AN EVALUATION OF FLOW AND TRANSPORT PROPERTIES FOR HYDRAULIC FRACTURING FLUIDS IN POROUS MEDIUM SYSTEMS

Caroline E. Tapscott

A thesis submitted to the faculty at the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Department of Environmental Sciences and Engineering.

Chapel Hill
2015

Approved by:
Cass T. Miller
Orlando Coronell
John Bane
ABSTRACT

CAROLINE E. TAPSCOTT: AN EVALUATION OF FLOW AND TRANSPORT PROPERTIES FOR HYDRAULIC FRACTURING FLUIDS IN POROUS MEDIUM SYSTEMS
(Under the direction of Cass T. Miller)

Hydraulic fracturing, or fracking, is a technology being applied across the US to increase the permeability of shale deposits containing natural gas by injecting a multicomponent, non-Newtonian mixture into the subsurface to induce fractures. The purpose of this work was to assess the behavior of non-Newtonian fluids used in fracking. Guar gum was chosen as a model fracking compound. Rheological properties of guar gum solutions were analyzed and column experiments were performed to determine the pressure drop as a function of fluid velocity. Guar gum was found to alter the viscosity of the flushing solution by more than two orders of magnitude in some cases. A Cross model was fit to the viscosity data and dispersion was found to decrease with increasing viscosity. Preliminary collaborative work has been done to model the observed systems at the pore scale. Comparing these results to the column-scale observations made shows relatively good agreement.
ACKNOWLEDGMENTS

There are many people whose help and support have been essential to my success over the past couple of years. First, I want to thank my advisor, Dr. Casey Miller, for giving me guidance and encouragement throughout the past two years and for believing in me even when I doubted myself. I would also like to thank Dr. Orlando Coronell and Dr. John Bane, who have provided valuable insight which has helped me shape this document into a final thesis.

Additionally, I would like to thank the members of Dr. Miller’s lab group who have helped me through my experiences both in the lab and in the classroom: Scott Hauswirth, Zineb Bouzoubaa, Amanda Dye, Pam Schultz, Tim Weigand, Sydney Bronson, and Mikayla Armstrong. I especially want to thank Scott, who has given me advice through every step of this experience and without whom I genuinely would not have made it through this process. Also, I want to thank Zineb for spending long hours collecting rheometer data with me, and Amanda for working on the modeling side of this study and for reminding me not to work too hard.

Finally, I want to thank my parents, John and Sally, and my siblings, John and Sarah, for always providing me with unconditional love and support, but especially through this process.
# TABLE OF CONTENTS

LIST OF TABLES ...................................................... vii

LIST OF FIGURES ................................................... viii

LIST OF ABBREVIATIONS ......................................... ix

CHAPTER 1: INTRODUCTION ........................................ 1

1.1 Overview of Hydraulic Fracturing ............................. 1

1.2 Study Objectives .............................................. 2

CHAPTER 2: BACKGROUND .......................................... 4

2.1 Natural Gas Trends ............................................. 4

2.2 Hydraulic Fracturing .......................................... 7

2.3 Fracturing Fluid ................................................ 8

2.3.1 Fluid Properties ............................................ 10

2.3.2 Guar Gum .................................................. 13

CHAPTER 3: EXPERIMENTAL METHODS ......................... 15

3.1 Guar gum solutions ............................................ 15

3.2 Column Experiments .......................................... 16

3.2.1 Column setup ............................................. 16

3.2.2 Pressure transducer calibration ........................... 18

3.2.3 Tracer tests ................................................ 18

3.2.4 Column flow experiments ................................. 19

3.3 Rheometer ..................................................... 21

CHAPTER 4: RESULTS ................................................ 23
LIST OF TABLES

2.1 Combustion Emissions (Pounds of Air Pollutant per Billion Btu of Energy) 5
2.2 Average Fracturing Fluid Composition 9
4.3 Column flow results for the 0.5 g/L filtered guar gum solution 27
4.4 Column flow results for the 3 g/L filtered guar gum solution 29
4.5 Column flow results for the 5 g/L filtered guar gum solution 31
4.6 Cross model parameters for rheometer data 35
5.7 Power law parameters calculated from rheometer data 46
LIST OF FIGURES

2.1 Chemical structure of guar gum ............................................. 13
3.2 Column setup ........................................................................ 17
4.3 Pressure transducer calibration curves ..................................... 23
4.4 Tracer test results and curve fits ............................................. 25
4.5 Column flow results for the 0.5 g/L filtered guar gum solution and water ....................................................... 28
4.6 Viscosity versus flow rate for the 0.5 g/L filtered guar gum solution and water ....................................................... 28
4.7 Column flow results for the 3 g/L filtered guar gum solution with standard deviation error bars ................................. 30
4.8 Column flow results for the 5 g/L filtered guar gum solution with standard deviation error bars ................................. 32
4.9 Column flow results ................................................................ 33
4.10 Viscosity calculated from Darcy’s law and column flow data ................................................................. 33
4.11 Rheometer results with lines fit ............................................. 34
4.12 Rheometer results for the 5 g/L guar gum unfiltered and filtered solutions ..................................................... 35
4.13 Cross model parameters fit to rheometer data ......................... 36
5.14 Rheology of a power law fluid in log-log scale [28] ..................... 37
5.15 Rheology of an Ellis fluid in log-log scale [28] ......................... 38
5.16 Rheology of a Carreau fluid in log-log scale [28] ....................... 39
5.17 Shear rate comparison of experimental data vs. previously published methods for 5 g/L guar gum ......................... 46
5.18 Shear rate comparison of experimental data vs. previously published methods for 3 g/L guar gum ......................... 47
5.19 Viscosity comparison of experimental data vs. previously published methods for 5 g/L guar gum ......................... 49
5.20 Viscosity comparison of experimental data vs. previously published methods for 3 g/L guar gum ......................... 49
5.21 Shear rate comparison of experimental data vs. previously published methods for 0.5 g/L guar gum ......................... 50
5.22 Viscosity comparison of experimental data vs. previously published methods for 0.5 g/L guar gum ......................... 51
LIST OF ABBREVIATIONS

