\dot{\gamma}$  (s<sup>-1</sup>) is the shear rate and  $\tau_o$  is the yield stress. Herschel-Bulkley model is convenient to use and very appropriate for many fluids because Newtonian, Power law and Bingham fluids are all considered special cases of this model as shown in Table 2.2. Herschel-Bulkley model has been used to model many materials including, blood, ink, food products, polymer suspensions, cellulosic slurries and straw suspensions, etc. (Pimenova and Hanley, 2004).

**Table 2.2 Special cases of Herschel-Bulkley model (Steffe, 1996)**

Fluid	$k$ (Pa.s <sup>n</sup> )	$n$ (-)	$\tau_o$ (Pa)
Herschel-Bulkley	>0	$0 < n < \infty$	>0
Newtonian	>0	1	0
Power law (Shear-thinning)	>0	$0 < n < 1$	0
Power law (Shear-thickening)	>0	$1 < n < \infty$	0
Bingham plastic	>0	1	>0

Another useful model for non-Newtonian fluids is the Casson model. This is an empirical model that does not obey Newton's law. It was originally proposed to describe the behaviour of pigment-oil suspensions but has been applied successfully to a large variety of suspensions like benonite, mycelial, polymer, including biomass suspensions. Casson model is also widely used for the determination of the rheological properties of molten chocolate (Steffe, 1996) but the most common fluid known to follow the Casson model is blood (Nguyen and Boger, 1992). The Casson model is a two parameter model shown in Equation (2.2) below. A fluid is said to follow the Casson model if a plot of  $\tau^{0.5}$  versus  $(\dot{\gamma})^{0.5}$  is linear, This feature of the model allows quick testing of the experimental data and determination of the model parameters. In some cases however, it has been reported that the linear relationship between,  $\tau^{0.5}$  and  $(\dot{\gamma})^{0.5}$  was obtained only in the shear rate region of about 400 -1000 $s^{-1}$  (Nguyen and Boger, 1992).

$$\tau^{0.5} = \tau_0^{0.5} + (k\dot{\gamma})^{0.5} \quad (2.2)$$

Another simple rheological model is the Bingham model. The Bingham model represents only the ideal case of non-Newtonian fluids in which the structure that helps the fluids in resisting irreversible deformation breaks down completely as soon as the applied shear stress overcomes a yield point. The Bingham model is shown in Equation (2.3)

$$\tau = \tau_o + k\dot{\gamma} \quad (2.3)$$

Where  $\tau_o$  (Pa) is the yield stress and  $k$  (Pa.s) is the Newtonian viscosity (consistency index). The model predicts that when the Bingham yield point is exceeded, the fluid flows like a liquid with constant viscosity.

The choice of a particular model for a given fluid depends on a number of factors such as the goodness of the model fit to experimental data which can be determined from  $R^2$  value, the simplicity of the constitutive equation involved, personal tastes, and most importantly, the intended use. It has been shown by many workers that over a restricted range of shear rate, typically from 10-1000  $s^{-1}$  the three models described above can adequately correlate the data for a given yield stress fluid (Nguyen, 1983). Therefore these three models Herschel-Bulkley, Casson and Bingham were applied in this study.

## 2.9 Rheometer

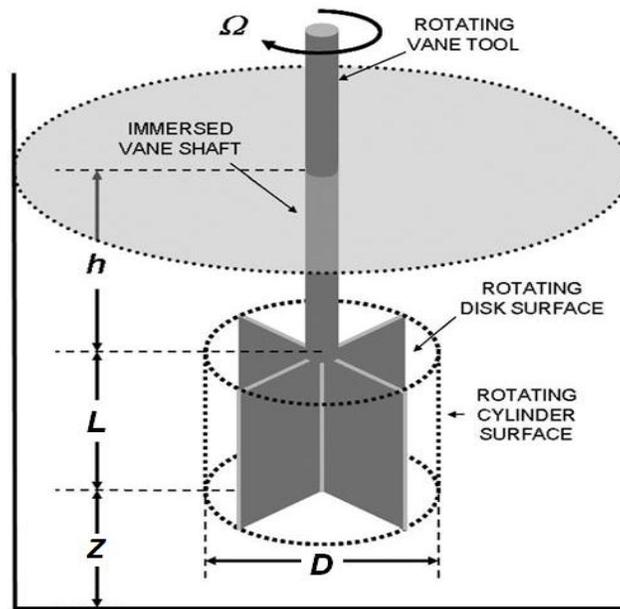
Varieties of rheometer are available for the determination of the rheological properties of materials, their performance and efficiencies depend on the right choice of geometry for the material being measured. Common geometries include coaxial cylinders (couette), cone and plate, concentric disk, and recently the vane.

The vane geometry (which was used in this study) was first introduced in the rheological property measurement of multiphase systems to eliminate the possibility of slip in 1936 by Russel as multiphase systems exhibit slip problems when tested at low shear rates with smooth surface geometries like cone plate (Zhu et al., 2005). Much later in 1985, Nguyen and Boger, further developed the use of the vane for measurements of the yield stress of concentrated suspensions, Vane geometry provide a convenient and relatively accurate means of making a direct measurement of the yield properties of concentrated suspensions. This is because the special geometry of the vane allows the material to yield within itself, rather than on the interface between the sample and the apparatus. Further studies also confirmed that the vane is not only suitable for yield stress measurements but also eliminates the possibilities of wall slip for a variety of materials including greases, oil-water emulsions and various suspensions (Keentok, 1982; Yoshimura et al., 1987; Barnes, 1999). Table 2.3 show examples of the application of the vane in rheological property measurement.

**Table 2.3 Uses of vane for yield stress determination in food and bioengineering systems**

<b>Type of food system</b>	<b>References</b>
Frozen ice cream	Briggs <i>et al.</i> , 1996
Fruit pectin jam	Houska <i>et al.</i> , 1997
Processes cheese analogue	Mleko and Foegeding, 2000
Apple pulps	Missaire <i>et al.</i> , 1990
Proteins foams	Pernell <i>et al.</i> , 2000
Various food	Rao and Steffe, 1997
Gellan gum gels, soybean protein	Truong and Daubert, 2000
Molten chocolate	Wilson <i>et al.</i> , 1993
Fermentation broth, ketchup	Leongpoi and Allen, 1992
Various fermentation broths	Mohseni <i>et al.</i> , 1997

Specifications have been established for the positioning of the vane during experimentation for accurate result prediction. (Nguyen and Boger, 1992; Liddel and Boger, 1996). Figure 2.4 show specifications for vane in cup geometry.



**Figure 2.4 Schematic of vane in cup showing vane specifications**

- (i) Ratio of the vane length ( $L$ ) to vane diameter ( $D$ ) should lie within 1.5 and 4.
- (ii) Depth of the vane surface from the surface of material ( $h$ ) can be zero, or the ratio of the vane length ( $L$ ) to the vane diameter ( $D$ ) should be greater than 1.0.
- (iii) Ratio of the height of vane from bottom of cup ( $Z$ ) to vane diameter ( $D$ ) should be greater than 0.5.

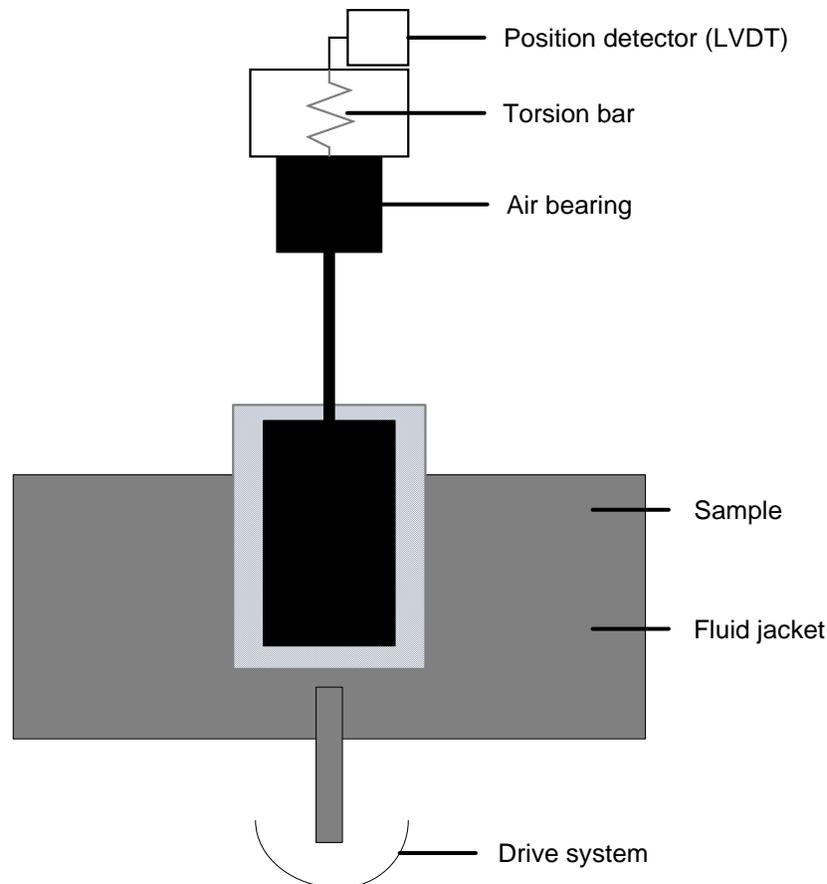
## 2.10 Principle of Operation the Rheometer

The rheometer can be operated in either the controlled shear rate or the controlled shear stress modes.

### 2.10.1 Controlled Shear Rate

In the controlled rate mode, rheometer operates as a constant speed motor with a torque detection system. Figure 2.5 shows the schematic of the controlled shear rate rheometer. The torsion bar is suspended on an air bearing to give a frictionless bearing. When the drive system turns, the resistance (viscosity) of the sample being measured tries to twist the torsion bar. By measuring the resultant twist and knowing the stiffness of the bar, the

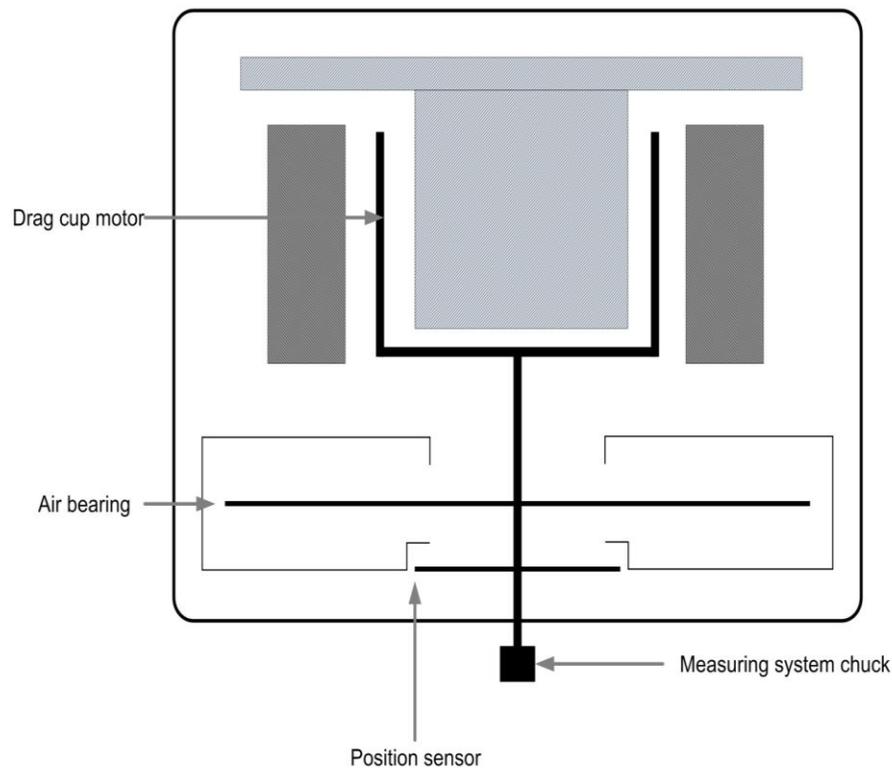
torque is measured. Since the rheometer is digitally based, the software automatically converts the measured torque to a shear stress when displaying the data.



**Figure 2.5 Principle of operation of a controlled shear rate rheometer**

### 2.10.2 Controlled Shear Stress

The controlled stress rheometer controls the stress and measures the strain. In this mode of operation, the rheometer works as a constant torque motor using a drag cup system. As the drive system turns, the resistance to the rotation of the measuring geometry caused by the viscosity of the sample being measured is detected by an angular position sensor attached to the shaft (Figure 2.6). Reading from the position sensor is converted to a strain. By monitoring the change of strain with time, the shear rate is obtained.



**Figure 2.6 Principle of operation of a controlled shear stress rheometer**

### 2.10.3 Calculation of Shear Rate and Shear Stress Form factors

The Bohlin rheometer works with torque and angular velocity. But because measurements are normally done based on shear stress and shear rates, a method is needed to convert from instrument numbers (torque and angular velocity) to rheology numbers (shear stress and shear rate). Each measuring system used on the Bohlin rheometer have its associated 'form factors' to convert torque to shear stress and to convert angular velocity to shear rate. If the shear stress form factor is  $C_1$  and the shear rate form factor  $C_2$ , then

$$\text{Shear Stress} = C_1 \times \text{Torque}$$

$$\text{Shear Rate} = C_2 \times \text{angular velocity}$$

$$\text{Viscosity} = \text{Shear Stress} / \text{Shear Rate}$$

Form factors calculations for some geometry are shown below.

### **Cone and plate**

$$C_1 = \frac{1}{2/3 \pi r^3} \quad (2.4)$$

$$C_2 = \frac{1}{\theta} \quad (2.5)$$

Where  $r$  = radius of cone,  $\theta$  = cone angle in radians

### **Parallel plates**

$$C_1 = \frac{1}{2/3 \pi r^3} \quad (2.6)$$

$$C_2 = \frac{3r}{4} \quad (2.7)$$

The rheometer software uses similar method to convert from instrument number to rheology number for all other geometries.

From the literature reviewed so far, it is obvious that there is a need to study the rheological behaviour of lignocellulose suspensions for them to be utilized successfully in the production of bioethanol and so far only limited research has being devoted to the study of other lignocellulose fiber suspensions aside from pretreated corn stover. Thus, this study which is based the rheology of wheat, Oats and malt barley straw suspensions will represent a first attempt in characterizing the rheological behaviour of Oats and malt barley suspensions.

## 2.10 Research Objectives

The objectives of this work were:

1. Determine the yield stress ( $\tau_0$ ) of untreated fiber suspensions.
2. Evaluate the effect of Xanthan gum when used as a viscosity modifier on the yield stress of straw suspensions.
3. Evaluate the change in yield stress of untreated straw suspensions resulting from change in suspension concentration and fiber size.
4. Determine the rheological model parameters of untreated straw suspensions with Xanthan gum.

# Chapter 3

## Material and Methods

This chapter covers material, sources of material, detailed experimental procedures and equipment applied in this work.

### 3.1 Material and Sources of Material

#### Straws

Oats and malt barley straws used in this study were 2007 spring sown, while the wheat straw was a 2005 spring cut. The straws were generously supplied by partners of the Agriculture and Agri-Food Canada, funding agency program: ABIP. They were received in dry condition, stacked in huge sacks with lengths of about 6–7 cm. They were stored in the same conditions as received for about three years before being used for this study.

#### Standard Viscosity Oil

A standard Newtonian viscosity oil (#12): Spectra Research Corporation, Missisauga, Canada) was used to calibrate the rheological measurement on the Bohlin CVOR rheometer. The oil has a viscosity of 1.074 Pa.s at 25°C (Bohlin Instruments, 1994)

#### Xanthan Gum

Xanthan gum used to increase the viscosity of water when making straw suspensions was supplied in powdered form by NovaXan ADM (Illinois, USA).

Solutions of 0.1 wt% – 0.5 wt % which were the range of concentrations that maintained their homogeneity long enough for rheological behaviour measurements, were used in this study.

## **3.2 Experimental Procedures**

### **3.2.1 Milling and Sieving**

About 900 g of straw was weighed and milled to approximately 1 mm size on a Retsch SM 100 Comfort milling instrument from Retsch GmbH Inc. (USA). Milled straw were stored in plastics bags and were later sieved using a stack of 8 metal sieves arranged in decreasing apertures (increasing mesh sizes: 8, 12, 20, 40, 60, 80, 100), with a solid collecting pan at the base and a lid at the top, according to a modified ASAE method (ASAE standard, 2003). Straw size is approximately 1-2 % smaller than the aperture of the sieve Merkus, (2009). For each straw type used, approximately 20 g of the milled straw was placed on the top most sieve, the stack of sieves was shaken manually to and fro 5 times, and then it was tilted and shaken 7 times, these 12 shakings made-up a set, each set was repeated 8 times. Milled straw fibers collected from a sieve were called by the name of that sieve mesh size (mesh size 20 means fibers retained on sieve #20, while mesh size -20 means fibers that pass through mesh 20).

### **3.2.2 Suspension Making**

For 5.0 wt% fiber concentration suspensions, one and half grams of Oats straw fibers of mesh size 40 were added in each 50mL plastic graduated cylinder containing 28.5 g of water at room temperature and manually stirred using a stirring rod until all fibers looked wet. Cylinders were left on the bench, measuring the height of the sedimented fibers and of the floating fibers for a maximum of 20 minutes. This procedure was repeated for fiber suspensions of 6.25 wt% to 20.0 wt% in increments of 0.25 wt%, for all mesh sizes and for wheat and malt barley straws.

Thinking of increasing the homogeneity of suspensions by increasing the dispersibility of the fibers, vortexing was used instead of manually shaking the suspensions. Twenty cylinders of fiber suspensions were placed on a multi-tube vortexer (VWR International, Bristol, USA) for 2 hours at a speed of 220 rpm. Again, all combinations of fiber

concentrations and mesh sizes were done, and the height of the sedimented fibers and of the floating fibers was measured for a maximum of 20 minutes.

Next, a Powermax General Purpose mixer (VWR International, Mississauga, Canada) was used, replacing the vortex mixer. This was good for only one cylinder at a time. The mixer was set at a speed of approximately 720 rpm, and ran for 300 s. All combinations of fiber concentrations and mesh sizes were done for the three straw types.