\dot{\gamma} \quad \text{shear rate}

\dot{\gamma}_{\text{app}} \quad \text{apparent shear rate}

\epsilon \quad \text{porosity}

\eta \quad \text{viscosity}

\eta_0 \quad \text{viscosity at zero shear}

\eta_{\text{app}} \quad \text{apparent viscosity}

\eta_{\infty} \quad \text{viscosity at infinite shear}

\kappa \quad \text{intrinsic permeability}

\rho \quad \text{density}

\sigma \quad \text{standard deviation}

\tau \quad \text{shear stress}

\tau^* \quad \text{shear stress at the transition between Newtonian and power law behavior}

A \quad \text{cross section area}

C \quad \text{concentration}

g \quad \text{gravitational acceleration}

h \quad \text{hydraulic head}

K \quad \text{Power law flow consistency index}

L \quad \text{column length}

n \quad \text{flow behavior index}

P \quad \text{pressure}

q \quad \text{darcy velocity}
$Q$  flow rate

$\mathcal{T}$  tortuosity
CHAPTER 1: INTRODUCTION

1.1 Overview of Hydraulic Fracturing

Natural gas is a vital component of meeting energy demands in the United States. It accounts for about 27% of the nation’s total energy, and natural gas production from shale formations is a rapidly growing trend in domestic oil and gas exploration [36]. The U.S. has extensive natural gas reserves in the form of shale gas that have previously been unobtainable due to the nature of the reservoirs. Recent advances in technologies such as horizontal drilling and hydraulic fracturing have allowed these previously unavailable reservoirs to become economically viable.

Hydraulic fracturing, commonly referred to as fracking, is a process that involves the injection of a fracturing fluid under high pressure into a shale formation containing large amounts of natural gas. This causes the formation to fracture, thereby increasing the permeability of the formation. The increased permeability allows natural gas to flow more easily through the shale formation so that it can be extracted. Fracturing fluid contains proppants, such as sand or ceramic beads, which hold open the fractures after the fluid is no longer pumped through the formation. Once this occurs, fluids flow back to the surface until the pressure becomes stable, after which natural gas can be produced continually until the gas in the formation is depleted [34].

Fracking has become a wildly polarizing subject in recent years. Often media portrayal of
fracking greatly simplifies a complex process, which can contribute to strong opinions both for and against fracking. The advancement of fracking technologies has allowed for increased use of those technologies in areas with a history of conventional oil and gas production as well as in new areas with unconventional reservoirs. This has led to growing concern among the general population about the potential effects fracking might have on human and environmental health. Much of these concerns are about the possible pollution of ground or surface waters during fracking processes [37]. Additionally, there is concern related to the disposal of flow back waters created during the fracturing process, which often contain carcinogenic chemicals [32]. There is also uncertainty in the environmental impacts of fracking, which leads to concerns over expanding fracking practices. However, evaluating the environmental impacts of fracking is complicated.

Despite the possible negative impacts fracking may have on aquatic or terrestrial systems, there are positive aspects as well. Compared to other fossil fuels, natural gas is more efficient and clean burning. Combustion of natural gas produces lower carbon dioxide (CO$_2$) emissions than both oil and coal as well as lower combustion byproducts such as nitrogen oxides (NO$_x$), sulfur dioxide (SO$_2$), and particulate matter [34]. Increased use of natural gas as an energy source in the U.S. would decrease the amount of CO$_2$ emissions and decrease the global warming burden.

1.2 Study Objectives

Although fracking practices across the U.S. are becoming more widespread, there are still many questions concerning fracking systems. One of these questions involves the lack of understanding of non-ideal fluids such as fracturing fluids. A more complete understanding
of properties relating to the flow and transport of these non-ideal fluids can help create a better understanding of fracking systems. The goal of this work is to advance fundamental understanding of the behavior of commonly used fracking fluids in porous media systems. The specific objectives of this work are: (1) to identify a model fracking fluid that is typical of industrial applications, (2) to characterize the physicochemical properties of the fluid, (3) to experimentally observe the flow behavior in model systems, (4) to evaluate dispersion in fracking displacement systems, and (5) to model the observed behavior.
2.1 Natural Gas Trends

Natural gas makes up a significant portion of energy demands in the United States. Currently, around 27% of the total national energy demand is met by natural gas, and this number is expected to rise in the coming years [36]. Natural gas is gas made up of a mixture of hydrocarbons that is mostly methane, but also includes ethane, propane, and butane, among other gases [34]. This mixture of gases is colorless and odorless. It releases a relatively large amount of energy when burned, while producing less CO\textsubscript{2} than other fossil fuels, making it a desirable source of energy.

Natural gas is found in rock formations, called reservoirs, deep below the Earth’s surface. Conventional natural gas is often associated with oil deposits [34]. Conventional natural gas reservoirs are generally sand or carbonate formations that contain natural gas in the pore spaces of the formation. The gas is able to move through the pore space to the wellbore without fracking [12, 34]. It is extracted via drilling, and processed to remove impurities, as well as any sand or water that may have traveled with the gas. It is then transferred across the country via natural gas pipelines to be used in residential, industrial, commercial, and transportation sectors.