De-aeration was introduced as a means to improve the wettability of the fibers. Consequently, the suspensions in their respective cylinders were placed in a cylindrical chamber where vacuum was applied for approximately one hour. After which the cylinders were removed and agitated for 120 s using the Powermax General Purpose mixer at a speed of approximately 720 rpm. Fibers were totally sedimented approximately 60s after mixing was stopped. Again, all combinations of fiber concentrations and mesh sizes were done for the straw types.

To further enhance homogenous suspension formation, the suspension preparation method was modified to also include addition of Xanthan gum to the dispersing water, at 0.1 wt% to 0.5 wt%, in increments of 0.1 wt%. After mixing, the suspensions remained suspended for about 20 minutes. These homogeneous Xanthan gum-straw suspensions needed to be made fresh, prior to each measurement of the rheological properties. This time, only 5.0 wt% to 10.0 wt% fiber concentration were evaluated in 0.25 wt% increments at 20, 40, 60, 80 and 100 mesh size and for all three types of straw.

### 3.2.3 Suspension Preparation Procedure Tested

- Dispersion and manual mixing
- Dispersion and vortexing
- Dispersion and mechanical mixing
- Dispersion, de-aeration and mechanical mixing

Variables tested in this study were fiber sizes and concentrations for untreated and pretreated Oats, wheat and malt barley straw suspensions. This is shown in Table 3.1. However only the rheological behaviour of the conditions that appear in bold on the table were studied due to equipment limitation.

**Table 3.1 Fiber conditions evaluated**

<b>Straw type</b>	<b>Mesh size (mm)</b>	<b>Fiber size (<math>\mu\text{m}</math>)</b>	<b>[Suspension] (wt %)</b>
Oats	8	2380	5-7.5
Wheat	12	1680	5-10
Malt barley	16	1190	5-10
	20	841	5-12.5
	<b>40</b>	<b>420</b>	5-12.5
	-40	<420	5-12.5
	<b>60</b>	<b>250</b>	5-12.5
	80	177	5-20
	<b>100</b>	<b>149</b>	5-20

### 3.2.4 Mild Acid Pretreatment

Some pretreated straws were also evaluated. Eight grams of milled straw fibers was weighed on a digital balance and added to 2.64ml aqueous solution of 0.1 wt%  $\text{H}_2\text{SO}_4$  in a 250 ml Erlenmeyer flask. The flask was covered with a clean foam plug, swirled gently and placed inside a steam pressure sterilizer (All American Pressure Sterilizer, Wisconsin Aluminum, USA) containing distilled water preheated to 40 °C. The sterilizer was placed on a heater and the heat turned on. The temperature of the sterilizer was maintained at 126 °C, at a pressure  $1.24 \times 10^5$  Pa (18 psi). After 15 minutes, the flask was transferred from the sterilizer to an ice bath and left there for 5 minutes, after which the contents of the flask were strained using a domestic strainer. The solid fraction of the mixture was transferred into a 140 ml beaker and about 80 ml of distilled was water added to the beaker. The pH of the solution was adjusted to about 4.7 by the addition of 0.03g/ml NaOH solution made from 97% pure NaOH pellets. The mixture was strained again and the fibers were air dried for 48 hours. They were stored in a plastic container until used for straw suspension production.

### 3.3 Yield Stress Measurement

Preliminary tests on the Bohlin CVOR 150-900 rheometer (Malvern Instruments Ltd, Worcestershire, United Kingdom) showed that the rheometer could only analyze suspensions made from fibers of mesh 40 to 100 (i.e fiber sizes of approximately 150 -490  $\mu\text{m}$ ) of 5.0 wt% and 7.5 wt% fiber concentration. Therefore rheological testing was limited to suspensions made from fibers of these mesh sizes and concentrations even though these conditions may not be applicable in the industry. Initial measurements of 5.0 wt% and 7.5 wt% fiber suspensions of all three types of straw, for mesh size of 40, 60, and 100 were done in both the controlled shear stress mode and the controlled shear rate mode. However, the controlled shear rate mode was discontinued as it produced noisy data. For the controlled shear stress mode, minimum and maximum shear stresses of 0.1 Pa and 50 Pa were set. This range was divided into 20 sample points at the discretion of the experimenter, which the instrument arbitrarily assigned to levels of constant shear stress. The length of time during which the shear rate of each sample point was applied i.e., delay time, was 5 s. An additional time of 10 s, called maximum time out on the instrument, was set to enable the measurement to attain a steady-state shear rate at that level. Whether or not the instrument reached a steady state, it moved to the next shear stress level after that time out. Delay time and maximum time out setting was done at the discretion of the experimenter, based on information from preliminary test results which showed that within these time frames, the rheometer attain steady state.

The rheometer was first initialized by pressing the “up arrow” button, which lowered the measuring system of the rheometer. The “up arrow” button was pressed a second time, to lift the measuring system allowing the insertion of the testing geometry (vane) into the chuck of the measuring system. Then the test geometry (vane) was selected on the software. Approximately 10ml of Xanthan gum–straw suspensions were poured into the testing cup and the testing cup placed in the sample chamber. The vane shaft was fitted to the chuck of the measuring system and the rheometer zeroed, by pressing the zero button. Zeroing is done once for the entire testing period so long as the system is not shut down in-between tests and the testing geometry not changed. As soon as the test temperature stabilized (after approximately 300 s) the run was started by clicking the start button. At

each level of shear stress, the instrument calculated the steady state value of shear rate from the angular velocity of the shaft of the measuring geometry, and the instantaneous velocity from the ratio of shear stress to shear rate. At the end of each run, the test data (constant shear stress and shear rate, and instantaneous viscosity at each level) was copied and saved into an excel file and the sample discarded. A fresh sample solution was used for each run. All runs were done in triplicates.

Yield stress values for the straw suspensions were determined from extrapolating the shear stress-shear rate curve to zero shear rate and from Herschel Bulkley, Casson and Bingham model parameters.

To study the effect of measurement time on the yield stress of suspensions, the test above was repeated using delay times of 180 s and 270 s and maximum time out of 180 s and 270s.

### 3.3.1 Rheometer Calibration

About 1ml of the standard viscosity oil was pipetted into the 4° angle and 40 mm diameter cone and plate testing geometry (CP 4°/40), using a minimum shear stress of 0.3 Pa and a maximum shear stress of 30 Pa, the test was carried out on the rheometer in the controlled shear stress mode at a temperature of 25°C.

For Xanthan gum solution, a 4° angle and 40 mm diameter cone and plate testing geometry (CP 4°/40) was used for the experiment with approximately one millilitre Xanthan gum solutions of 0.1 wt% to 0.5 wt% concentration, in increments of 0.1 wt%.

### 3.3.2 Modeling

All model parameters were estimated using Polymath 6.0 version software, a user friendly numerical computation package. The data (shear stress versus shear rate), and Herschel Bulkley (Equation (2.1)), Casson (Equation (2.2)) and Bingham (Equation (2.3)) models were inserted in the program together with estimates of the parameters. These values were iterated until they converged.

# Chapter 4

## Results and Discussion

This work is divided into two parts: qualitative evaluation of making of straw suspensions that remain homogeneous long enough to measure their yield stress, and quantitative determination of the yield stress of straw suspensions.

### 4.1 Making Suspensions

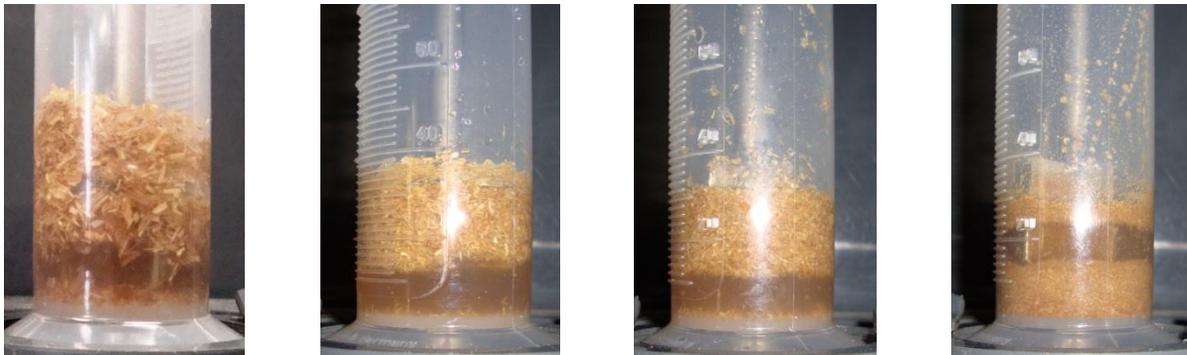
Several factors were considered in the attempt to produce homogenous straw suspensions, ranging from fiber size, suspension concentration and process conditions. However after preliminary test on the rheometer, it was discovered that the rheometer could not measure the rheological properties of some of these suspensions because the vane could not be lowered into them thus the work was restricted to suspensions made from fibers of mesh sizes 40, 60, and 100 and fiber concentration 5.0–7.5 wt% as a result of equipment limitation.

Dispersion of the fibers in water without mixing did not produce homogenous suspensions for fiber concentrations of 5, 10, 20 and 40 wt% tested. This is shown in Figure 4.1.



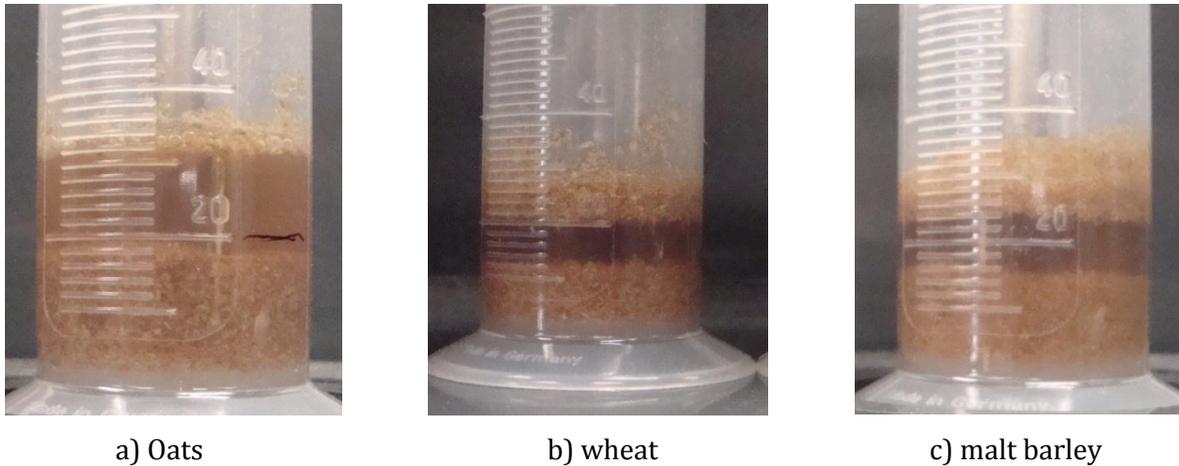
**Figure 4.1 Oats straw suspensions of mesh size 60 and concentrations of 5, 10, 20 and 40 wt % made by dispersion.**

Manual mixing was introduced afterward, but homogeneous suspensions were not obtained. Figure 4.2 shows straw suspensions made by dispersion and manual mixing.



**Figure 4.2 Oats straw suspensions of 5.0 wt% fiber concentration made from mesh size a) 12, b) 20, c) 40 and d) 60 by dispersion and manual mixing.**

Mechanical mixing was also introduced in the attempt to make homogenous suspensions. However, this was not achieved as can be seen in Figure 4.3. The suspensions were non-homogenous, most of the fibers in the suspension floated 5 minutes after mixing stopped. Floating of fiber could be partly due to density difference between the fibers and the dispersion medium and partly as a result of air trapped in the dispersion medium. For 7.5 wt% fiber concentration, similar results as shown in Table 4.1 were obtained. Table for same condition as shown in Table 4.1 with 7.5 wt% fiber concentration is shown in Table A1.



**Figure 4.3 Suspensions of a) Oats, b) wheat and c) malt barley straws produced by dispersion and mechanical mixing.**

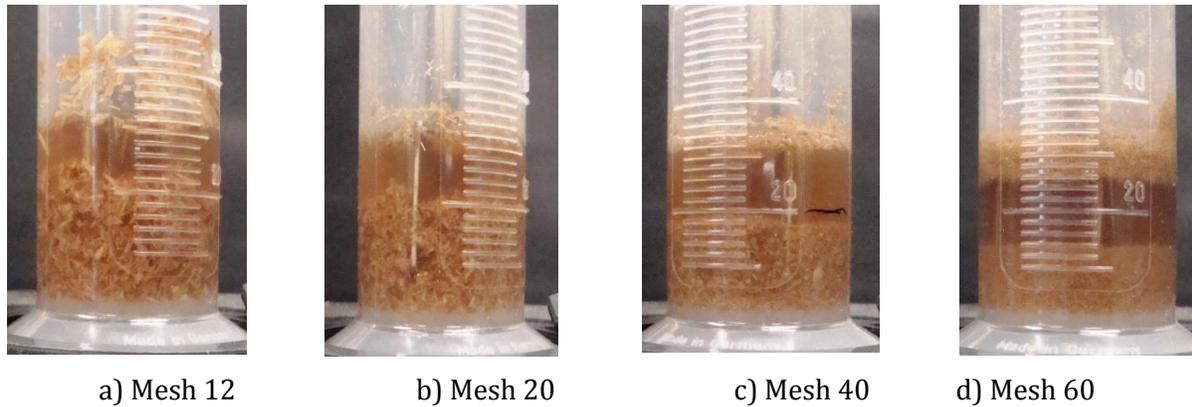
Table 4.1 shows the characteristics of Oats suspensions made by dispersion and mechanical mixing.

**Table 4.1 Characteristics of 5.0 wt% Oats straw suspension made by dispersion in water and mechanical mixing**

<b>Fiber mesh size (mm)</b>	<b>Mixing speed (rpm)</b>	<b>Height of floating fibers (cm)</b>	<b>Height of sediment (cm)</b>
12	163	2.0	Negligible
20	159	1.0	Negligible
40	151	0.4	Negligible
-40	140	0.3	1.0

De-aeration was introduced to eliminate air trapped in the water used as the dispersion medium, which was assumed to be partly responsible for the fibers floating in the water. Figure 4.4 show the characteristics of suspensions with 5.0 wt% fiber concentrations while Table 4.2 shows the characteristics of Oats straw suspensions of 5.0 wt% fiber concentration made by dispersion, mechanical mixing for 2 minutes and placed in the vacuum for 30 minutes. Suspensions of 6.25 and 7.5 wt% fiber concentrations were also

made and their characteristics did not differ from those of 5.0 w% fiber concentrations. This is shown in Table A2. They were non-homogenous with floating and sedimented fibers.



**Figure 4.4 Oats straw suspensions of 5.0 wt% fiber concentration made from mesh size a) 12, b) 20, c) 40 and d) 60 by dispersion, mechanical mixing and placed in the vacuum.**

**Table 4.2 Characteristics of 5.0 wt% Oats straw suspensions made by dispersion, mechanical mixing and de-aeration**

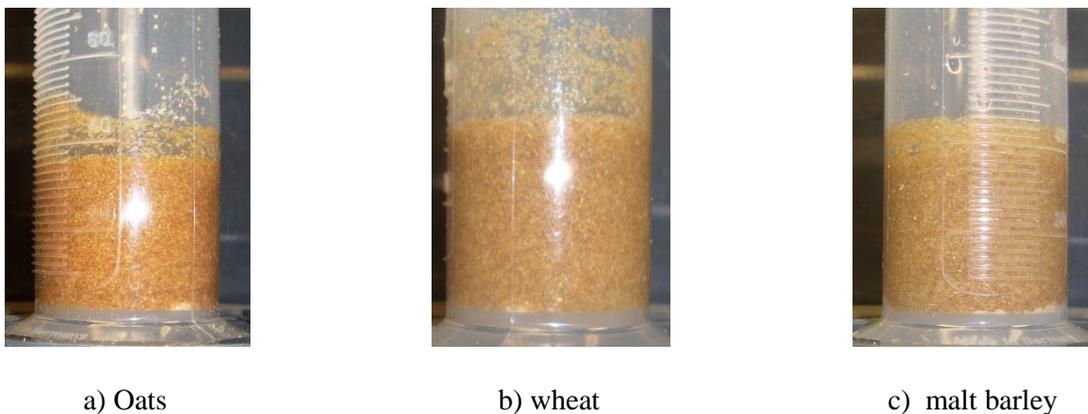
Fiber mesh size (mm)	Mixing speed (rpm)	Height of floating fibers (cm)	Height of sediment (cm)
12	163	Negligible	2.0
20	163	Negligible	1.9
40	164	0.1	1.5
-40	168	0.2	1.4

Acid pretreated fibers were also used in suspension preparation; the characteristics of suspension made from acid pretreated fibers did not differ from those of untreated fibers. Table 4.3 show characteristics of acid pretreated straw suspensions while the figure showing this condition is Figure A1.

**Table 4.3 Characteristics of Oats straw suspensions made from 5.0 wt% acid pretreated fibers concentrations**

Fiber mesh size (mm)	Preparation Condition	Height of floating fibers (cm)	Height of sediment (cm)	Mixing speed (rpm)
20	De-aerated	Negligible	0.5	176
40	De-aerated	Negligible	0.5	180
20	Non de-aerated	0.5	Negligible	174
40	Non de-aerated	0.7	Negligible	182

Because none of the conditions above produced homogenous suspensions, as in all cases, the less dense fibers floated while the denser ones sedimented, Xanthan gum from 0.1 – 0.5 wt% was introduced to enhance homogenous suspension formation, (Figure 4.5) making the yield stress measurement possible.