Natural gas is a desirable energy source for many reasons. It is a versatile and efficient fuel that can be used for many functions. It has a well established infrastructure, which
allows for safe and reliable transportation across the country, and a high British thermal unit (Btu) content [34]. Additionally, it is the cleanest burning fossil fuel, as shown in Table 2.1 [35]. Coal and oil are composed of more complex organic molecules than natural gas, which produce combustion byproducts with higher quantities of CO₂, NOₓ, SO₂ and particulate matter. Combustion of natural gas produces roughly half as much CO₂ as coal and 30% less CO₂ than oil when comparing pounds of CO₂ emitted per billion Btu of energy produced. Moreover, natural gas only emits about a quarter of the NOₓ produced by coal or oil, by the same comparison [35]. The increasing emphasis on reducing global greenhouse gas emissions makes these traits highly desirable. Also, the U.S. has a large amount of natural gas reservoirs, making it a reliable source of energy. Ninety seven percent of the natural gas consumed in the U.S. is produced in North America, and 84% is produced within the U.S. [34].

Table 2.1: Combustion Emissions
(Pounds of Air Pollutant per Billion Btu of Energy)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Natural Gas</th>
<th>Oil</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>117,000</td>
<td>164,000</td>
<td>208,000</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>40</td>
<td>33</td>
<td>208</td>
</tr>
<tr>
<td>Nitrogen Oxides (NOₓ)</td>
<td>92</td>
<td>448</td>
<td>457</td>
</tr>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>0.6</td>
<td>1,122</td>
<td>2,591</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>7.0</td>
<td>84</td>
<td>2,744</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.750</td>
<td>0.220</td>
<td>0.221</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.000</td>
<td>0.007</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Unconventional gas is natural gas that has been previously inaccessible due to the nature of the formations in which it is found. These formations are typically made of shale,
tight sands, or coal beds and have inherently low permeability, which restricts the flow of fluids [12]. Natural gas in these formations has become economically viable in recent years as a result of advances in drilling technologies and in hydraulic fracturing. The main difference between conventional natural gas and unconventional natural gas reservoirs is that unconventional gas formations are both the source of and reservoir for natural gas [32]. Also, the production of unconventional gas employs horizontal drilling and hydraulic fracturing to gain access to gas trapped in formations [20]. Fewer horizontal wells are needed to achieve the same amount of well coverage using only vertical drilling, thus reducing the amount of surface disturbances [34].

Increased use of these technologies has led to increased shale gas production and lower natural gas prices, which has contributed to faster growth for industrial production [36]. Unconventional gas is predicted to become an ever-increasing portion of the U.S. natural gas reserves, while conventional gas reservoirs are declining [34, 36]. In 2007, unconventional gas production accounted for 46% of the total national natural gas production [34].

Shale gas plays a key role in unconventional gas sources. The continental U.S. contains a wide distribution of organic shale formations that are capable of containing large amounts of natural gas [34, 36]. Natural gas has been produced from shale formations in the U.S. since the 1930s, but production has greatly increased in recent years as advances in hydraulic fracturing have greatly facilitated and become essential to the process [20]. Shale gas has since become the largest factor in the shift towards unconventional gas recovery. In 2010, shale gas accounted for approximately 23% of the U.S. natural gas supply [12]. It is expected that shale gas will become an even more important part of the U.S. energy outlook in coming years as hydraulic fracturing technologies become more advanced.
2.2 Hydraulic Fracturing

Hydraulic fracturing, or fracking, is a process used to increase the productivity of a well by overcoming barriers to the flow of fluids to the wellbore. The process is begun by drilling a well vertically to depths in the range of around 1,000 to over 5,000 m \cite{15, 34}. The depth of the well is dependent on the location and the shale formation being drilled. After the desired depth is reached, the well is then drilled horizontally. Horizontal drilling is used to access more exposure to a shale formation.

To induce fractures in the shale formation, fracturing fluids are injected at high pressures. The fracking fluids include proppants, which can be small grains of sand or ceramic beads, that enter the fractures and hold them open. Fracking fluids are injected in stages. The high pressures used to inject the fluid initiate fractures, and then proppants are added to increase fracture sizes. Initially, fine grained proppants are added to the fluid. These fine grain particles are better able to travel deep into fractures in order to extend the cracks \cite{34}. Coarse grained proppants are added in subsequent stages to prop fractures open while the fine grained proppants travel deeper into the fractures. Pressures and flow rates used to inject the fracturing fluid vary depending on the characteristics of the shale formation.

After the injection of the fracking fluid is complete and pressure is reduced, the fluid in the well begins to flow back to the wellbore due to the difference in pressure. This fluid is referred to as flowback water and includes any fluid that returns to the surface both before and while the well is in production \cite{37}. Flowback water is composed of a mixture of the original fracking fluid combined with any natural water that had been in the formation, and it may also contain dissolved components of the formation itself \cite{7}. Additionally, flowback
water can contain large amounts of salts, made up of sodium, calcium, chloride, and bromide ions; trace metals, such as barium, strontium, and iron; and organic hydrocarbons [9, 30].

As production of the well goes on, the amount of flowback water returning to the surface lessens and the amount of natural gas increases. However, fracking fluid cannot be completely recovered from the well, and often the produced water contains flowback of fracking fluid for long periods of time after production of the well is initiated [34].

2.3 Fracturing Fluid

Fracturing fluids are made up of a mixture of water, chemical additives, and proppants. While the exact chemical makeup of fracking fluids varies depending on the characteristics of the shale formation, they are generally roughly 99% water as shown in Table 2.2 [6]. A list of chemicals used in fracking fluids in the U.S. is available through the FracFocus Chemical Disclosure Registry; complete lists of chemicals vary from site to site and in states where disclosure of chemicals is not a requirement, well site information is provided on a voluntary basis [6].