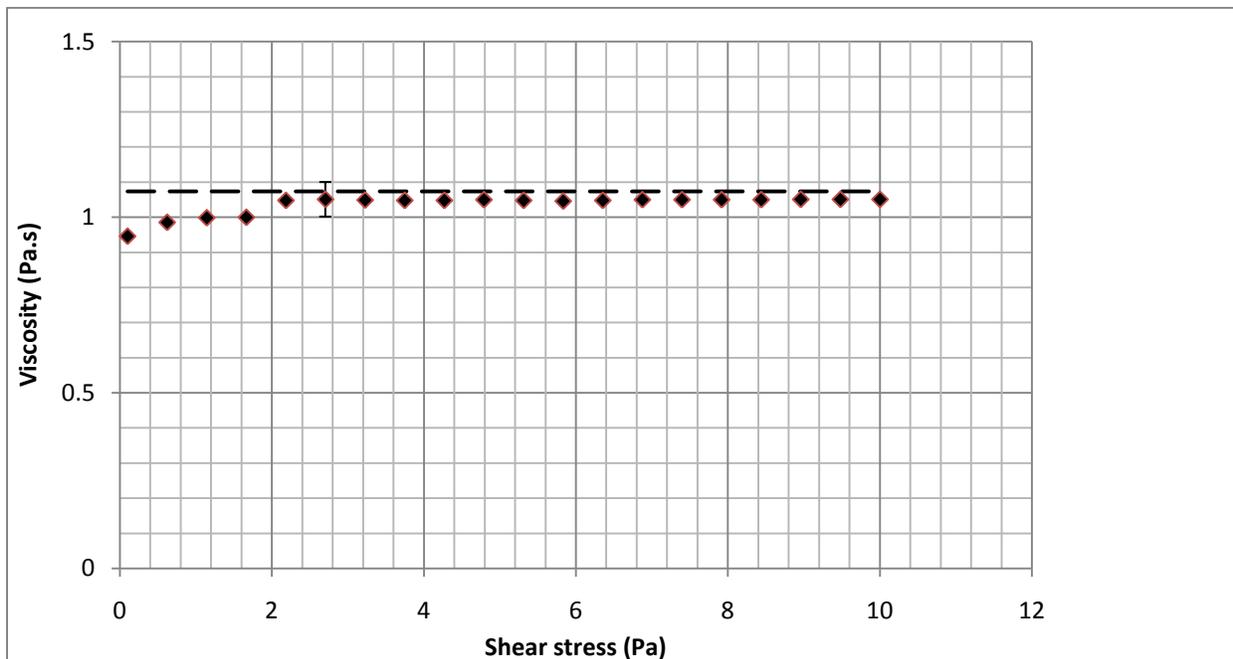
**Figure 4.5 Suspensions of a) Oats, b) wheat and c) malt barley straws produced by dispersion and mechanical mixing with the addition of Xanthan gum**

## 4.2 Measuring Yield Stress of Straw Suspensions

### 4.2.1 Calibration

The rheometer was first calibrated using standard viscosity oil with nominal viscosity of 1.074 Pa.s at 25°C, purchased from Malvern Instruments Ltd.

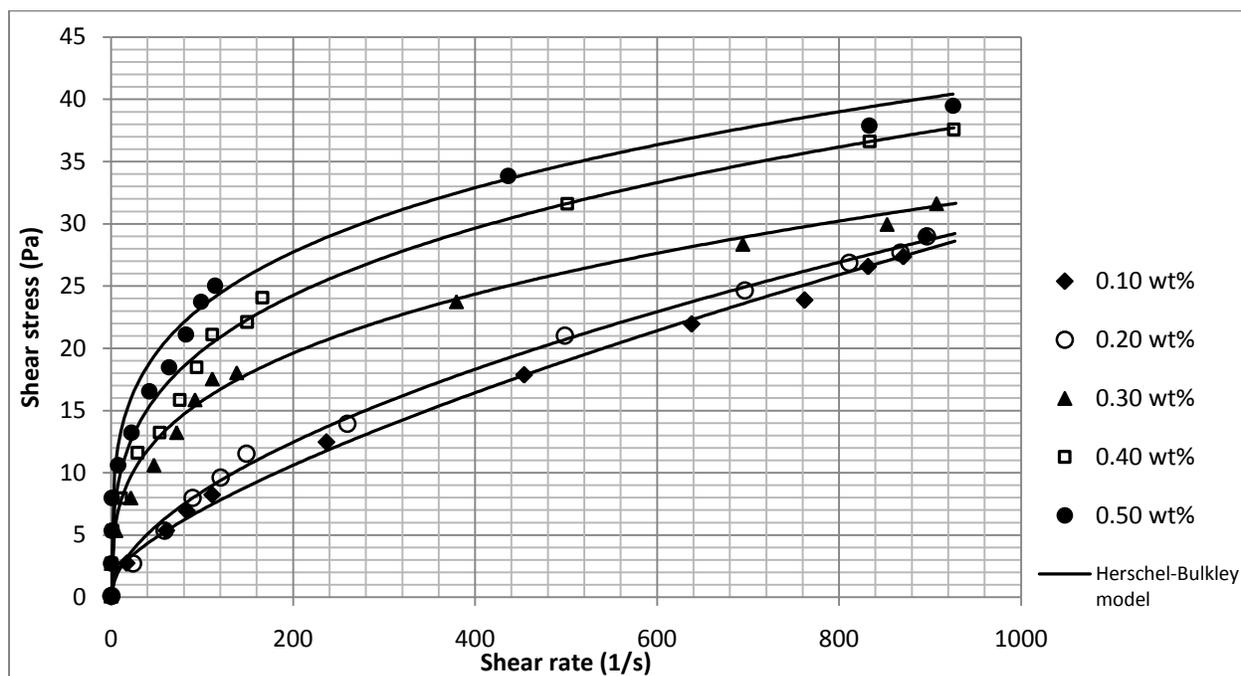
Figure 4.6 shows variable oil viscosity at shear stress less than 2 Pa. This could be a result of inertia which produces a time lag before equilibrium is attained in the moving part of the rheometer's measuring system. As soon as this effect wore off; the viscosity became Newtonian, and remained constant with increasing stress across two decades of applied stress. An average viscosity of 1.036 Pa.s was recorded for this test. This value falls within the  $\pm 5\%$  range of viscosities for the test oil specified for the Bohlin rheometer (Bohlin Instruments, 1996). Thus the rheometer performance was judged to be within the manufacturer's specification.



**Figure 4.6 Calibration curve of standard viscosity oil, with 4°/40mm diameter cone and plate instrument. Min. stress = 0.10 Pa, max. stress = 10 Pa at 25 °C.**

#### 4.2.2 Rheological Characterization of Xanthan gum Solution

Xanthan gum solutions of concentrations 0.10-0.50 wt% were rheologically characterized. Figure 4.7 shows the viscometric curves (representation of the shear stress as a function of shear rate) for aqueous solutions of 0.10-0.50 wt% Xanthan gum.



**Figure 4.7 Rheogram for 0.10% - 0.50 wt% concentration Xanthan gum solution, with 40/40 mm diameter cone and plate instrument. Min. stress = 0.1 Pa, max. stress = 50 Pa at 25 °C.**

For 0.30 wt% Xanthan gum solution, the data points follow a vertical at zero shear rate, up till a shear stress of about 7 Pa and starts to curve at shear rates greater than zero (approximately  $10 \text{ s}^{-1}$ ), which seem to be indicative of the presence of a yield stress. Solutions of 0.40 and 0.50 wt% Xanthan gum both displayed similar behaviour with their data points starting to curve out at about 8 Pa thus their yield stresses will be around 8 Pa. For 0.10-0.20 wt% solutions, there did not seem to be a stress required to be overcome to initiate movement. These observations agree with the work of Garcia-Ochoa and Casas (1994), who investigated the steady shear flow properties of aqueous solutions of Xanthan gum over a of shear rate range of  $0\text{-}100 \text{ s}^{-1}$  and concentrations of 1-2 wt% and reported a yield stress range of 0.2-0.8 Pa. Their results also show that sufficiently dilute Xanthan gum

solutions show a region of Newtonian viscosity at low shear rates and more concentrated solutions appear to exhibit yield stress.

The higher yields stress values exhibited by Xanthan gum solutions of 0.30 wt% -0.50 wt% may have come from the large number of hydrogen bonds in the structure of Xanthan gum compound responsible for the stability of the compound and its resistance to flow (Song *et al.*, 2006). The group of Song (2006) also suggested that increase in yield stress may also arise from intermolecular association due to acetate residue. Marcotte *et al.* (2001) and Ramaswamy and Ahmed (2004) also reported a high effect of concentration on the yield stress of Xanthan gum solutions.

Herschel-Bulkley (HB), Casson (Cs) and Bingham (Bh) models were used to fit experimental data. These are all flow models with yield stresses and were employed to make quantitative evaluation of the flow behaviour of the suspensions. These three models all have applicability and ability to describe the shear flow behaviour of Xanthan gum solutions. However Herschel-Bulkley gave the best average regression coefficient ( $R^2$ ) of 0.9965 for 0.10 -0.50 wt% concentrations (Table B1), hence analysis of experimental results was based on Herschel-Bulkley model (Table 4.4).

The curve passing through the data points (Figure 4.7) is the Herschel-Bulkley model obtained from Equation (2.1), used to determine model parameters ( $k$ ,  $n$  and  $\tau_0$ ). Experimental and model data agree reasonably well.

**Table 4.4 Rheological model parameters of Xanthan gum solution for shear stress range of 0.1 – 50 Pa obtained from Herschel- Bulkley model**

[Xanthan gum] (%)	Consistency index, $k$ (Pas <sup><math>n</math></sup> )	Flow behaviour index, $n$	Yield stress, $\tau_0$ (Pa)	Regression coefficient $R^2$ (-)
0.1	0.02	0.8	0.5	0.9944
0.2	0.5	0.7	0.7	0.9959
0.3	0.5	0.5	0.8	0.9921
0.4	0.8	0.5	1.2	0.9912
0.5	1.2	0.4	1.3	0.9969

The yield stress ( $\tau_0$ ) and consistency index ( $k$ ) both increased with increasing Xanthan gum concentration, which is a typical characteristic of yield stress fluids (Garcia-Ochoa and Casas, 1994). The group of Pakzad also found an increasing yield stress of 1.789-7.4 Pa and consistency of 3-14 Pa.s<sup>n</sup> with increase in Xanthan gum concentration of 0.5-1.5 wt% in their work with yield stress fluids (Table 4.5). However, the flow index ( $n$ ) decreased with increasing Xanthan gum concentration indicating a progressive increase in the shear-thinning behaviour of Xanthan gum solution. As  $n$  tends to 1, the shear-thinning nature of Xanthan gum becomes less pronounced and Newtonian behaviour is achieved at 1.

**Table 4.5 Rheological Properties of Xanthan Gum (Pakzad et al., 2008)**

[Xanthan gum] (%)	Consistency index, $k$ (Pa.s <sup>n</sup> )	Flow behaviour index, $n$	Yield stress, $\tau_0$ (Pa)
0.5	3	0.11	1.789
1.0	8	0.12	5.254
1.5	14	0.14	7.455

Rheological model parameters of Xanthan gum solutions obtained using Casson and Bingham models are shown in Table B1. Both models also showed an increasing yield stress of 0.98-2.22 Pa for increasing Xanthan gum concentrations of 0.10-0.50 wt% but with lower R<sup>2</sup> values.

The effect of change in shear stress value on the rheological behaviour of Xanthan gum solutions tested with the same solution conditions of Table 4. 4 and a lower stress range of 0.01 – 10 Pa, is shown in Table 4.6. Since yield stress is defined as the stress needed to initiate movement, it should be measured at very low shear stress. The measurement was done in triplicates, so as to obtain the confidence interval for the yield stress that can be compared with result from the previous test. (Table 4.6)

**Table 4.6 Yield stress of triplicate Xanthan gum solutions for shear stress range of 0.01 – 10 Pa obtained from Herschel- Bulkley model**

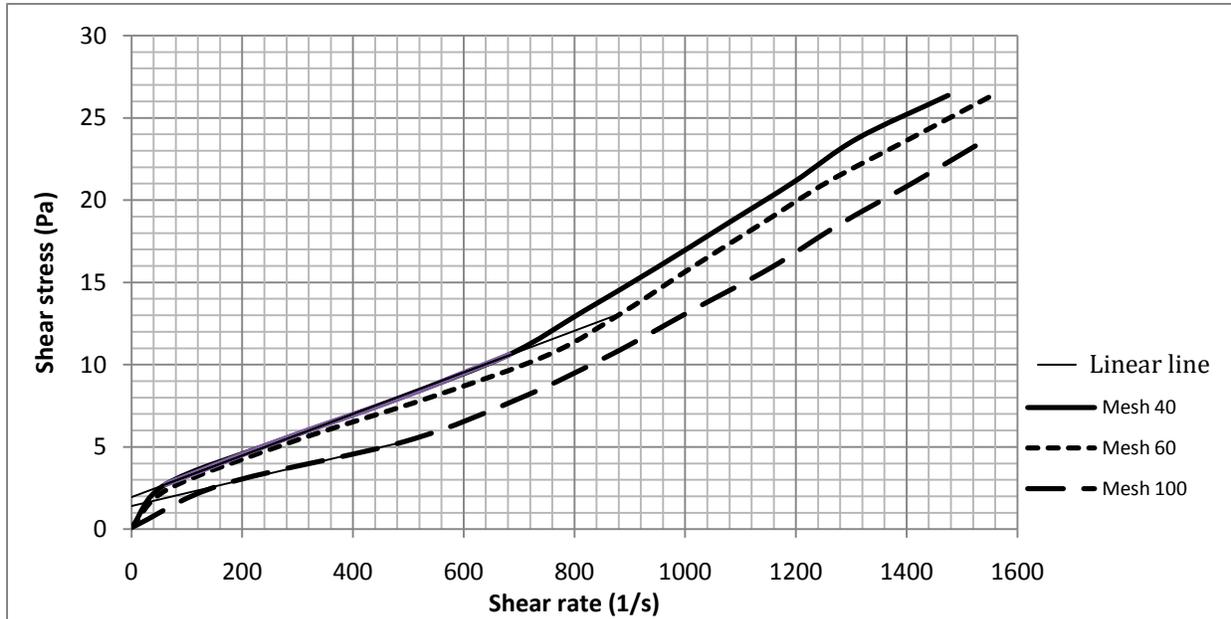
[Xanthan gum] (%)	Yield stress (Pa)				Yield stress $\pm$ Confidence interval (Pa)
	$\tau_{o1}$	$\tau_{o2}$	$\tau_{o3}$	$\tau_{oav}$	
0.1	0.40	0.44	0.42	0.42	0.40 $\pm$ 0.09
0.2	0.60	0.64	0.66	0.63	0.60 $\pm$ 0.16
0.3	0.75	0.76	0.77	0.77	0.75 $\pm$ 0.10
0.4	1.20	1.10	1.10	1.33	1.20 $\pm$ 0.28
0.5	1.34	1.30	1.37	1.33	1.34 $\pm$ 0.13

Using 95% probability (95% probability calculation is shown in Table B2), the yield stress of triplicate Xanthan gum solutions at each strength was found to be independent of the maximum value of shear stress during the two controlled shear stress runs (0.1-50 Pa; 0.01-10 Pa). All subsequent measurements were done at 0.10 -50 Pa.

Variation of yield stress with Xanthan gum concentration measured in the controlled stress mode at a min. stress of 0.01 Pa and a max stress of 10 Pa, with error bars indicating reproducibility of experimental data is shown in Figure B2.

#### 4.2.3 Rheological Measurements of Straw Suspensions

Since the rheometer can be used in a controlled shear stress or a controlled shear rate modes to determine the yield stress, these two modes of operation were assessed. Figure 4.8 is an example of the behaviour of 5.0 wt% Oats straw fibers of mesh size 40, 60, and 100 suspended in 0.1 wt% Xanthan gum solution with a controlled shear stress mode.



**Figure 4.8 Viscometry curves (controlled shear stress) for 5.0 wt% Oats straw suspension with 0.1 wt% Xanthan gum for fiber of mesh sizes 40, 60 and 100 obtained using the vane and cup measuring instrument. Min. stress = 0.1Pa, max. stress = 50 Pa at 25°C.**

In the absence of vertical data points, another way of trying to determine yield stress is extrapolation of the linear portion of the shear stress-shear rate data to zero shear rate. For Oats straw suspension made from fibers of mesh 40 yielding can be said to occur at the point where the shape of the curve just changes tending towards linearity. This is read on the graph as approximately 2 Pa. Oats straw suspensions made from fibers of mesh 60 and 100 also follow similar trend, therefore the yield stress of suspensions of mesh 60 is also approximately 2 Pa. This may be because of the closeness in the sizes of fiber from mesh 40 and 60 bearing in mind that the mesh gives a size distribution. Also the consistency index value ( $k$ ) from the Herschel Bulkley model for suspensions made from fibers of mesh 40 and 60 are approximately equal. However, it doesn't seem that suspension from mesh 100 needs to overcome any stress to flow from visually observing the flow curve, but extrapolation of the curve to zero shear rate gave a yield stress of 1.3 Pa. Extrapolation lines for suspensions of mesh 40 and mesh 60 overlapped was not shown on Figure 4.8. Evaluation of the yield stresses using Herschel-Bulkley, Casson and Bingham models produced yield stress values ranging from 0.41Pa - 4.48 Pa (Table 4.7).

**Table 4.7 Rheological model parameters for 5.0 wt% Oats straw suspensions with 0.10 wt% Xanthan gum**

Mesh size	Parameter	Herschel-Bulkley	Bingham	Casson	Extrapolation
40	$\tau_0$	0.96	4.48	4.38	2.0
	k	0.1	0.12	0.11	-
	n	1.2	-	-	-
	R <sup>2</sup>	0.9941	0.9798	0.9798	-
60	$\tau_0$	0.84	3.84	3.84	2.0
	k	0.05	0.42	0.11	-
	n	1.2	-	-	-
	R <sup>2</sup>	0.9937	0.9874	0.9874	-
100	$\tau_0$	0.41	2.05	2.05	1.3
	k	0.001	0.02	0.13	-
	n	1.3	-	-	-
	R <sup>2</sup>	0.9982	0.9563	0.9563	-

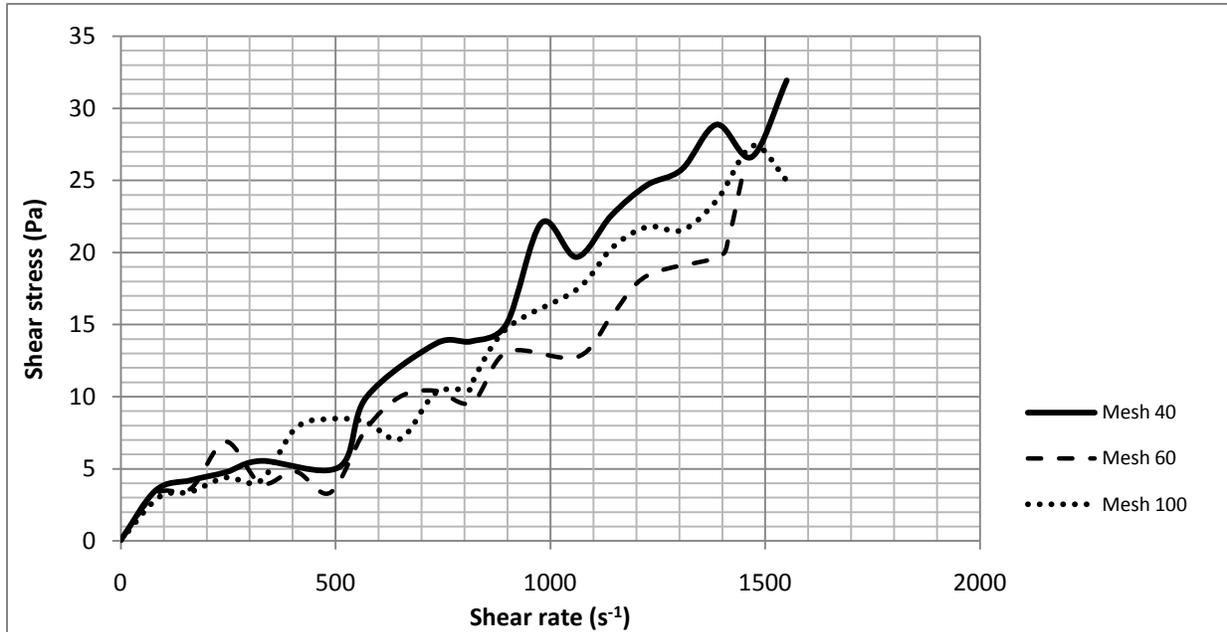
From Table 4.7, we noticed a reducing suspension consistency from 0.1–0.001 Pa.s<sup>n</sup> in mesh 40–100 and a corresponding reduction in yield stress, for the three mesh sizes. The reduction in consistency may be attributed to the near absence of fiber entanglement in water, common with smaller fibers, resulting in weaker suspension structure, this can also lead to decrease in yield stress. This finding agrees with the result of the group of Viamajala (2009) who reported lower yield stress values for corn stover slurry containing smaller particles than those containing larger particles at the same solid concentration. However, flow behaviour index ( $n$ ) was the same for suspensions from mesh 40 and 60 (1.2) and increased for mesh 100 (1.3) this shear-thickening behaviour is unexpected as a number of researchers have reported a shear-thinning behaviour for pretreated corn stover suspensions and slurries Knutsen and Liberator, (2009) and moreso because the Xanthan gum solutions from which the straw suspensions were made is shear-thinning. It

is unclear whether the interaction between Xanthan gum solution and the fibers is responsible for this shear-thickening effect. However, the group of Viamajala (2009) suggested that corn stover slurries might exhibit shear-thickening behaviour at high shear rates, but this high shear rate value was not reported. Also from Table 4.7, we observed that yield stress values obtained from Bingham and Casson models are approximately equal, while those from Herschel Bulkley models were significantly lower, this is due to the power relationship between shear stress and shear rate in the Herschel Bulkley model because the flow behaviour index  $n > 1$ , shear stress value increases faster in Herschel Bulkley model than in Bingham and Casson models where shear stress varies linearly with shear rate. For extrapolated yield stress values, differ from model values most likely because extrapolation value is dependent on the sensitivity of the measuring instrument.

Other 5.0 wt% Oats straw suspensions at various Xanthan gum strengths showed similar behaviour to 5.0 wt% suspension with 0.1 wt% Xanthan gum (Figures B2-B5).

Table 4.8 shows the comparison of rheological model parameters obtained from Herschel-Bulkley, Casson and Bingham models for 5.0 and 7.5 wt% concentration Oats straw suspensions with 0.10 wt% Xanthan gum.

Figure 4.9 shows a plot of shear stress vs. shear rate obtained from a controlled shear rate experiment for 5.0 wt% Oat straw suspensions with fibers from mesh 40, 60 and 100. As can be seen from the figure, controlled shear rate mode produced “noisy data”.



**Figure 4.9** Viscometry curves (controlled shear rate) for 5.0 wt% Oats straw suspension with 0.1 wt% Xanthan gum for fiber of mesh sizes 40, 60 and 100 obtained using the vane and cup measuring instrument. Min. stress = 0.1Pa, max. stress = 50 Pa at 25°C.

This behaviour is hard to explain as both the controlled shear stress and shear rate modes were expected to produce similar results. This pattern repeated in all straw suspensions regardless of concentration and fiber size. Since noisy data were difficult to interpret and may lead to error in results, therefore the controlled shear stress mode was used for the remainder of the experiments. Flow curves for 5.0 wt% concentration Oats straw suspensions with varying Xanthan gum strengths obtained from viscometry measurement in the controlled rate mode are shown in Figures B6-B9.

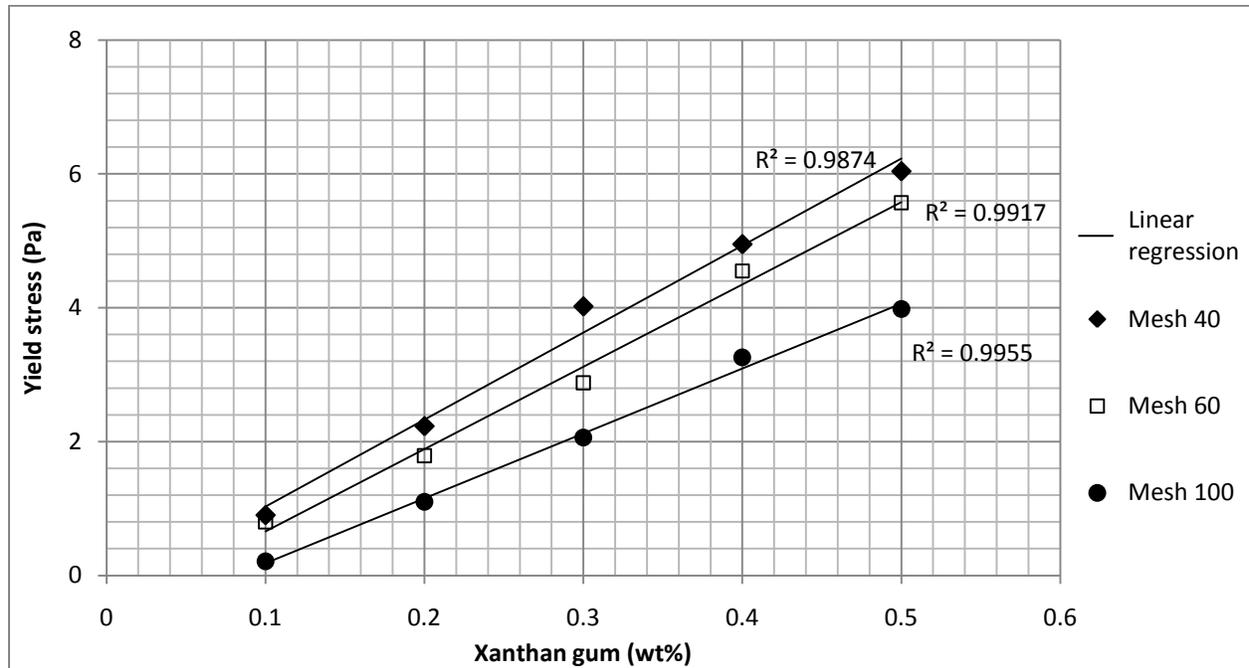
**Table 4.8 Yield stress of 5.0 and 7.5 wt% concentration Oats straw suspension containing 0.1 wt% Xanthan gum**

Straw Concentration (wt %)	Mesh Size (mm)	Yield stress (Pa)			
		Extrapolation	HB	Bh	Cs
5.0	40	2	0.96	4.8	4.38
	60	2	0.84	3.84	3.84
	100	1.3	0.41	2.05	2.05
7.5	40	20	4.38	12.90	12.93
	60	10	3.94	2.20	2.25
	100	4	2.64	1.58	1.62

Data from Table 4.8 shows that, Oats straw suspensions of 7.5 wt% concentrations and mesh sizes 40, 60 and also followed similar pattern as 5 wt% concentration, decreasing yield stress value with increasing mesh size. Casson and Bingham models produced higher yield stress values which are nearly identical, and larger in comparison to those of Herschel-Bulkley models. However, Herschel-Bulkley model seems to give the most accurate yield stress value based on  $R^2$  values (Table 4.7). Moreover extrapolated yield stress values are often less accurate than actual yield stress values as they are dependent on the sensitivity of the measuring instrument. Rheological model parameters for 7.5 wt% fiber concentration and 0.1-0.5 wt% Xanthan gum concentrations are shown in Table B6.

#### 4.2.4 Effect of Fiber Size and Concentration on Yield Stress of Oats Straw Suspension

The effect of fiber size on the yield stress of Oats straw suspensions is shown in Figure 4.10.



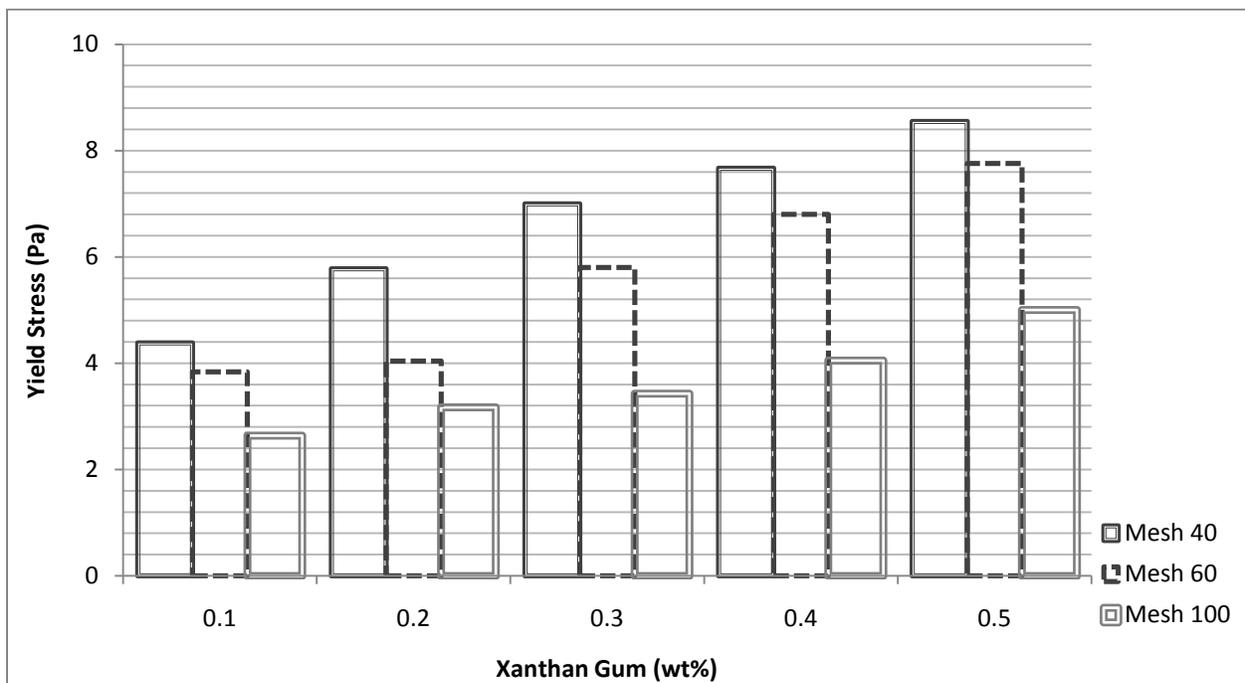
**Figure 4.10 Effect of fiber size on yield stress of 5.0 wt% concentration oats straw suspension**

This figure clearly show that higher yield stress values (0.1-0.8 Pa) are obtained from suspensions made from larger fiber sizes (Mesh 100 - mesh 40) for 5.0 wt% Oats straw suspension and 0.10 wt% Xanthan gum, the same increasing yield stress (2.64-4.38 Pa) with increase in fiber sizes was also obtained for oats straw suspensions made with 7.5 wt% fiber concentration (Figure 4.11). This may be as a consequence of increased strength of the chain structure formed by larger fibers in water. Results from Herschel-Bulkley, Casson and Bingham models and extrapolation are all agreement (Figure B6 and B7), showing increasing yield stress (1.2-4.2 Pa) as fiber sizes increase from mesh 100 – mesh 40. This observation is in agreement with the results of Bashir, (2008) who studied the yield stress of concentrated wheat straw suspensions and reported that yield stress of concentrated wheat straw suspensions increased from 2.3-3 Pa as fiber size increased from 0.42-2.38mm, even though he employed the ramp test method. Dalpke and Kerekees

(2005), Bennington et al. (1990) and Wikstrom and Rasmuson (1998) all reported similar trend of increasing yield stress with fiber length in fiber suspensions.

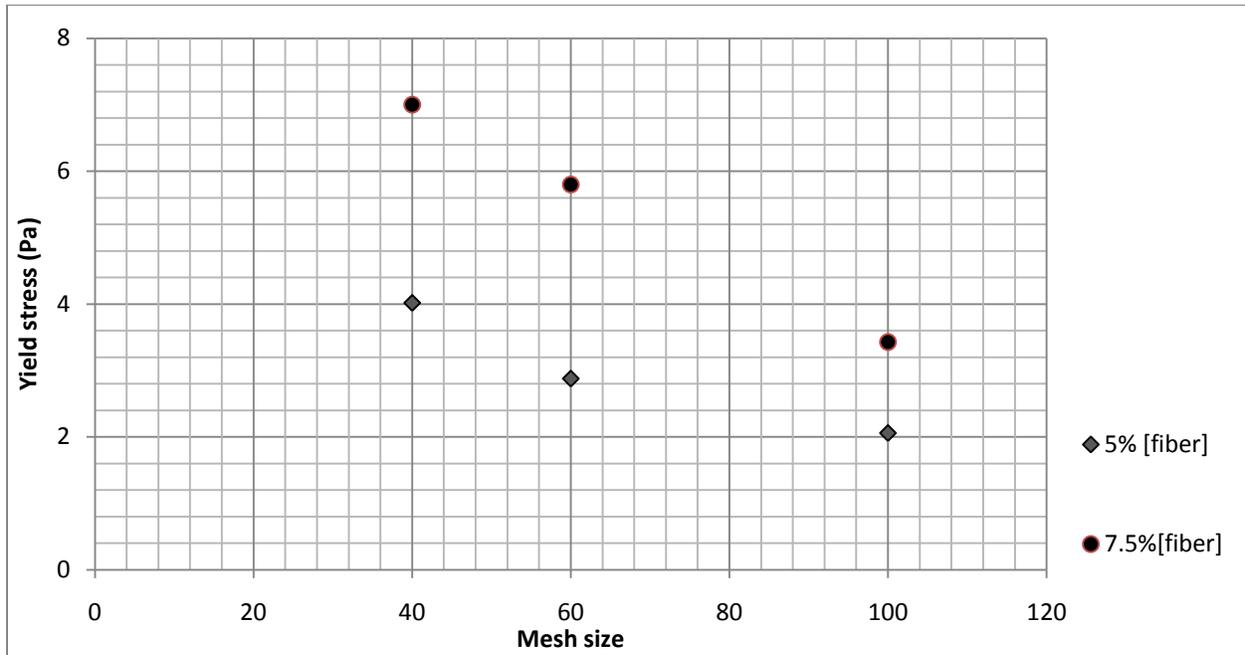
Also from Figure 4.10, we observed a linear correlation between yield stress and Oats straw suspensions made from fibers of mesh 40 – mesh 100 containing Xanthan gum concentration of 0.1 wt% - 0.5 wt% with  $R^2$  ranging from 0.9874 – 0.9955. All though the relationship between yield stress and Xanthan gum concentration without Oats straw is not linear (Table 4.4), this difference in behaviour may be due to fiber interaction with Xanthan gum solution.

Yield stress also evidently increased with increase in fiber concentration, Figure 4.11.



**Figure 4.11 Effect of fiber size on yield stress of 7.5 wt% concentration Oats straw suspension**

Yield stresses obtained from suspensions of 7.5wt% concentration were higher in the three mesh sizes evaluated when compared to those obtained from suspension of 5.0 wt% concentration of same mesh sizes (Figure 4.12).



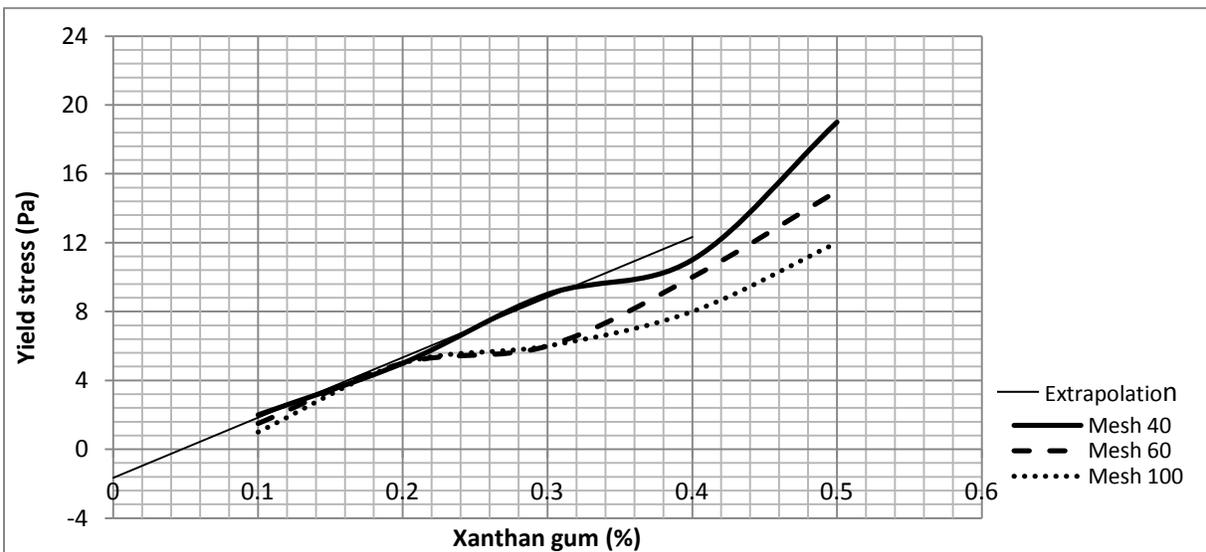
**Figure 4.12 Effect of fiber concentration on yield stress of Oats straw suspensions**

This increase in yield stress with increase in concentration may be attributed to stronger suspension structure which requires higher stress to initiate flow resulting in higher yield stress values. The trend is the same for all the suspensions with different Xanthan gum strengths tested and agrees with the work done by Pimenova and Hanley (2004), who used a helical impeller to study the rheological properties of corn stover suspension (a lignocellulose suspension) and obtained yield stress ranging from 0.152-22.9 Pa for corn stover suspensions of concentration range of 5.0-17.0 wt%. Knutsen and Liberator (2009) also reported the same concentration dependency of yield stress in their work on rheology of high-solids slurry for biorefinery applications. The slurries were made from pretreated corn stover without Xanthan gum. However, the sensitivity of yield stress to concentration is also not specific to lignocellulose suspension alone as it has also been shown for fermentation broths by Allen and Robinson (1990). While Bennington et al. (1990) and Alderman et al. (1991) presented similar results for paper pulp and bentonite gels.