Chemicals are added for different purposes to obtain a fluid with desired characteristics. These chemicals are comprised of a wide range of classes, including gelling agents, surfactants, friction reducers, antibacterial agents, acids, and corrosion inhibitors, among others [11, 25]. These additives are included to serve specific purposes. For example, friction reducers allow the fracking fluid to be pumped at higher flow rates and lower pressures than if water alone was used. Antibacterial agents, or biocides, prevent biological growth in the fractures, corrosion inhibitors prevent corrosion of metal pipes, and acids are used to remove drilling damage near the wellbore caused by pores becoming plugged with drilling
Table 2.2: Average Fracturing Fluid Composition

<table>
<thead>
<tr>
<th>Component category</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>99.2</td>
</tr>
<tr>
<td>gellant</td>
<td>0.5</td>
</tr>
<tr>
<td>acid</td>
<td>0.07</td>
</tr>
<tr>
<td>corrosion inhibitor</td>
<td>0.05</td>
</tr>
<tr>
<td>friction reducer</td>
<td>0.05</td>
</tr>
<tr>
<td>clay controller</td>
<td>0.034</td>
</tr>
<tr>
<td>cross linker</td>
<td>0.032</td>
</tr>
<tr>
<td>scale inhibitor</td>
<td>0.023</td>
</tr>
<tr>
<td>breaker</td>
<td>0.02</td>
</tr>
<tr>
<td>iron control</td>
<td>0.004</td>
</tr>
<tr>
<td>biocide</td>
<td>0.001</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.984</td>
</tr>
</tbody>
</table>

mud or casing cement [34].

While the vast majority of fracking fluid is made up of water, an important compound in the mixture is the gelling agent. This gelling agent is most commonly a polymer or cross-linked polymer that increases the viscosity of the solution [5, 18]. An increased viscosity is needed to keep the proppants suspended in solution. An added bonus to using a gelling agent is that there is decreased occurrence of fluid leakoff, or the loss of fracking fluid to any permeable rock surrounding the fracture, for a wide range of reservoir temperatures and permeabilities [18, 27]. However, these solutions can leave behind a high amount of residue if they are too viscous [22, 38].
2.3.1 Fluid Properties

In order to fully understand the complexity of fracking fluid flow, it is important to have a general understanding of fluid dynamics. Newtonian fluids are the simplest to understand when it comes to viscosity. A Newtonian fluid is a fluid that displays a linear relationship between shear stress and rate of strain following

\[ \tau = \eta \frac{du}{dy}, \quad (2.1) \]

where \( \tau \) is the shear stress in the fluid, \( \eta \) is a proportionality constant, which is the dynamic viscosity, and \( \frac{du}{dy} \) is the rate of strain of the fluid. This relationship dictates that the viscosity, \( \eta \), of Newtonian fluids is constant with respect to the applied shear stress.

Flow of Newtonian fluids through porous media can be described by Darcy’s law

\[ Q = \frac{-\kappa A \Delta P}{\eta L}, \quad (2.2) \]

where \( Q \) is the flow rate, \( \kappa \) is the intrinsic permeability, \( A \) is the cross sectional area of the flow column, \( \eta \) is the dynamic viscosity of the fluid, \( \Delta P \) is the difference in pressure over the porous media, and \( L \) is the length of the porous media. This equation relies on the direct proportionality relationship between flow rate and pressure difference over the system.

Darcy’s law can be written in terms of a darcy velocity or flux, \( q \) by dividing through by \( A \) to get

\[ q = \frac{-\kappa}{\eta} \nabla P \quad (2.3) \]
where $\nabla P$ is the pressure gradient. This equation describes the flow of a fluid through a porous medium given a pressure gradient, but it no longer applies if the fluid is non-ideal.

There are different types of non-ideal, or non-Newtonian, fluids. Non-Newtonian fluids have a viscosity that is dependent on shear rate and, therefore, is no longer constant. This makes describing the flow properties of non-Newtonian fluids complicated. Two common classes of non-Newtonian fluids are shear thickening liquids and shear thinning liquids. Shear thickening liquids exhibit an increased viscosity as the shear rate increases. Shear thinning fluids are fluids whose viscosity decreases with increased shear rates. These types of fluids are often used in oil-field applications, including in hydraulic fracturing [16, 19, 23, 28, 29].

Two common relationships used to describe non-Newtonian fluids are the power law and the Cross model. Both of these provide an expression for an apparent or effective viscosity that is dependent on shear rate. For power law fluids, shear stress, $\tau$, is given by

$$
\tau = K \left( \frac{\partial u}{\partial y} \right)^n
$$

(2.4)

where $K$ is the flow consistency index, $\partial u/\partial y$ is the shear rate, also written as $\dot{\gamma}$, and $n$ is a flow behavior index that is dimensionless and reflects the closeness to Newtonian flow. The apparent viscosity, $\eta_{app}$ is given by

$$
\eta_{app} = K \left( \frac{\partial u}{\partial y} \right)^{n-1}.
$$

(2.5)

When the flow behavior index is equal to one, the power law simplifies to Eqn (2.1), which means the fluid is Newtonian [28]. A flow behavior index less than one means that $\eta_{app}$
decreases as shear rate increases and therefore applies to a shear thinning fluid. Conversely, a flow behavior index greater than one means that $\eta_{app}$ increases as shear rate increases, so this applies to shear thickening fluids. The power law is appealing due to its simplicity, but it is also limited in its ability to describe the behavior of real fluids. Because of this limitation, the power law only describes fluid behavior well over a limited range of shear rates and does not produce good results at high or low shear rates for fluids of common interest [28].