Results from Herschel-Bulkley, Casson and Bingham models and extrapolation all show reasonable agreement of increasing yield stress with increase in fiber concentration. In all cases, yield stress values from Casson and Bingham models were higher than those obtained from Herschel-Bulkley model. However, extrapolated yield stress values were the largest (Table B7).

#### 4.2.5 Extrapolation of Results obtained from Oats Straw Suspensions with 0.1-0.5 wt% Xanthan gum to 0.0 wt% Xanthan gum suspensions.

Figure 4.13 is a plot of yield stress vs. Xanthan gum concentration for 5.0 wt% concentration Oats straw suspensions (mesh sizes 40, 60 and 100) with Xanthan gum concentration of 0.10 - 0.50 wt%.



**Figure 4.13 Extrapolation of results obtained from 5.0 wt% concentration Oats straw suspensions with 0.1-0.5 wt% Xanthan gum to 0.0 wt% Xanthan gum suspension.**

The linear portion of each curve was extrapolated to 0.0 wt% Xanthan gum to obtain the yield stress of Oats straw suspension without Xanthan gum. Results obtained shows that extrapolation is inadequate for predicting yield stresses of suspensions with low fiber concentration ( $\leq 5.0$  wt%) and small fiber sizes ( $\leq 149$   $\mu\text{m}$ , mesh 100) as these results were negative values (Figure 4.13). This may be due to the low consistency of these suspensions; therefore their yield stresses could not be dictated. But for suspension of 7.5 wt% fiber concentration, 18 Pa was obtained for mesh 40; 3.8 Pa for mesh 60, while mesh 100 could

not be evaluated as the suspension is also has low consistency. Figure B13 shows extrapolation to 0.0 wt% Xanthan gum concentrations for suspension of 7.5 wt% fiber concentration while Table B8 shows the extrapolation data.

In this study, 5.0 wt% Oats straw suspensions was the basis of evaluations so far, while at 0.3 wt% Xanthan gum concentration, the rheological flow behaviour of this suspension became very evident. Therefore this condition was used as a reference for assessing the flow behaviour of other straw suspensions.

#### 4.2.6 Wheat and Malt barley Straw Suspensions

Wheat and malt barley straw suspensions of 5.0 wt% fiber concentrations and 0.3 wt% Xanthan gum concentrations were also evaluated at same suspension and test conditions as the Oats straw suspension. Table 4.9 shows the rheological model parameter for Oats, wheat and malt barley straw suspensions.

**Table 4.9 Rheological model parameters of Oats, wheat and malt barley straw suspensions of 5 wt% concentration and 0.3 wt% Xanthan gum**

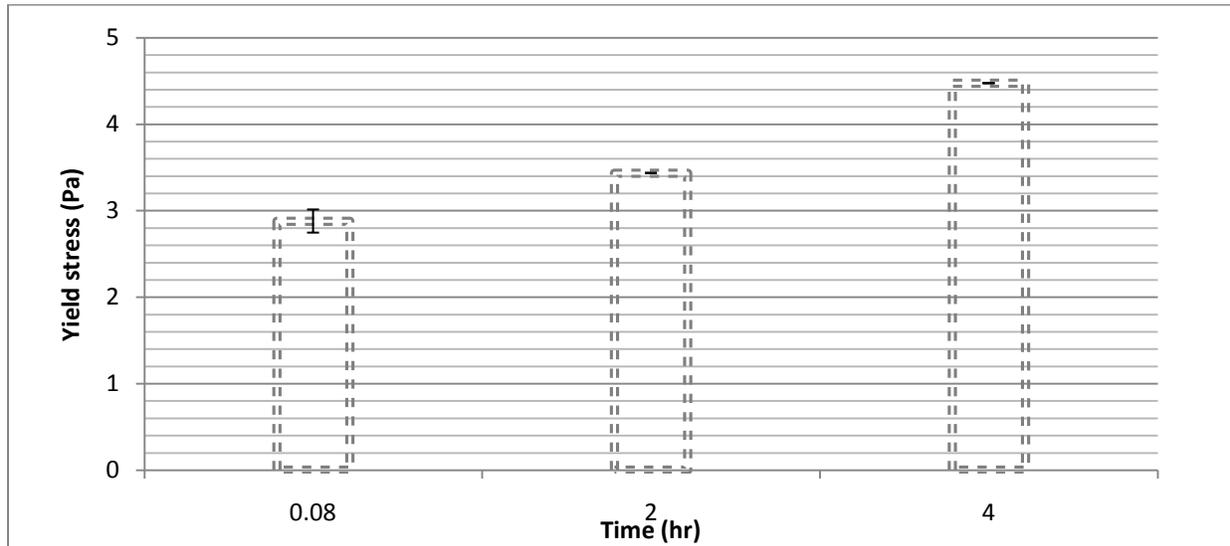
Model	Mesh size	Suspension type	$\tau_0$ (Pa)	k (Pas <sup>n</sup> )	n (-)	$\tau_0$ range at 95% Probability
Herschel-Bulkley	40	Oats straw	4.1	0.05	0.90	4.10±0.26
		Wheat straw	4.2	0.03	0.82	
		Malt barley straw	4.04	0.3	1.04	
	60	Oats straw	3.08	0.03	0.96	3.08±0.64
		Wheat straw	3.28	0.05	1.20	
		Malt barley straw	3.33	0.2	0.95	
	100	Oats straw	3.04	0.01	1.10	3.04±0.44
		Wheat straw	2.5	0.005	1.20	
		Malt barley straw	2.82	0.04	1.20	

Casson	40	Oats straw	4.79	0.14		4.79±0.10
		Wheat straw	4.75	0.17		
		Malt barley straw	4.70	0.16		
	60	Oats straw	3.11	0.12		3.11±0.30
		Wheat straw	3.15	0.20		
		Malt barley straw	3.25	0.14		
	100	Oats straw	2.63	0.10		2.63±0.14
		Wheat straw	2.68	0.10		
		Malt barley straw	2.31	0.12		

Wheat and malt barley suspensions seem to exhibit similar behaviour as Oats straw suspension. All three suspensions yield stress values are statistically the same based on 95% probability for both Herschel Bulkley and Casson models. They also exhibited decreasing consistency ( $k$ ) with fiber size with the exception of wheat straw whose  $k$  fluctuated for mesh 40 and 60 which may be attributed to the size distribution of the fibers in both suspensions. Oats and wheat straw suspensions from mesh 40 both showed shear-thinning behaviour, while suspension from malt barley showed a Newtonian behaviour. For mesh 60, Oats and malt barley suspensions also showed shear-thinning behaviour while the behaviour of wheat straw suspension was shear-thickening. For mesh 100, all three straw suspensions showed thickening behaviour which is strange and difficult to explain. The similarities in the behaviour of these straw suspensions could be attributed to their similar chemical composition, as they are all composed of cellulose, hemicellulose and lignin. Statistical analysis for Table 4.9 is shown in Table B10.

#### 4.2.7 Effect of Measurement Time on Yield Stress of Oats Straw Suspension

So far in this study, the test time has been 300 s. To investigate the effect of measurement time on the behaviour of Oats straw suspension, 5.0 wt% Oats straw suspension with 0.3 wt% Xanthan gum was tested for extended times of two and four hours.

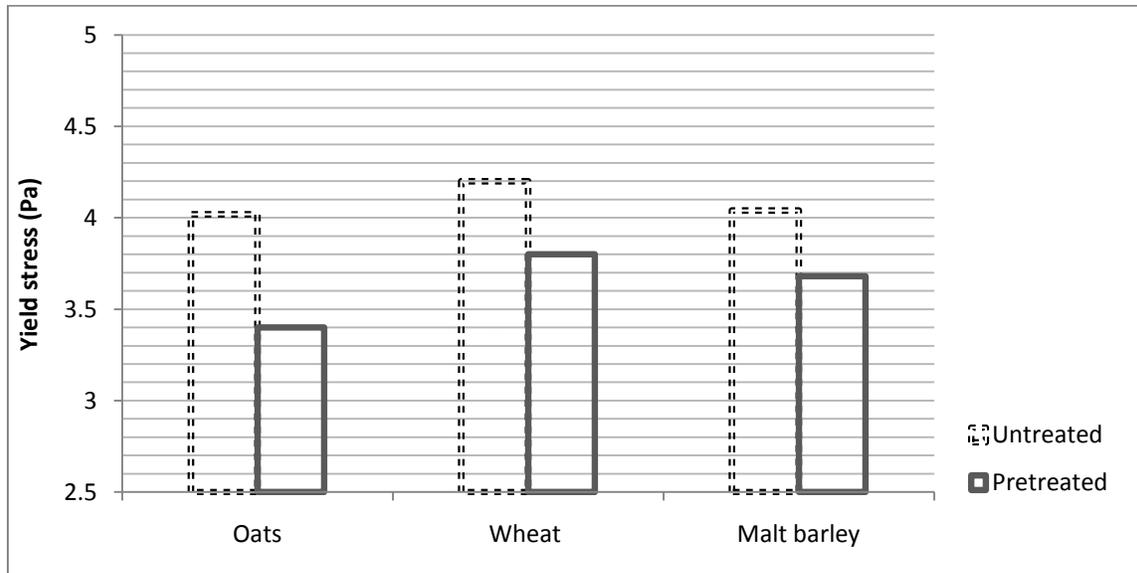


**Figure 4.14 Effect of measurement time on the yield stress of 5.0 wt% concentration Oats straw suspension (mesh 60) with 0.3 wt% Xanthan gum.**

As its evidence from Figure 4.14, yield stress increased with time, this may be because, the fibers absorb water with time into their hydrophilic polymer matrix and water entrained within the micro-pores in the cell wall or macro-pores within the plant tissues can increase their internal and external surface area which invariably leads to increase in their sizes and as we have observed from previous results, yield stress increase with increase in fiber size. Time dependency of straw suspensions has not been a point of interest in most work done on straw suspensions as it has hardly being referred to in most studies.

#### 4.2.8 Yield Stress of Pretreated Oats Straw Suspension

Test straws were acid pretreated to study the effect of pretreatment on the yield stress of suspensions made with pretreated straws. Figure 4.15 shows the chart of yield stress of pretreated and untreated straw suspensions.



**Figure 4.15 Yield stresses of pretreated and untreated straw suspensions of 5.0 wt% concentration (mesh 60) and 0.3 wt% Xanthan gum concentration for Oats, wheat and malt barley straws.**

As can be seen from the chart, pretreatment decreases yield stress in all three straw suspensions, the effect being most evident in Oats straw suspension. The reduction in yield stress seen after pretreatment maybe due to disruption in lignin structure, which reduces the binding effect of lignin on the straws. Also acid pretreatment greatly reduces hemicellulose content and removes water soluble sugars thereby weakening the straw considerably. Hence suspensions made from pretreated straws will most likely possess lower yield stresses. This results agrees with the work of the group Viamajala et al (2009), who studied the rheology of untreated and dilute acid pretreated corn stover suspensions made from fibers of mesh -20 and -80, and obtained lower yield stresses for suspensions made from pretreated fibers.



# Chapter 5

## Conclusion and Recommendations

### 5.1 Conclusion

In this work, the characteristics of straw suspensions made from Oats, wheat and malt barley straws of fiber sizes 0.15mm-4.20mm and concentrations 5.0-10.0wt% using different preparation techniques were studied. The effect of Xanthan gum added to these suspensions to enhance suspension homogeneity was also investigated. The Bohlin rheometer was used to evaluate the rheological properties of these straw suspensions, while in addition to direct measurements and extrapolation, Herschel-Bulkley, Casson and Bingham models were employed in analyzing experimental results. From the analysis of the results obtained, it can be concluded that

- Sedimentation prevents uniform straw suspension formulation, thereby impeding rheological measurements of pretreated and untreated cereal straw suspensions.
- Addition of Xanthan gum to the dispersion medium resulted in cereal straw suspensions that remained homogenous long enough for their rheological behavior to be determined.
- Cereal straw suspensions analyzed contained varying magnitude of yield stress based on the suspension properties.
- For all straw types and suspension concentrations analyzed, yield stress exhibited a high concentration and fiber size dependence.

- Herschel-Bulkley model most accurately predicted the rheological behavior of all suspensions analyzed when compared with Casson and Bingham models based on the  $R^2$  values obtained from modeling experimental data.

## 5.2 Recommendations

In the future, it is recommended that

- Straw suspensions made from larger fiber sizes  $>420 \mu\text{m}$  and higher fiber concentration be studied because the value of yield stress obtained from suspensions of fiber sizes  $<420 \mu\text{m}$  is relatively small and may not result in significant changes to the mixing behavior of straw suspensions during enzymatic hydrolysis.
- Rheological behaviour in terms of shear thinning or thickening of untreated cereal straw suspensions be re-examined, because even though a number of researchers has reported a shear thinning behaviour for pretreated corn stover suspension, the behaviour of untreated Oats, wheat and malt barley straw suspensions obtained from this study varied from their result.
- The effect of measurement time on the yield stress of untreated straw suspensions be reinvestigated for validation.
- Rheological behaviour of pretreated Oats, wheat and malt barley straws should also be studied.

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# Appendix A

## Suspension Preparation

**Table A1 Characteristics of 7.5 wt% concentration Oats straw suspensions made by dispersion and mechanical mixing**

Mesh size (mm)	Height of floating fiber (cm)	Height of sediment (cm)	Mixing speed (rpm)
12	2.5	Negligible	155
20	2.3	0.2	163
40	2.3	0.2	163
-40	Indeterminate	Indeterminate	167



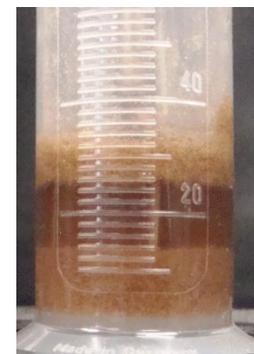
a) Mesh size 12



b) Mesh size 20



c) Mesh size 40



d) Mesh size 60

**Figure A1 Oats straw suspensions of 7.5 wt% fiber concentration made from mesh a) 12, b) 20, c) 40 and d) 60 by dispersion, mechanical mixing and placed in the vacuum.**

**Table A2 Characteristics of Oats straw suspensions made by dispersion, mechanical mixing for 2minutes and placed in the vacuum for 30minutes**

Straw concentration (w/v)	Mesh size (mm)	Height of floating fiber (cm)	Height of sediment (cm)	Mixing speed (rpm)
6.25%	12	Negligible	2.0	159
	20	Negligible	2.2	164
	40	Negligible	1.9	169
	-40	Negligible	1.7	170
7.5%	12	Indeterminate	2.3	155
	20	Indeterminate	2.3	163
	40	Indeterminate	2.4	163
	-40	Indeterminate	2.3	167



Mesh size 20



b) Mesh size 40



c) Mesh size 20



d) Mesh size 40

**Figure A2 Oats straw suspensions of 5.0 wt% acid pretreated fiber concentration; a) and b) were placed in the vacuum, while c) and d) were not.**

# Appendix B

## Yield Stress Measurement

Effect of change in shear stress value on the rheological behaviour of Xanthan gum solutions tested with the same solution conditions of Table 4.4 and a lower stress range of 0.01 – 10 Pa.

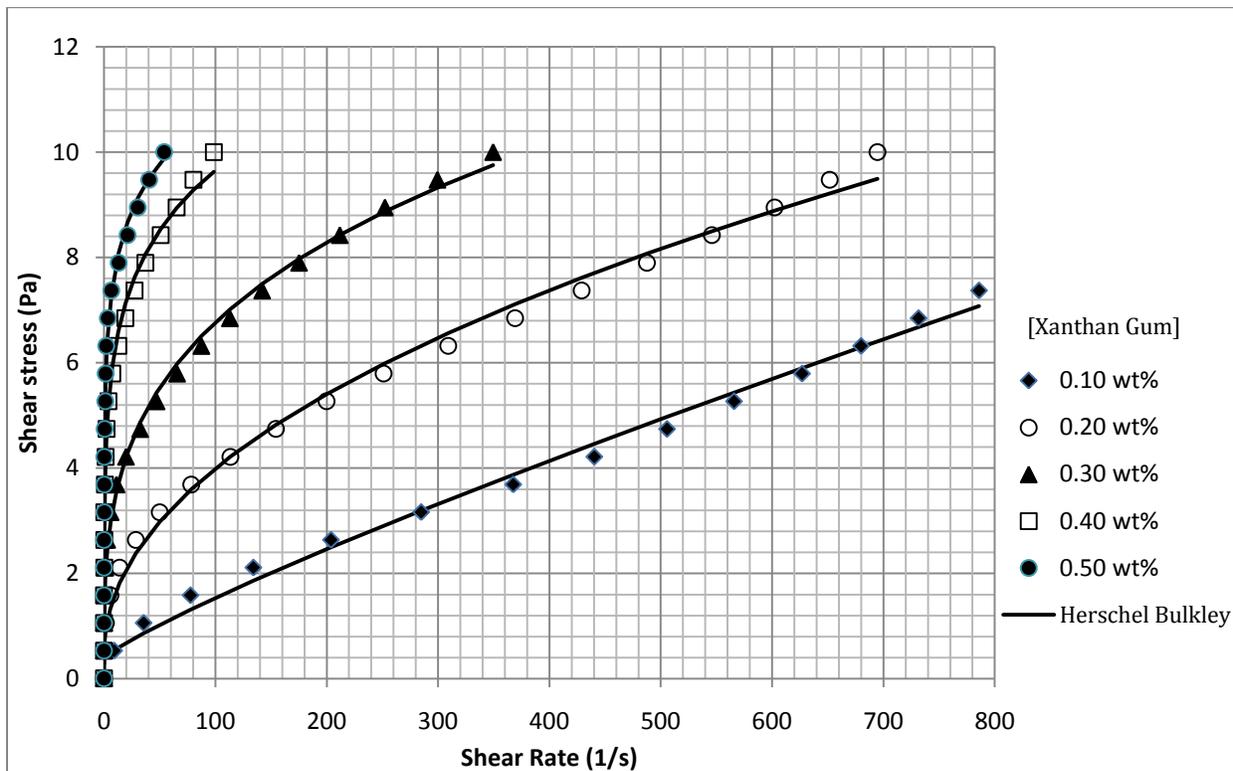


Figure B1 Rheogram for 0.1% - 0.5 wt% concentration Xanthan gum solution, obtained using 4<sup>o</sup>/40 mm diameter cone and plate instrument, min. stress 0.01 Pa, max. stress 10 Pa at 25 °C.