The Cross model is another option for describing non-Newtonian fluids that can exhibit both Newtonian and power law type behaviors. It provides an equation for $\eta_{app}$ according to

$$\eta_{app} = \frac{\eta_0}{1 + (\eta_0 \dot{\gamma}/\tau^*)^{1-n}} \quad (2.6)$$

where $\eta_0$ is the viscosity at zero shear rate, $\dot{\gamma}$ is the shear rate, $\tau^*$ is the shear stress at the transition between Newtonian and power law behavior, and $n$ is the flow behavior index [13]. At low shear rates, $\eta_0 \dot{\gamma} \ll \tau^*$, and the fluid behaves like a Newtonian fluid. At high shear rates, $\eta_0 \dot{\gamma} \gg \tau^*$, and the fluid behaves like a power law fluid.

The rheological properties of fracking fluids are of vital importance to the fracturing process. These properties, in large part, determine the parameters of the fractures created by hydraulic fracturing [16]. Fracking fluids must be viscous enough to keep the proppant from settling prematurely, but fluids that are too viscous could clog the fractures and rock pores. Additionally, excessively viscous fluids are more likely to remain in the fracture after the fracturing process is complete, which reduces the conductivity of the fracture [22].
2.3.2 Guar Gum

A commonly used gelling agent in fracking fluids is guar gum. Guar gum is a polysaccharide and is used as a thickening agent across a broad range of disciplines. It is commonly used in the food, textile, and pharmaceutical industries, and more recently in hydraulic fracturing. Guar gum is derived from guar beans, which have historically been grown in India and Pakistan, and more recently in the United States. The powdered guar gum is obtained by removing the beans from their casing via water or acid soaking. The beans are ground to remove the embryo, which is then ground further into a powder [14].

![Chemical structure of guar gum](image)

Figure 2.1: Chemical structure of guar gum

Guar gum is a type of polysaccharide called galactomannon, which is characterized by a mannose backbone and galactose side chains, as shown in Figure 2.1. The molecular weight of guar gum varies from 440,000 to 650,000 Da, depending on the polysaccharide chain length [2]. Guar gum is an appealing choice as a thickening agent, in addition to its viscosity-enhancing capabilities, because it is a natural polysaccharide. This means that it is relatively low cost and has high capability to withstand mechanical and thermal
Guar gum is water soluble and changes the physical characteristics of its solutions. The addition of low quantities of guar gum can result in greatly increased viscosities of solutions. These changes in viscosity of the solvent are due to the high molecular weight polymeric nature of gums [2, 40]. Guar gum is a shear thinning fluid, which means that its apparent viscosity decreases as shear rate increases. The range of guar gum concentrations used in fracking fluids is generally between 0.5 g/L and 5 g/L [6].
CHAPTER 3: EXPERIMENTAL METHODS

3.1 Guar gum solutions

The guar gum solutions used in these experiments were prepared by weight. Guar gum solutions of 0.5, 3, and 5 g/L were prepared by weighing out the appropriate amount of solid guar gum (S-4500-G industrial grade guar gum), which was then mixed with deionized water to get the desired concentration. Sodium Azide (NaN$_3$, Aldrich Chemical 19993-1) was added to each solution, at an amount of 0.02% to prevent biological growth from occurring. Each solution was then well mixed using a blender to break apart the large clumps of guar gum, resulting in a frothy solution. The solutions were allowed to mix further using a magnetic stir bar until the solution appeared visibly homogeneous. This occurred over a period of 4-48 hours, depending on the concentration of the solution.

Once the guar gum in each solution had fully dissolved and air bubbles had settled out, the solutions were filtered through a 1.5 micron glass fiber filter (Baxter Scientific Products Filter Paper, grade 394 glass fiber) into a preweighed vacuum flask. Prior to filtering, the 3 and 5 g/L solutions were centrifuged in 50 mL plastic centrifuge vials at 4600 rpm for approximately 1.5 hours to allow a majority of the large particles to settle out. Each filter was weighed before and after filtering the solution. Additionally, the vacuum flask, which caught the filtrate, was weighed before and after filtering. These weights were then used to determine the amount of guar gum remaining in solution.
Guar gum solutions of 1, 2, and 4 g/L were also prepared in order to be tested on a rheometer. The 4 g/L solution was prepared using the same methods as the previous solutions, and 0.02% NaN₃ was added to this solution. The 1 and 2 g/L solutions were made using serial dilutions of the 3 g/L solution, since the amount needed of these solutions for testing on the rheometer was much less than the amount needed to run column flow experiments. Each of these solutions was filtered through a 1.5-micron syringe filter (Whatman GD/X syringe filter 934-AH).

3.2 Column Experiments

3.2.1 Column setup

Column experiments were conducted in a vertically oriented glass column (ACE Glass) with 2.5-cm inside diameter, as shown in Figure 3.2. The column was set up by first inserting a polytetrafluoroethylene (PFTE) plunger with a wetted o-ring seal and a steel mesh filter into the bottom of the column. Next, the column was filled with 20/30 Accusand, and the mass of sand added was recorded. Then, a second plunger with o-ring and a steel mesh filter was inserted into the top of the column. An air compressor was then used to vibrate the sand, which removed air pockets. The compressor was used to agitate the column until all air pockets had been removed, after which the top plunger was further pushed in until firmly touching the sand.

Each plunger contained a 2-mm inside diameter tube that was connected to a three-way valve. The line feeding the bottom end led to a programmable syringe pump (PHD 4400 programmable pump), while the line on the top end was open to the atmosphere during
experiments. A stainless steel tube with 2-mm inside diameter leading to a collection flask was connected to the top end three-way valve to ensure the outlet height remained constant throughout all experiments.

After the sand was fully compacted, the length of the filled column was measured and found to be 26.55 cm. The mass of sand added to the column was divided by the density of the sand to calculate the pore volume of the column, which was found to be 44.49 mL. Additionally, the porosity of the column was calculated by dividing the pore volume by the total volume of the column; this was found to be 0.340. After the column was packed with sand, CO$_2$ was then pumped through the column upwards to displace the air in the system. Next, de-ionized (DI) water was pumped through the column, upwards, at a rate
of 10 mL/hr to displace the CO$_2$, until at least 5 and up to 10 pore volumes of water moved through the system.

### 3.2.2 Pressure transducer calibration

Calibration provides a way to convert the pressure value obtained by the data acquisition program, in mV, to psi. There were two pressure transducers used over the course of these experiments, and both were calibrated using a water-filled manometer. In both cases, the pressure transducers (Omega PX800-010GV, Omega PX800-001GV) recorded the pressure at various heights of water. The relationship between cm H$_2$O and psi, 

\[ 1 \text{cm H}_2\text{O} \approx 0.0142 \text{ psi}, \tag{3.7} \]

was used to make a calibration curve relating mV to psi.

### 3.2.3 Tracer tests

A series of tracer tests was performed on the column using a stock solution of tritiated water (T$_2$O), a radioactive form of H$_2$O where the hydrogen atoms are replaced with tritium ($^3$H or T), and guar gum solutions of varying concentrations. The results of the tracer tests were used to measure column properties such as porosity and dispersivity. Initially, T$_2$O was pumped upwards through the column at a flow rate of 10 mL/hr. Samples were collected in 20 mL plastic scintillation vials, which were numbered and weighed prior to the experiment. Samples were taken every 2.5 mL, or every 15 minutes, until approximately two pore volumes had been pumped through the column. They were then weighed again.
and mixed with 7.5 mL scint cocktail (ScintiSafe 30% LSC-Cocktail) and analyzed on a scintillation counter (Packard 1900 TR Liquid Scintillation Analyzer) to determine the disintegrations per minute (DPM). Finally, this value for each sample was divided by the volume of the sample to find DPM per mL.

Next, a 0.5 g/L guar gum solution made with regular DI water was pumped through the column to replace the T$_2$O, also at 10 mL/hr for approximately two pore volumes. Then, a tritiated 3 g/L guar gum solution was pumped through the column in the same manner, displacing the 0.5 g/L solution. Finally, a 5 g/L guar gum solution was pumped through the column. During each of these three steps, samples were collected every 2.5 mL, or 15 minutes, until approximately 2 pore volumes had been collected. The samples were processed and counted as described above. Additionally, the pressure of the column system was recorded continuously throughout the process using a pressure transducer.

### 3.2.4 Column flow experiments

A series of column flow experiments was conducted throughout this study, in which filtered 0.5, 3, or 5 g/L guar gum solutions were pumped through the column using a 60-mL plastic syringe. The solutions were pumped upwards at various flow rates using the programmable pump. The column pressure was measured during this process using a pressure transducer (Omega PX800 Series). The pressure transducer was located on the line between the pump and the inlet to the bottom of the column, and the column outlet was open to the atmosphere.

The pressure transducer recorded a reading every second. The pressure at each flow rate was determined by allowing the solution to be pumped at a given flow rate for a period of
at least 40 seconds while the pressure reading was stable. This resulted in a collection of at least 40 pressure readings for each flow rate. These readings were then averaged over the stable time period for each individual flow rate, giving a single point for each flow rate. A baseline pressure corresponding to the hydrostatic pressure of the column was obtained by taking a pressure reading at no flow through the column. This value was subtracted from the readings where there was flow in the column, giving a pressure difference or drop over the length of the column. This measurement was then converted to psi.

In cases where the pressure was too low to obtain an accurate reading, a meter stick manometer was used to record the pressure instead. In these cases, a pressure reading was taken every 10 minutes, until the pressure readings were stable for three consecutive readings. The height of the column outlet was subtracted from the height of the stable pressure reading at the inlet to obtain the measurement for the pressure drop in psi.

These experiments were repeated three times for each guar gum solution over the same range of flow rates. Two of the three replicates were done in increasing flow rate order, while the third was performed in decreasing flow rate order. This was done to ensure that there was no pressure build up occurring as flow rates increased. After one set of triplicate experiments was completed, the solution in the column was replaced with the next solution. The 0.5 g/L solution experiments were done first, followed by the 5 g/L solution. To switch from the 0.5 g/L solution to the 5 g/L solution, 5 g/L guar gum was flushed upwards at a flow rate of 10 mL/hr for 3 pore volumes. Pressure readings were taken continuously throughout this process and became stable after just over 2 pore volumes.

Again, a set of triplicate experiments was run using the 5 g/L solution, after which the solution was replaced with 3 g/L guar gum. To minimize unstable density driven flow
effects, the 3 g/L solution was pumped downwards. One syringe full, or about 60 mL, of dyed 3 g/L guar gum was pumped downwards at 10 mL/hr. The solution was dyed using red food coloring so that the front could be easily tracked moving through the column. After the colored solution made it all the way through the column and was exiting through the bottom outflow, the flow direction was switch back to being upwards. Uncolored 3 g/L guar gum was flushed through the column upwards at 10 mL/hr for about 2 pore volumes, at which point no colored solution was left in the column. Again, pressure readings were taken continuously while the solution was flowing upwards and became stable after the first upward pore volume.

3.3 Rheometer

The rheological properties of guar gum solutions of concentrations 0.5, 1, 2, 3, 4, and 5 g/L were measured using a rheometer (TA Instruments AR-G2 6J3194). Each solution was tested at least twice, with at least one run being an unfiltered solution and a second being a filtered solution of the same concentration. The samples were tested at 22 degrees Celsius, using a 40 mm cone to find apparent viscosities of each solution over a range of shear rates in both ascending and descending directions. The resulting sets of data were each fit to the Cross model Eqn (2.6).