Table B1 is the rheological parameters of Xanthan gum solution obtained using Herschel-Bulkley, Casson and Bingham models.

**Table B1 Herschel-Bulkley parameters of Xanthan gum solutions determined from a controlled shear stress range of 0.1 – 50 Pa, and at T=25°C**

Model	[Xanthan gum] (%)	Consistency index, k (Pas <sup>n</sup> )	Flow behaviour index, n	Yield stress $\tau_0$ (Pa)	Regression coefficient (R <sup>2</sup> )
Herschel-Bulkley	0.1	0.02	0.8	0.5	0.9944
	0.2	0.5	0.7	0.7	0.9959
	0.3	0.5	0.5	0.8	0.9921
	0.4	0.8	0.5	1.2	0.9912
	0.5	1.2	0.4	1.3	0.9969
Casson	0.1	0.1	-	1.03	0.9627
	0.2	0.2	-	1.1	0.9678
	0.3	0.4	-	1.3	0.9548
	0.4	1.3	-	1.9	0.9428
	0.5	1.8	-	2.2	0.9868
Bingham	0.1	0.03	-	0.98	0.9657
	0.2	0.008	-	1.1	0.9666
	0.3	0.5	-	1.2	0.9755
	0.4	0.9	-	1.8	0.9564
	0.5	1.3	-	2	0.9788
	0.1	0.03	-	0.98	0.9657

**Table B2 Rheological model parameters of Xanthan gum solution in triplicate for shear stress range of 0.01 – 10 Pa obtained from Herschel- Bulkley model**

Replicate	[Xanthan gum] (%)	Consistency index, k (Pas <sup>n</sup> )	Flow behaviour index, n	Yield stress $\tau_0$ (Pa)	Regression coefficient (R <sup>2</sup> )
1	0.1	0.1	0.1	0.40	0.9936
	0.2	0.4	0.5	0.60	0.9940
	0.3	1.1	0.4	0.75	0.9957
	0.4	2.0	0.3	1.2	0.9909
	0.5	3.5	0.3	1.34	0.9952
2	0.1	0.2	0.4	0.44	0.9940
	0.2	0.4	0.1	0.64	0.9936
	0.3	1.07	0.4	0.77	0.9917
	0.4	2.01	0.25	1.06	0.9908
	0.5	3.53	0.33	1.31	0.9952
3	0.1	0.2	0.1	0.42	0.9960
	0.2	0.4	0.2	0.66	0.9968
	0.3	1.3	0.4	0.77	0.9951
	0.4	2.2	0.3	1.1	0.9922
	0.5	3.55	0.33	1.37	0.9968

Table B3 is an extract from Table B2 and contain data used in calculating the confidence interval for 0.1-0.5% Xanthan gum solution.

**Table B3 Data used in the calculation of confidence interval for 0.1-0.5 wt% Xanthan gum solution**

[Xanthan gum] (%)	Yield stress, $\tau_o$ (Pa)				Standard deviation	Maximum error	Confidence interval
	$\tau_{o1}$	$\tau_{o2}$	$\tau_{o3}$	$\tau_{oav}$			
0.1	0.40	0.44	0.42	0.42	0.02	0.049	0.42±0.09
0.2	0.60	0.64	0.66	0.63	0.03	0.076	0.63±0.16
0.3	0.75	0.76	0.77	0.77	0.02	0.049	0.77±0.1
0.4	1.20	1.10	1.10	1.33	0.58	0.143	1.33±0.28
0.5	1.34	1.30	1.37	1.33	0.04	0.087	1.33±0.13

$$\text{Maximum error } (E) = t(\alpha/2) * \left( \frac{\text{stdev}}{\sqrt{n}} \right) \quad \text{Hodges and Lehmann (2005)}$$

Where stdev =standard deviation

n = sample size = no. of replicates (3)

$t(\alpha/2) = 4.303$  (obtained using two-tailed distribution table because sample size is < 30)

*Confidence interval = Mean ± E*

The data of Table 5 in the chapter of Results and Discussion is based on the calculations from Table B3.

**Table B4 Viscometric data for Xanthan gum solution for  
shear stress range of 0.01-10 Pa**

Replicate 1		Replicate 2		Replicate 3	
Shear Rate (1/s)	Shear Stress (Pa)	Shear Rate (1/s)	Shear Stress (Pa)	Shear Rate (1/s)	Shear Stress (Pa)
0.1 wt% Xanthan gum					
0.0051	0.0100	0.0047	0.0100	0.0020	0.0100
0.2958	0.5358	0.2462	0.5358	0.166	0.5358
1.7560	1.0620	1.4720	1.0620	0.8589	1.0620
5.6690	1.5870	4.7860	1.5870	3.0970	1.5870
14.050	2.1130	11.680	2.1130	9.0460	2.1130
28.580	2.6390	24.210	2.6390	20.610	2.6390
49.840	3.1650	43.590	3.1650	36.880	3.1650
78.220	3.6900	69.130	3.6900	60.020	3.6900
113.50	4.2160	101.20	4.2160	88.790	4.2160
154.4	4.742	139.2	4.742	124.1	4.742
199.9	5.268	182.4	5.268	165.1	5.268
250.9	5.794	231.1	5.794	209.4	5.794
309.00	6.3190	288.800	6.3190	259.50	6.3190
369.10	6.8450	346.90	6.8450	317.500	6.8450
428.90	7.3710	409.300	7.371	376.3	7.371
487.60	7.8970	471.900	7.897	435.8	7.897
545.90	8.4230	533.00	8.4230	495.30	8.4230
602.20	8.9480	592.40	8.9480	556.80	8.9480
651.60	9.4740	641.80	9.4740	616.80	9.4740

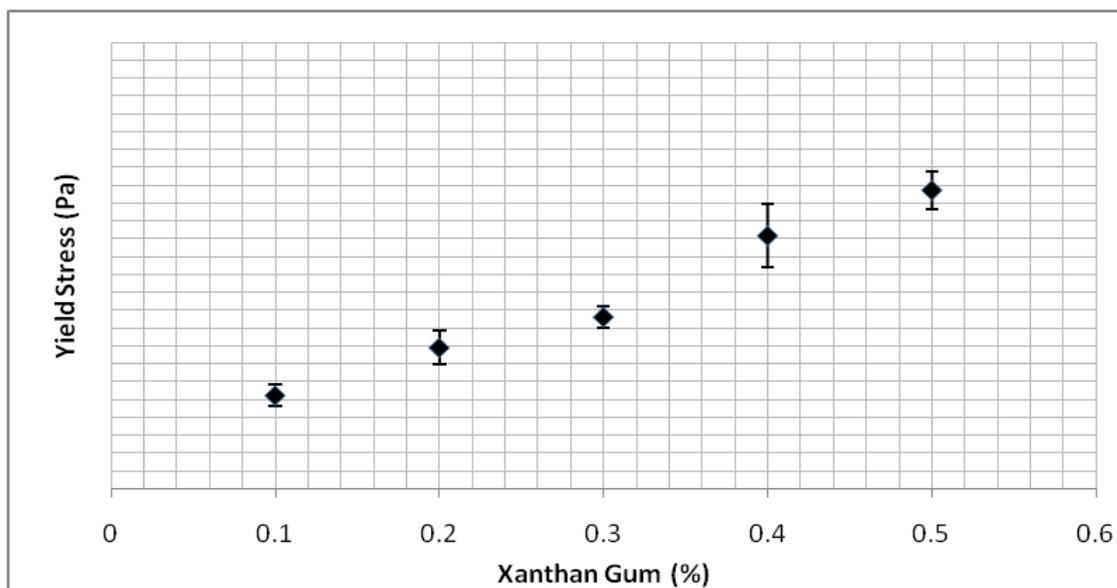
694.70	10.000	688.40	10.000	669.70	10.000
0.2 wt% Xanthan gum					
0.0595	0.0100	0.0684	0.0100	0.0658	0.0100
9.2170	0.5358	10.430	0.5358	9.2440	0.5358
35.660	1.0620	39.200	1.0620	36.490	1.0620
77.760	1.5870	85.170	1.5870	80.400	1.5870
134.20	2.1130	144.70	2.1130	139.40	2.1130
203.90	2.6390	217.20	2.6390	212.10	2.6390
284.90	3.1650	300.90	3.1650	296.70	3.1650
367.60	3.690	385.20	3.6900	381.30	3.6900
440.40	4.2160	460.20	4.2160	460.20	4.2160
505.70	4.7420	503.10	4.7420	532.90	4.7420
565.90	5.2680	578.20	5.2680	600.70	5.2680
627.00	5.7940	639.50	5.7940	661.50	5.7940
680.00	6.3190	691.80	6.3190	717.40	6.3190
731.60	6.8450	742.40	6.8450	774.60	6.8450
785.90	7.3710	793.40	7.3710	831.10	7.3710
840.40	7.8970	844.20	7.8970	886.70	7.8970
892.10	8.4230	896.00	8.4230	941.30	8.4230
944.70	8.9480	947.10	8.9480	995.00	8.9480
990.90	9.4740	1000.0	9.4740	1047.0	9.4740
1035.0	10.000	1052.0	10.000	1099.0	10.000
0.3 wt% Xanthan gum					
0.0011	0.0100	0.0012	0.0100	0.0010	0.0100

0.0476	0.5358	0.0491	0.5358	0.0469	0.5358
0.1227	1.0620	0.1303	1.0620	0.1237	1.0620
0.3906	1.587	0.4123	1.5870	0.3859	1.5870
1.2080	2.113	1.326	2.113	1.212	2.113
2.8660	2.639	3.212	2.639	2.913	2.639
5.9230	3.165	6.523	3.165	5.968	3.165
11.290	3.6900	12.680	3.6900	11.420	3.6900
19.730	4.2160	22.100	4.2160	20.060	4.2160
32.440	4.7420	34.750	4.7420	32.400	4.7420
47.230	5.2680	51.840	5.2680	48.340	5.2680
65.640	5.7940	72.980	5.7940	68.930	5.7940
87.440	6.3190	96.370	6.3190	93.210	6.3190
113.00	6.8450	121.60	6.8450	119.40	6.8450
142.00	7.3710	150.60	7.3710	147.00	7.3710
175.10	7.8970	182.60	7.8970	176.60	7.8970
211.70	8.4230	218.70	8.4230	210.50	8.4230
252.20	8.9480	258.80	8.9480	248.70	8.9480
299.30	9.4740	304.20	9.4740	294.10	9.4740
349.30	10.000	352.00	10.000	342.80	10.000
0.4 wt% Xanthan gum					
0.0008	0.0100	0.0008	0.0100	0.0008	0.0100
0.0155	0.5358	0.0148	0.5358	0.0155	0.5358
0.0268	1.0620	0.0264	1.0620	0.0268	1.0620
0.0412	1.5870	0.0416	1.5870	0.0412	1.5870

0.0674	2.113	0.0678	2.1130	0.0674	2.1130
0.1267	2.6390	0.1274	2.6390	0.1267	2.6390
0.2763	3.1650	0.2818	3.1650	0.2763	3.1650
0.6482	3.690	0.6564	3.690	0.6482	3.690
1.274	4.216	1.319	4.216	1.274	4.216
2.2240	4.7420	2.2280	4.7420	2.2240	4.7420
3.9380	5.2680	3.9000	5.268	3.938	5.268
7.6020	5.7940	7.4810	5.7940	7.602	5.794
13.740	6.3190	12.920	6.3190	13.740	6.3190
21.540	6.8450	19.220	6.8450	21.540	6.8450
31.400	7.3710	27.520	7.3710	31.400	7.3710
44.050	7.8970	37.240	7.8970	44.050	7.8970
58.600	8.4230	50.790	8.4230	58.600	8.4230
75.000	8.9480	65.170	8.9480	75.000	8.9480
94.040	9.4740	80.430	9.4740	94.040	9.4740
115.50	10.000	98.540	10.000	115.50	10.000
0.5 wt% Xanthan gum					
0.0004	0.0100	0.0006	0.0100	0.0003	0.0100
0.0083	0.5358	0.0101	0.5358	0.0096	0.5358
0.0144	1.0620	0.0160	1.0620	0.0156	1.0620
0.0204	1.5870	0.0226	1.5870	0.0217	1.5870
0.0289	2.1130	0.0308	2.1130	0.0303	2.1130
0.0426	2.6390	0.0449	2.6390	0.0443	2.6390
0.0708	3.1650	0.0732	3.1650	0.0721	3.1650

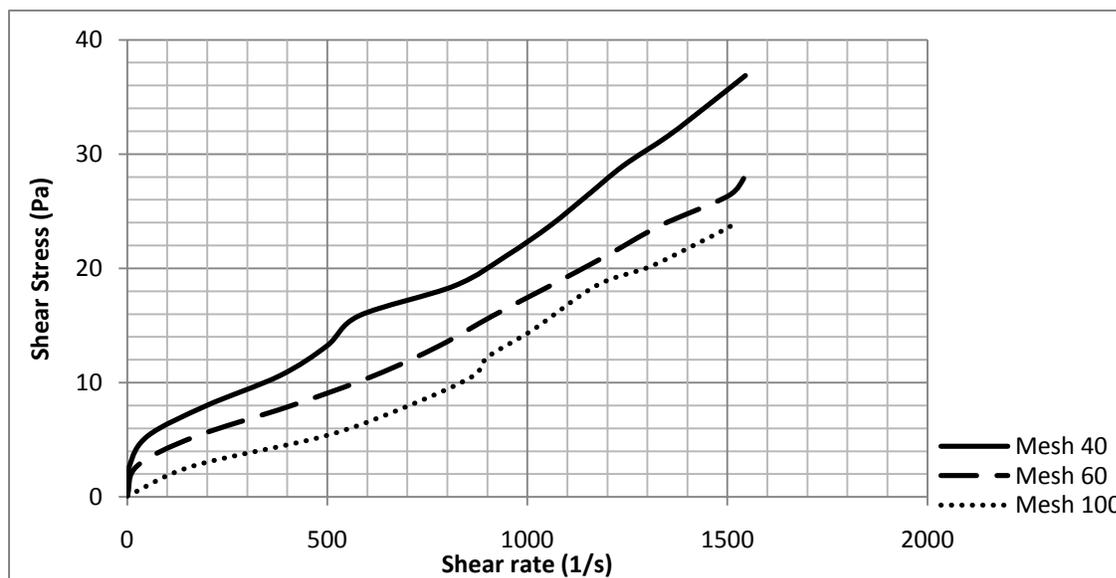
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0.1384	3.6900	0.1414	3.6900	0.1354	3.6900
0.3071	4.2160	0.3212	4.2160	0.2919	4.2160
0.6241	4.7420	0.6470	4.7420	0.6178	4.7420
1.0040	5.2680	1.0730	5.2680	1.0330	5.2680
1.4350	5.7940	1.6070	5.7940	1.5150	5.7940
2.0550	6.3190	2.4020	6.3190	2.1780	6.3190
3.3560	6.8450	4.1250	6.8450	3.7030	6.8450
6.4900	7.3710	7.8610	7.3710	7.0580	7.3710
13.110	7.8970	15.020	7.8970	13.630	7.8970
21.080	8.4230	22.450	8.4230	21.180	8.4230
30.230	8.9480	31.010	8.9480	29.950	8.9480
40.500	9.4740	41.210	9.4740	40.540	9.4740
53.850	10.000	52.610	10.000	52.590	10.000

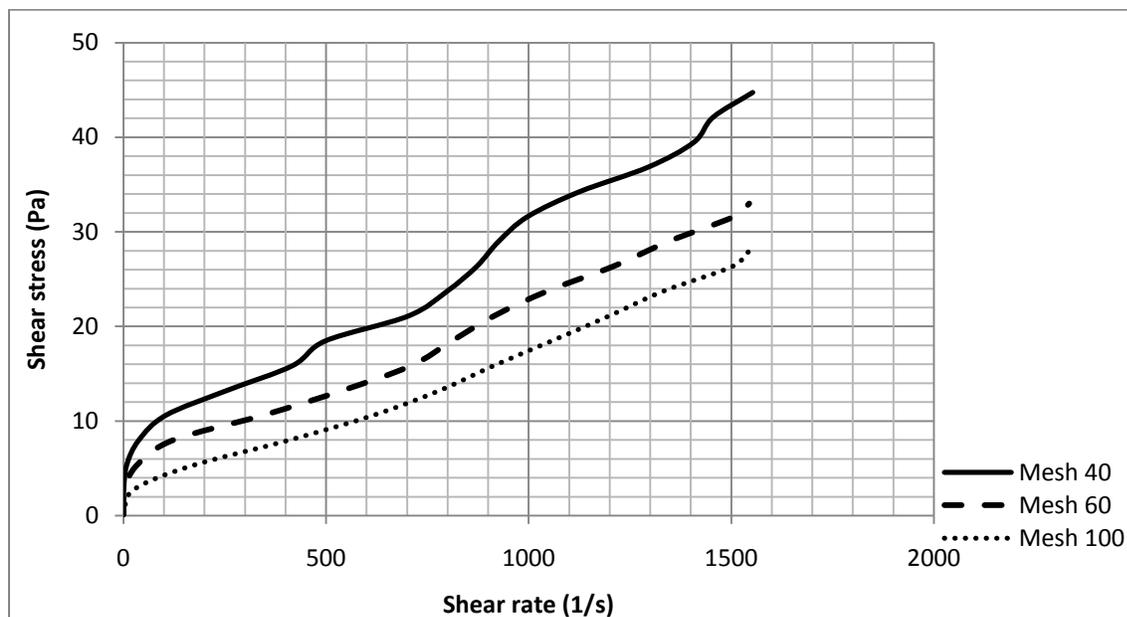


**Figure B2** Variation of yield stress with Xanthan gum concentration measured in the controlled stress mode at a min. stress of 0.01 Pa and a max stress of 10 Pa, with error bars showing reproducibility of experimental data