The Cross model equation found for each concentration solution was combined into one equation which included concentration as a variable. This was done by finding a statistical fit for the parameters in the Cross model equation ($\eta_0$, $\tau^*$, and $n$), resulting in an equation for each parameter that is a function of concentration (C). The resulting equation followed the form:
\[ \eta = \frac{\eta_0 (C)}{1 + (\eta_0 (C) \dot{\gamma}/\tau^*(C))^{1-n(C)}}. \]  

(3.8)
CHAPTER 4: RESULTS

4.1 Column experiments

4.1.1 Pressure transducer calibration

Both calibrations provided a relationship between voltage (mV) and pressure (psi) using a meter stick manometer setup. The first calibration was done for a transducer, T1, capable of recording pressures up to 10 psi. In this case, pressures were recorded at 10 cm intervals from 1 m of water up to 2 m of water, and additionally at 50 cm and 0 cm water. The resulting calibration curve (Figure 4.3a) displayed a linear trend between mV and psi. The slope for the curve using this method was 0.1052, and the intercept was -0.3342. This calibration resulted in an R² of 0.9988.

\[
y = 0.1052x - 0.3342
\]

\[
R^2 = 0.99878
\]

(a) Pressure transducer calibration for transducer T1

The second calibration also provided a relationship between voltage (mV) and pressure...
(psi) using a water manometer setup. The transducer used in this calibration, T2, was capable of recording pressures up to 1 psi and allowed for more sensitive measurement of low pressures. As with the first calibration, pressures were recorded at 10 cm intervals over a range of 15 cm to 75 cm. The calibration curve resulting from this method can be seen in Figure 4.3b, which shows a slope of 0.0637 and an intercept of -0.2186. The R$^2$ value for this curve was 0.9997.

4.1.2 Tracer test results

The results found by the tracer tests can be seen in Figure 4.4, which shows the tracer results for each concentration guar gum solution (GG) compared to the T$_2$O tracer results (H3). The time for each test was started when the syringe pump was started. At time $t = 0$, the solution of interest was at the valve connected to the tubing extending from the bottom of the column. There was approximately 12.4 cm of tubing between this valve and the bottom of the porous media filling the column. Thus, the time was adjusted for all tracer tests to account for the time it took for the fluid to reach the bottom boundary of the column. Additionally, the radiation concentrations (in DPM per mL) were normalized for each solution. The greatest dispersivity resulted from the T$_2$O tracer test. In this case, the dispersion coefficient was 0.404 cm$^2$/hr. The dispersivity decreased going from T$_2$O to 0.5 g/L guar gum, giving a dispersion coefficient of 0.279 cm$^2$/hr. The dispersivity decreased again after replacing the 0.5 g/L guar gum with tritiated 3 g/L guar gum. The dispersion coefficient after this step was 0.227 cm$^2$/hr. Finally, the dispersion coefficient after replacing the tritiated 3 g/L guar gum with 5 g/L guar gum was 0.234 cm$^2$/hr.
Figure 4.4: Tracer test results and curve fits
4.1.3 Column flow experiment results

Table 4.3 shows the averaged pressure difference and standard deviation for each flow rate. The standard deviation was calculated using a compounded error method; the standard deviation was calculated for the stable pressure period of each flow rate. This resulted in three standard deviations corresponding to one flow rate. The total standard deviation for a single flow rate was calculated using the equation

$$
\sigma_T = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}
$$

(4.9)

where $\sigma_T$ is the total standard deviation and $\sigma_1$, $\sigma_2$, and $\sigma_3$ are the standard deviations for the first, second, and third replicates, respectively. The standard deviation did not vary much, ranging from 0.031 at the lowest to 0.040 at the highest. These values are relatively high compared to the difference between each average pressure drop value. The average pressure difference increased linearly with flow rate for the 0.5 g/L guar gum solution, as shown in Figure 4.5. Additionally, the average pressure drop versus flow rate for DI water is shown in Figure 4.5. Water is a Newtonian fluid and has a linear relationship between pressure difference and flow rate.

The apparent viscosity was calculated using the pressure drop data and Darcy’s law Eqn (2.2). Figure 4.6 shows these viscosities calculated for the 0.5 g/L guar gum solution and for DI water plotted against flow rate. The viscosity for water is relatively constant, as it should be since it is Newtonian. The viscosity of water from these experiments was found to be about 0.90 cP, which is close to the known viscosity value for water at 22 degrees Celsius (0.95 cP). This figure also shows that the viscosity of the 0.5 g/L guar gum solution
Table 4.3: Column flow results for the 0.5 g/L filtered guar gum solution