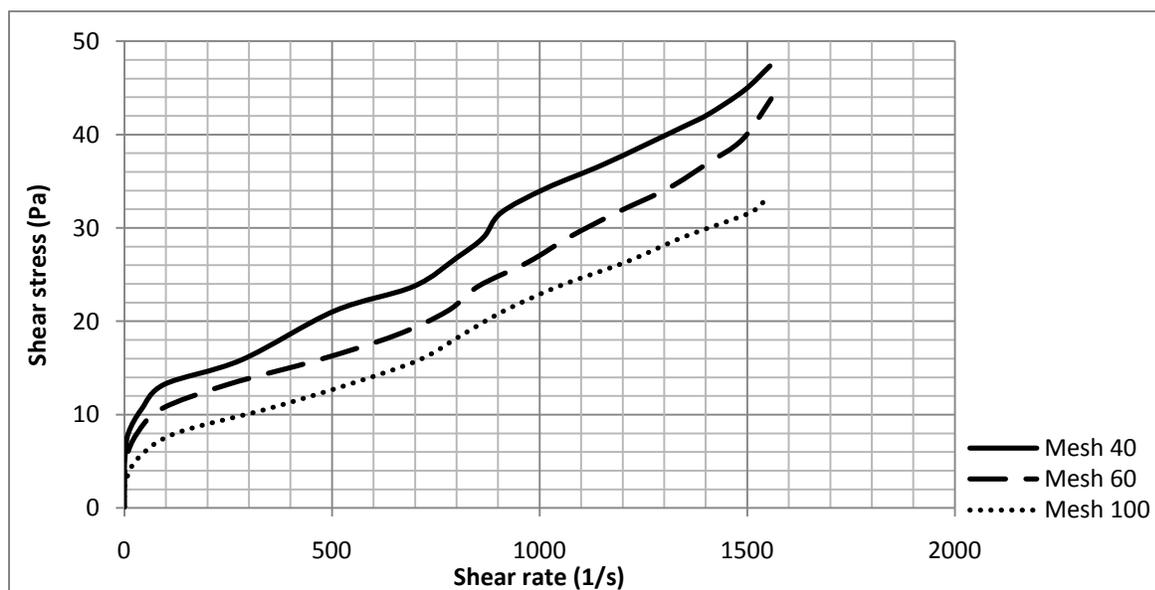
**Viscometry curves (controlled shear stress) for 5 wt%  
concentration Oats straw suspensions**



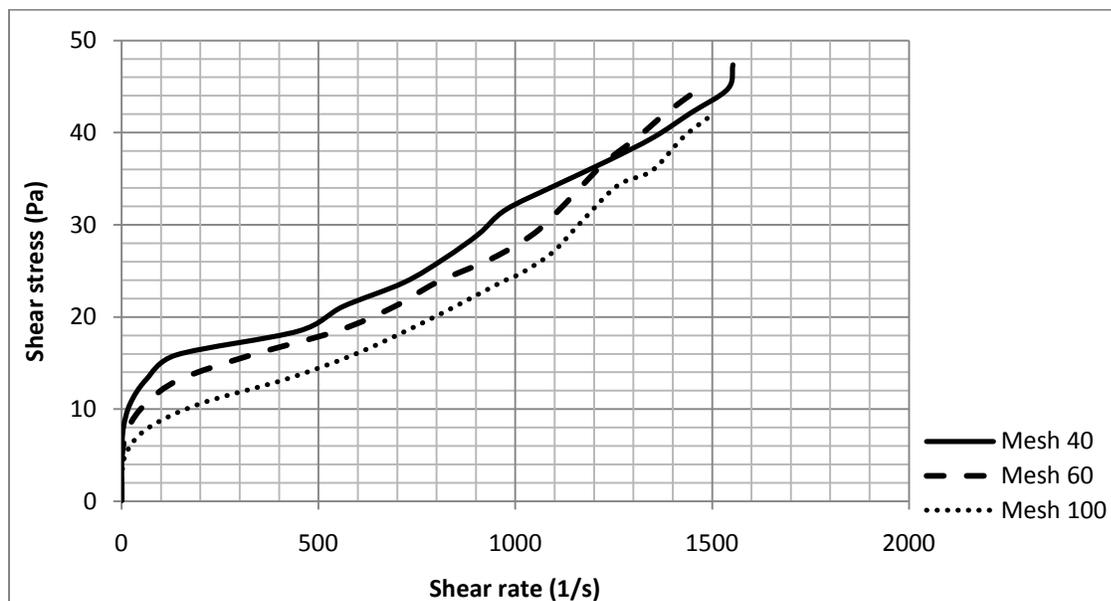
**Figure B3** Viscometry curves (controlled shear stress) for 5.0 wt% Oats straw suspension with 0.2 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



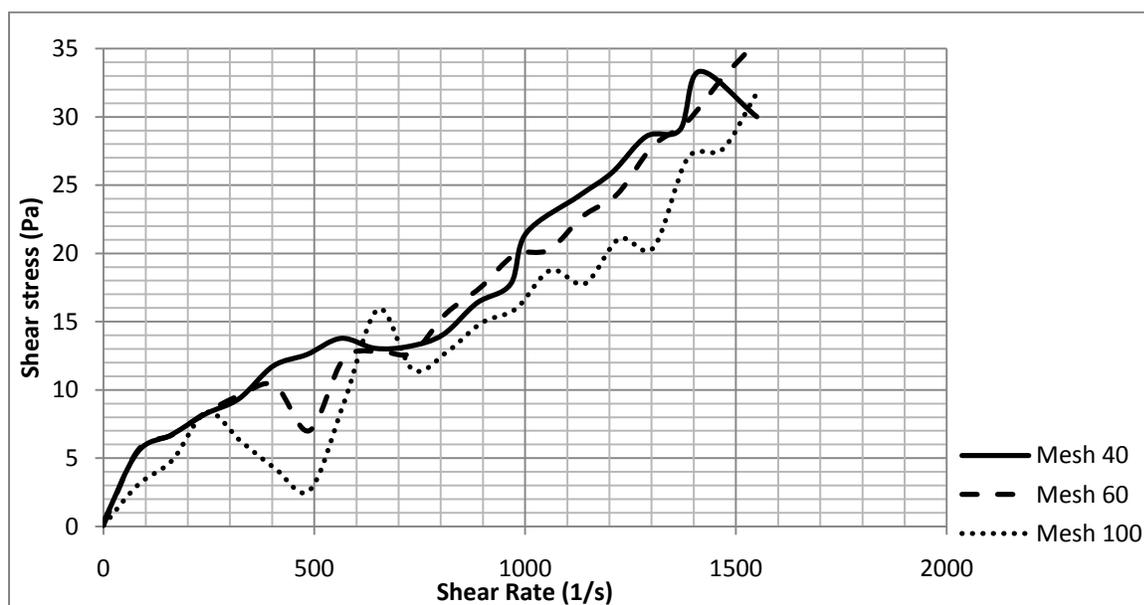
**Figure B4** Viscometry curves (controlled shear stress) for 5.0 wt% Oats straw suspension with 0.3 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



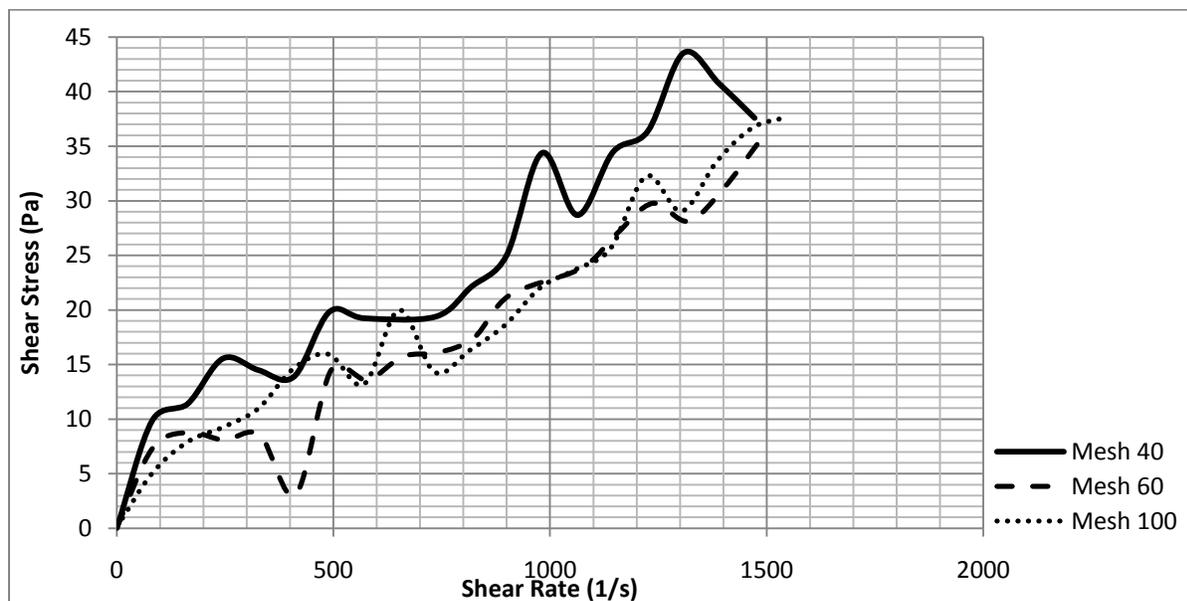
**Figure B5** Viscometry curves (controlled shear stress) for 5.0 wt% Oats straw suspension with 0.4 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



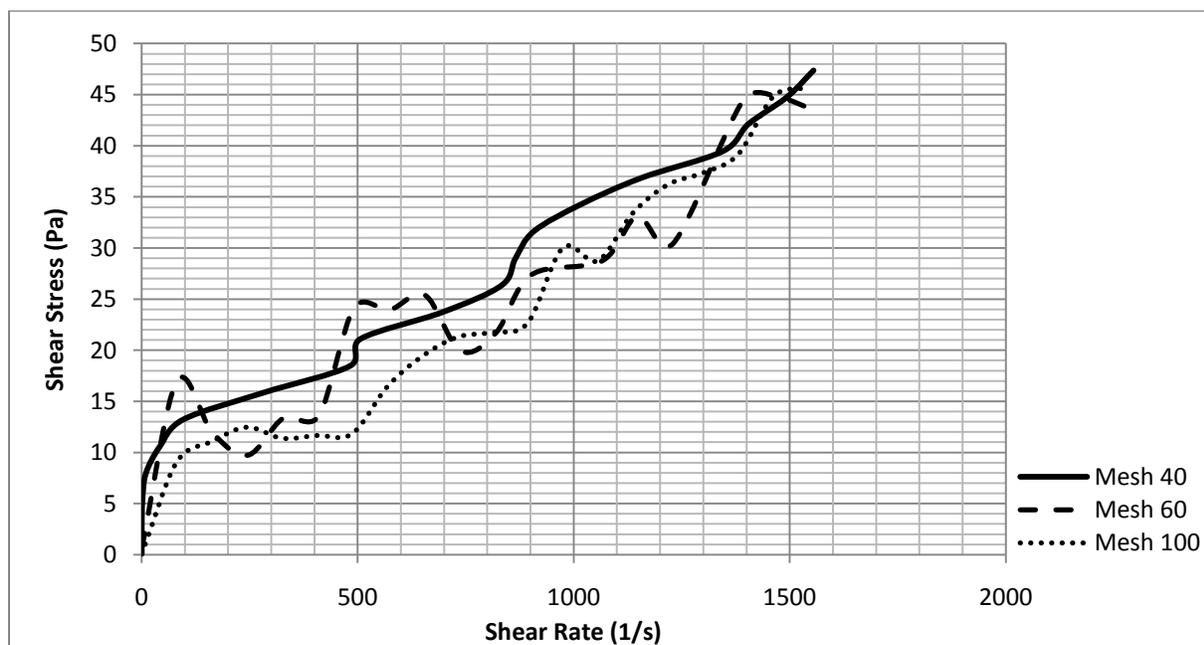
**Figure B6** Viscometry curves (controlled shear stress) for 5.0 wt% Oats straw suspension with 0.5 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



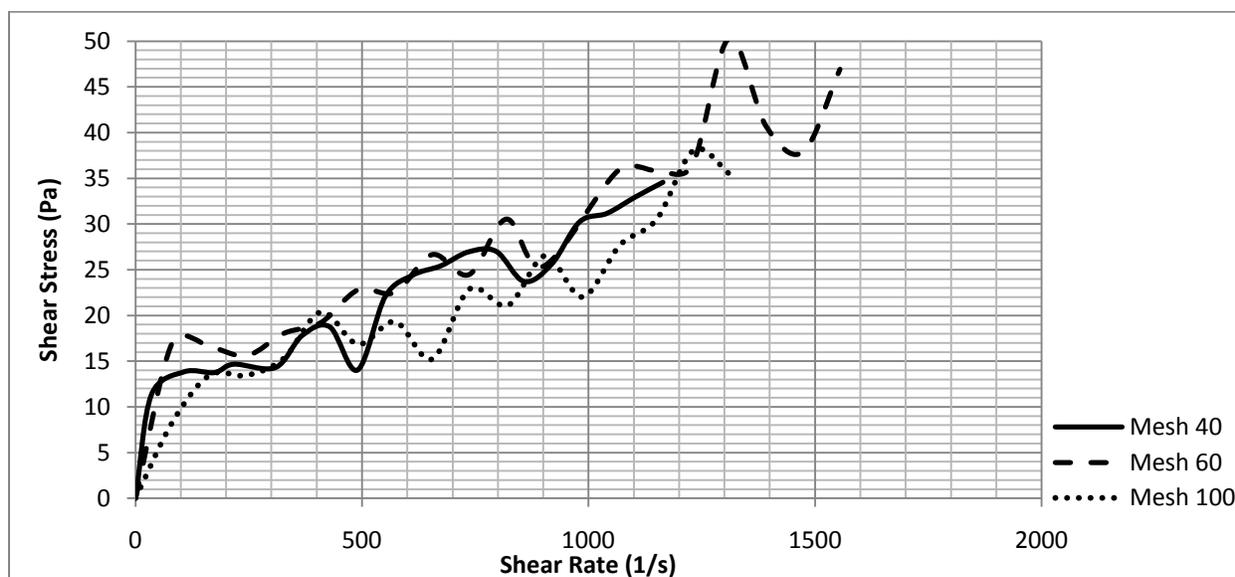
**Figure B7** Viscometry curves (controlled shear rate) for 5.0 wt% Oats straw suspension with 0.2 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



**Figure B8** Viscometry curves (controlled shear rate) for 5.0 wt% Oats straw suspension with 0.3 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



**Figure B9** Viscometry curves (controlled shear rate) for 5.0 wt% Oats straw suspension with 0.4 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.



**Figure B10** Viscometry curves (controlled shear rate) for 5.0 wt% Oats straw suspension with 0.5 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1Pa, max. stress 50 Pa at 25°C.

**Table B5** Rheological model parameters for 5 wt% concentration Oats straw suspensions

Mesh size	Parameter	Herschel-Bulkley	Bingham	Casson	Extrapolation
0.1 wt% Xanthan gum					
40	$\tau_0$	0.96	4.48	4.38	2.00
	k	0.01	0.12	0.11	-
	n	1.20	-	-	-
	R <sup>2</sup>	0.9941	0.9798	0.9798	-
60	$\tau_0$	0.84	3.84	3.84	1.5
	k	0.05	0.42	0.11	-
	n	1.2	-	-	-
	R <sup>2</sup>	0.9937	0.9874	0.9874	-
100	$\tau_0$	0.41	2.05	2.05	1.0

	k	0.001	0.02	0.13	-
	n	1.35	-	-	-
	R <sup>2</sup>	0.9982	0.9563	0.9563	-
0.2 wt% Xanthan gum					
40	$\tau_0$	2.23	6.00	6.00	4.8
	k	0.02	0.02	0.14	-
	n	1.04	-	-	-
	R <sup>2</sup>	0.9932	0.9780	0.9789	-
60	$\tau_0$	1.79	4.04	4.04	5.0
	k	0.01	0.02	0.13	-
	n	1.14	-	-	-
	R <sup>2</sup>	0.9921	0.9898	0.98898	-
100	$\tau_0$	1.1	2.65	2.65	5.0
	k	0.003	0.02	0.14	-
	n	1.2	-	-	-
	R <sup>2</sup>	0.9984	0.9807	0.9807	-
0.3 wt% Xanthan gum					
40	$\tau_0$	4.02	6.60	6.60	9
	k	0.05	0.03	0.12	-
	n	0.90	-	-	-
	R <sup>2</sup>	0.9845	0.9850	0.9580	-
60	$\tau_0$	2.88	3.14	3.14	6.0
	k	0.03	0.02	0.14	-
	n	0.96	-	-	-

	R <sup>2</sup>	0.9862	0.9859	0.9859	-
100	$\tau_0$	2.06	3.17	3.17	6.0
	K	0.01	0.02	0.14	-
	n	1.15	-	-	-
	R <sup>2</sup>	0.9923	0.9769	0.9769	-
0.4 wt% Xanthan gum					
40	$\tau_0$	4.95	7.98	7.98	11
	k	0.12	0.03	0.16	-
	n	0.79	-	-	-
	R <sup>2</sup>	0.9780	0.9689	0.9689	-
60	$\tau_0$	4.55	4.91	4.91	10.0
	k	0.05	0.02	0.14	-
	n	0.94	-	-	-
	R <sup>2</sup>	0.9772	0.9768	0.9768	-
100	$\tau_0$	3.26	3.33	3.33	9.0
	k	0.03	0.02	0.15	-
	n	1.12	-	-	-
	R <sup>2</sup>	0.9886	0.9704	0.9704	-
0.5 wt% Xanthan gum					
40	$\tau_0$	6.04	8.15	8.15	19
	K	1.93	0.03	0.18	-
	n	0.43	-	-	-
	R <sup>2</sup>	0.9687	0.9564	0.9564	-
60	$\tau_0$	5.57	6.33	6.3	15.0

	k	1.06	0.03	0.16	-
	n	0.87	-	-	-
	R <sup>2</sup>	0.9722	0.9703	0.9703	-
100	$\tau_0$	3.98	4.00	4.00	12.0
	K	0.6	0.02	0.16	-
	n	1.2	-	-	-
	R <sup>2</sup>	0.9869	0.9868	0.9868	-

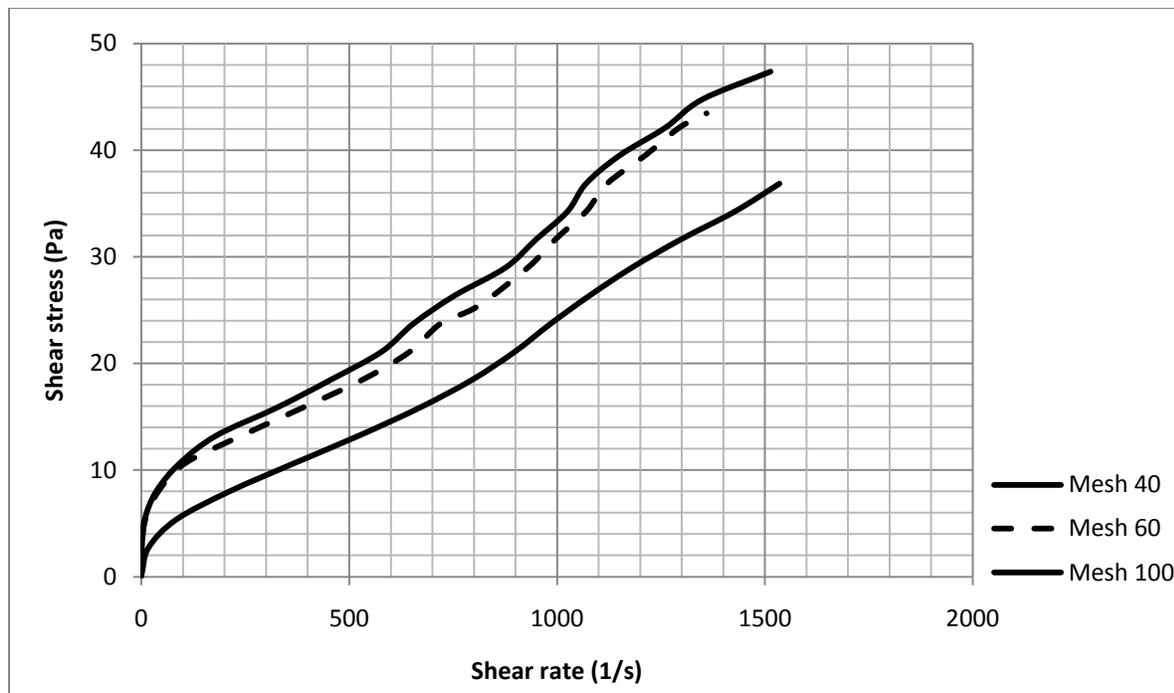
**Table B6 Rheological model parameters for 7.5 wt% concentration Oats straw suspensions**

Mesh size	Parameter	Herschel-Bulkley	Bingham	Casson	Extrapolation
0.1 wt% Xanthan gum					
40	$\tau_0$	4.38	12.90	12.93	20
	k	2.23	0.05	0.22	-
	n	0.13	-	-	-
	R <sup>2</sup>	0.9841	0.8417	0.8417	-
60	$\tau_0$	3.94	2.20	2.25	10.0
	k	0.96	0.03	0.17	-
	n	1.12	-	-	-
	R <sup>2</sup>	0.9881	0.9882	0.9882	-
100	$\tau_0$	2.64	1.58	1.62	4.0
	k	0.64	0.02	0.15	-
	n	1.14	-	-	-
	R <sup>2</sup>	0.9910	0.9890	0.9890	-

0.2 wt% Xanthan gum					
40	$\tau_0$	5.78	13.39	13.49	23
	k	1.8	0.04	0.20	-
	n	0.45	-	-	-
	R <sup>2</sup>	0.9941	0.8355	0.8355	-
60	$\tau_0$	4.01	5.10	5.17	10.0
	k	1.0	0.03	0.17	-
	n	0.87	-	-	-
	R <sup>2</sup>	0.9869	0.9842	0.9703	-
100	$\tau_0$	3.17	5.14	5.17	10.0
	k	0.8	0.03	0.17	-
	n	0.87	-	-	-
	R <sup>2</sup>	0.9858	0.9842	0.9703	-
0.3 wt% Xanthan gum					
40	$\tau_0$	7.0	16.9	17.6	30
	k	6.05	0.06	0.28	-
	n	0.31	-	-	-
	R <sup>2</sup>	0.9508	0.6220	0.6220	-
60	$\tau_0$	5.80	9.20	9.21	16.0
	K	2.01	0.03	0.18	-
	n	0.52	-	-	-
	R <sup>2</sup>	0.9808	0.9359	0.9360	-
100	$\tau_0$	3.43	9.15	9.15	15.0
	k	0.94	0.00	0.17	-

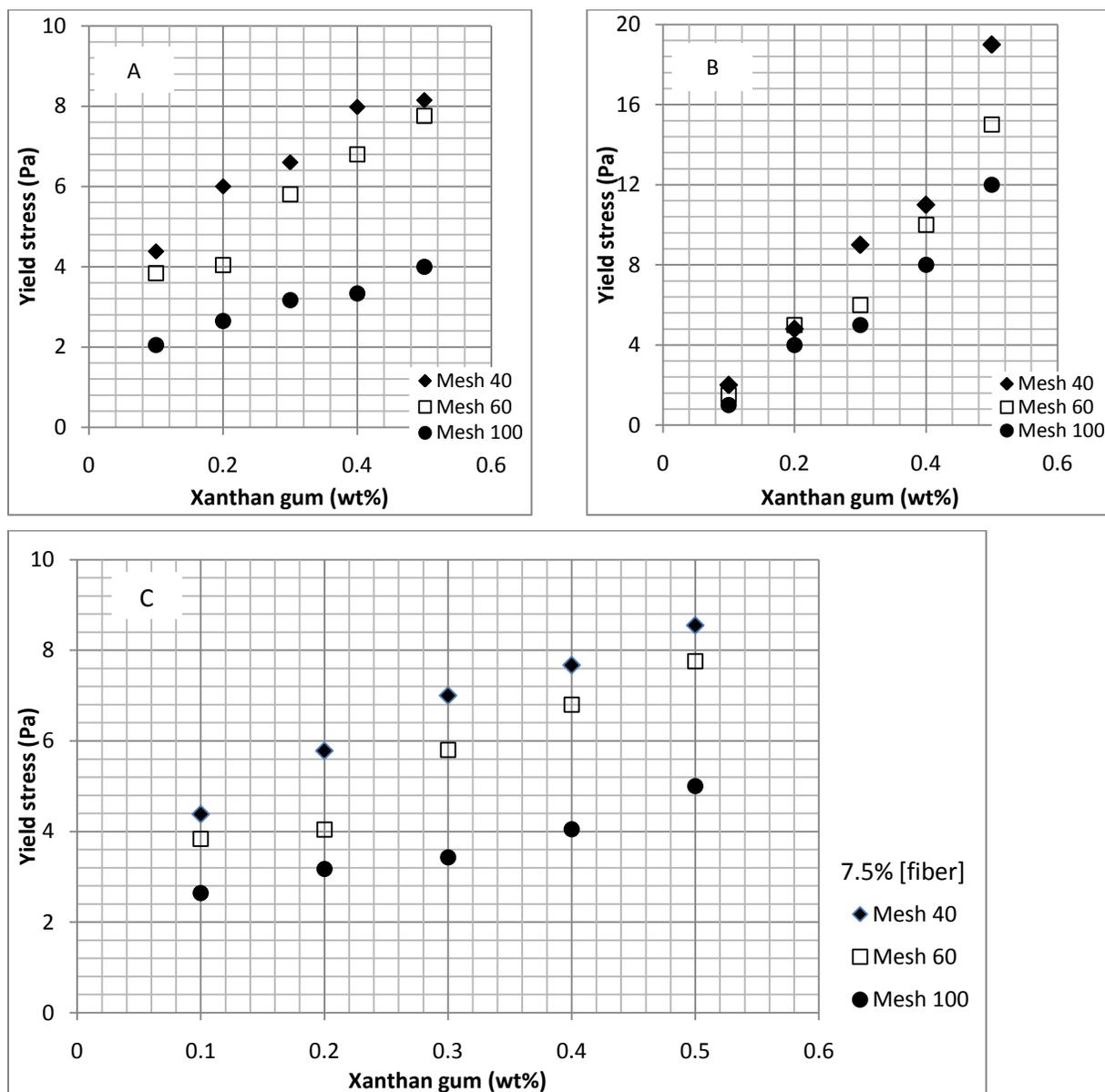
	n	0.53	-	-	-
	R <sup>2</sup>	0.9874	0.9472	0.9472	-
0.4 wt% Xanthan gum					
40	$\tau_0$	7.67	18.66	18.71	34
	k	10.90	0.12	0.52	-
	n	0.25	-	-	-
	R <sup>2</sup>	0.9805	0.5627	0.5627	-
60	$\tau_0$	6.80	12.00	12.00	24.0
	k	3.90	0.04	0.2	-
	n	0.35	-	-	-
	R <sup>2</sup>	0.9852	0.8820	0.8820	-
100	$\tau_0$	4.05	10.96	11.00	20.0
	k	2.02	0.03	0.18	-
	n	0.37	-	-	-
	R <sup>2</sup>	0.9827	0.8824	0.8824	-
0.5 wt% Xanthan gum					
40	$\tau_0$	8.55	18.76	18.76	38
	k	10.89	0.08	0.28	-
	n	0.23	-	-	-
	R <sup>2</sup>	0.9493	0.5560	0.5560	-
60	$\tau_0$	7.76	13.77	13.97	29.0
	k	5.91	0.05	0.2	-
	n	0.31	-	-	-
	R <sup>2</sup>	0.9852	0.8121	0.8121	-

100	$\tau_0$	5.00	12.00	12.00	24.0
	k	4.00	0.03	0.3	-
	n	0.30	-	-	-
	R <sup>2</sup>	0.9894	0.8622	0.8622	-



**Figure B11 Viscometry curves (controlled shear rate) for 7.5 wt% Oats straw suspension with 0.1 wt% Xanthan gum for fiber sizes a) mesh 40; b) mesh 60; and c) mesh 100 obtained using the vane and cup measuring instrument. Min. stress 0.1 Pa, max. stress 50 Pa at 25°C.**

### Effect of Fiber Size on the Yield Stress of Oat Straw Suspension



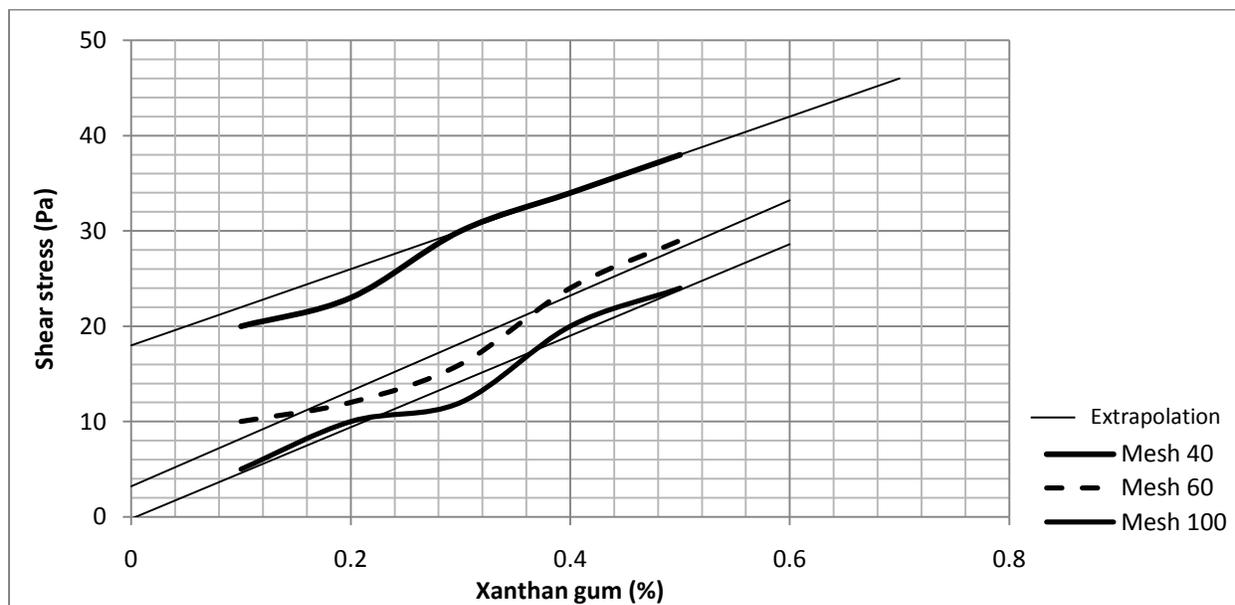
**Figure B12** Effect of fiber size on yield stress for Oats straw suspension of 5.0 and 7.5 wt% [fiber], yield stress evaluated from a) Casson model, b) extrapolation to zero shear rate and c) Herschel-Bulkley model.

**Table B7 Yield stress ( $\tau_0$ ) value from Herschel-Bulkley model, Casson model and Extrapolation to zero shear rate for 5.0 and 7.5 wt% Oats straw suspensions**

Model	Xanthan gum (wt %)	Yield stress ( $\tau_0$ )		
		Mesh 40	Mesh 60	Mesh 100
5% fiber concentration				
Herschel Bulkley	0.1	0.96	0.80	0.21
	0.2	2.23	1.79	1.1
	0.3	4.02	2.88	2.06
	0.4	4.95	4.55	3.26
	0.5	6.04	5.57	3.98
Casson	0.1	4.38	3.84	2.05
	0.2	6.00	4.04	2.65
	0.3	6.60	5.80	3.17
	0.4	7.98	6.80	3.33
	0.5	8.15	7.76	4.00
Bingham	0.1	4.48	3.84	2.05
	0.2	6.00	4.04	2.65
	0.3	6.60	5.80	3.17
	0.4	7.98	6.80	3.33
	0.5	8.15	7.76	4.00
Extrapolation	0.1	2.00	1.50	1.00
	0.2	4.80	5.00	5.00
	0.3	9.00	6.00	6.00
	0.4	11.00	10.00	9.00
	0.5	19.00	15.00	12.00

7.5% fiber concentration				
Herschel-Bulkley	0.1	4.38	3.84	2.64
	0.2	5.78	4.04	3.17
	0.3	7.00	5.80	3.43
	0.4	7.67	6.80	4.05
	0.5	8.55	7.76	5.00
Casson	0.1	12.93	2.25	1.62
	0.2	13.49	5.17	4.76
	0.3	17.60	9.21	9.50
	0.4	18.51	12.00	11.00
	0.5	18.76	13.90	12.00
Bingham	0.1	12.90	2.20	1.58
	0.2	13.39	5.10	4.96
	0.3	16.90	9.21	9.50
	0.4	18.66	12.00	10.96
	0.5	18.76	13.77	12.00
Extrapolation	0.1	20.00	10.00	4.00
	0.2	23.00	10.00	10.00
	0.3	30.00	16.00	15.00
	0.4	34.00	24.00	20.00
	0.5	36.00	29.00	24.00

**Extrapolation of Results obtained from Oats Straw Suspensions with 0.1-0.5 wt%  
Xanthan gum to 0% Xanthan gum suspension**



**Figure B13 Extrapolation of results obtained from 7.5 wt% Oats straw suspensions with 0.1-0.5% Xanthan gum to 0% Xanthan gum suspension**

**Table B8 Yield Stress ( $\tau_o$ ) from extrapolation to 0.0 wt% Xanthan gum concentration**

Xanthan (%)		$\tau_o$ (Pa)		
		Mesh 40	Mesh 60	Mesh 100
5% [fiber]				
0.1		2	1.5	1
0.2		5	5	5
0.3		9	6	6
0.4		11	10	8
0.5		19	15	12
0	$\tau_{o,ext}$ (Pa)	*	*	*
7.5% [fiber]				
0.1		20	10	5
0.2		23	12	10
0.3		30	16	12
0.4		34	24	20
0.5		38	29	24
0	$\tau_{o,ext}$ (Pa)	18	3.8	*

\* Value cannot be predicted by extrapolation

### Other Straw Suspensions Evaluated

**Table B9 Rheological model parameters for suspensions of 5.0 wt % fiber concentration and 0.3 wt% Xanthan gum concentration**

Mesh size	Parameter	Herschel-Bulkley	Casson	Extrapolation
Wheat straw suspension				
40	$\tau_0$	4.20	4.75	6.00
	k	0.03	0.17	-
	n	0.92	-	-
	R <sup>2</sup>	0.9962	0.9885	-
60	$\tau_0$	3.23	3.14	4
	k	0.05	0.2	
	n	1.2		
	R <sup>2</sup>	0.9975	0.9917	5
100	$\tau_0$	2.5	2.68	
	k	0.05	0.15	
	n	1.2	0.9980	
	R <sup>2</sup>	0.9985		
Malt barley suspension				
40	$\tau_0$	4.04	4.70	8.00
	k	0.02	0.16	-
	n	0.89	-	-
	R <sup>2</sup>	0.9899	0.9887	-
60	$\tau_0$	3.33	3.25	7
	k	0.03	0.14	-
	n	0.95	-	-

	R <sup>2</sup>	0.9984	0.9898	-
100	$\tau_0$	2.62	2.56	4.8
	k	0.04	0.13	-
	n	1.2	0.9895	-
	R <sup>2</sup>	0.9984	-	-

**Table B10 Statistical analysis for Oat straw suspension of 5.0 wt% fiber concentration and 0.3 wt% Xanthan gum**

Applied model	Mesh size	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_{av}$	Maximum error	Confidence interval
<b>Herschel-Bulkley</b>	40	4.02	4.18	4.2	4.1	0.1315	4.10±0.30
	60	2.88	3.33	3.03	3.08	0.323	3.08±0.64
	100	3.03	2.9	3.2	3.04	0.216	3.04±0.44
<b>Casson</b>	40	4.83	4.76	4.8	4.79	0.0503	4.80±0.10
	60	3.14	3	3.2	3.11	0.147	3.10±0.30
	100	2.62	2.59	2.68	2.63	0.066	2.63±0.14
<b>Extrapolation</b>	40	9	7	8	8	1.434	8.00±2.86
	60	6	5	6	5.667	0.83	5.67±1.66
	100	6	6	5	5.667	0.83	5.67±1.66