<table>
<thead>
<tr>
<th>Flow rate (mL/hr)</th>
<th>Average pressure difference (psi)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.065</td>
<td>0.032</td>
</tr>
<tr>
<td>25</td>
<td>0.074</td>
<td>0.032</td>
</tr>
<tr>
<td>50</td>
<td>0.085</td>
<td>0.031</td>
</tr>
<tr>
<td>75</td>
<td>0.102</td>
<td>0.031</td>
</tr>
<tr>
<td>100</td>
<td>0.119</td>
<td>0.038</td>
</tr>
<tr>
<td>125</td>
<td>0.135</td>
<td>0.038</td>
</tr>
<tr>
<td>150</td>
<td>0.148</td>
<td>0.037</td>
</tr>
<tr>
<td>175</td>
<td>0.159</td>
<td>0.035</td>
</tr>
<tr>
<td>200</td>
<td>0.171</td>
<td>0.036</td>
</tr>
<tr>
<td>250</td>
<td>0.195</td>
<td>0.033</td>
</tr>
<tr>
<td>300</td>
<td>0.220</td>
<td>0.037</td>
</tr>
<tr>
<td>350</td>
<td>0.243</td>
<td>0.034</td>
</tr>
<tr>
<td>400</td>
<td>0.266</td>
<td>0.035</td>
</tr>
<tr>
<td>450</td>
<td>0.290</td>
<td>0.032</td>
</tr>
<tr>
<td>500</td>
<td>0.311</td>
<td>0.035</td>
</tr>
<tr>
<td>550</td>
<td>0.337</td>
<td>0.037</td>
</tr>
<tr>
<td>600</td>
<td>0.364</td>
<td>0.032</td>
</tr>
<tr>
<td>650</td>
<td>0.395</td>
<td>0.039</td>
</tr>
<tr>
<td>700</td>
<td>0.412</td>
<td>0.036</td>
</tr>
<tr>
<td>800</td>
<td>0.464</td>
<td>0.034</td>
</tr>
<tr>
<td>900</td>
<td>0.518</td>
<td>0.040</td>
</tr>
<tr>
<td>1000</td>
<td>0.568</td>
<td>0.034</td>
</tr>
</tbody>
</table>
decreases with flow rate, which is as expected for shear thinning fluids.

![Graph showing pressure drop vs flow rate]

Figure 4.5: Column flow results for the 0.5 g/L filtered guar gum solution and water

![Graph showing viscosity vs flow rate]

Figure 4.6: Viscosity versus flow rate for the 0.5 g/L filtered guar gum solution and water

The average pressure difference and standard deviations corresponding to each flow rate for the 3 g/L guar gum solution can be found in Table 4.4. The standard deviation for each flow rate was calculated in the same manner as above, by averaging the three standard deviations found for a single flow rate in the repeated experiments. This resulted
in a relatively constant standard deviation of about 0.045. The pressure difference was not linearly related to flow rate for the 3 g/L solution. This can be seen in Figure 4.7. Pressures initially increased quickly, then began to increase at a slower rate as flow rates increased.

Table 4.4: Column flow results for the 3 g/L filtered guar gum solution

<table>
<thead>
<tr>
<th>Flow rate (mL/hr)</th>
<th>Average pressure difference (psi)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.155</td>
<td>0.048</td>
</tr>
<tr>
<td>10</td>
<td>0.246</td>
<td>0.041</td>
</tr>
<tr>
<td>20</td>
<td>0.407</td>
<td>0.042</td>
</tr>
<tr>
<td>30</td>
<td>0.539</td>
<td>0.044</td>
</tr>
<tr>
<td>40</td>
<td>0.674</td>
<td>0.048</td>
</tr>
<tr>
<td>50</td>
<td>0.793</td>
<td>0.045</td>
</tr>
<tr>
<td>60</td>
<td>0.896</td>
<td>0.040</td>
</tr>
<tr>
<td>70</td>
<td>1.003</td>
<td>0.038</td>
</tr>
<tr>
<td>80</td>
<td>1.100</td>
<td>0.041</td>
</tr>
<tr>
<td>90</td>
<td>1.196</td>
<td>0.042</td>
</tr>
<tr>
<td>100</td>
<td>1.275</td>
<td>0.040</td>
</tr>
<tr>
<td>125</td>
<td>1.479</td>
<td>0.042</td>
</tr>
<tr>
<td>150</td>
<td>1.671</td>
<td>0.047</td>
</tr>
<tr>
<td>175</td>
<td>1.851</td>
<td>0.042</td>
</tr>
<tr>
<td>200</td>
<td>2.024</td>
<td>0.048</td>
</tr>
<tr>
<td>225</td>
<td>2.171</td>
<td>0.043</td>
</tr>
<tr>
<td>250</td>
<td>2.317</td>
<td>0.043</td>
</tr>
<tr>
<td>275</td>
<td>2.464</td>
<td>0.043</td>
</tr>
<tr>
<td>300</td>
<td>2.603</td>
<td>0.047</td>
</tr>
<tr>
<td>400</td>
<td>3.090</td>
<td>0.049</td>
</tr>
<tr>
<td>500</td>
<td>3.530</td>
<td>0.049</td>
</tr>
</tbody>
</table>
Table 4.5 shows the average pressure difference and standard deviation corresponding to each flow rate for the 5 g/L guar gum solution. Again, standard deviations were found by calculating the compounded standard deviation, following Eqn (4.9). This method takes the square root of the sum of the standard deviation squared for each replicate at single flow rate. Standard deviations varied a bit more between each flow rate for the 5 g/L solution, ranging from 0.045 to 0.115. Despite this increased variation, the total standard deviation for each flow rate is still small compared to its average pressure drop value. Figure 4.8 shows that pressure difference and flow rate were not linearly related. As with the 3 g/L solution, pressure differences initially increased rapidly, then gradually increased at a slower rate as flow rate increased.

The results for the column flow experiments for all three concentrations can be seen in Figure 4.9. As expected, pressures increased with concentration. The pressure differences for the 5 g/L solution increased at a much quicker rate than both the 3 g/L and 0.5 g/L
Table 4.5: Column flow results for the 5 g/L filtered guar gum solution

<table>
<thead>
<tr>
<th>Flow rate (mL/hr)</th>
<th>Average pressure difference (psi)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.131</td>
<td>0.054</td>
</tr>
<tr>
<td>5</td>
<td>0.468</td>
<td>0.048</td>
</tr>
<tr>
<td>10</td>
<td>0.794</td>
<td>0.064</td>
</tr>
<tr>
<td>20</td>
<td>1.369</td>
<td>0.069</td>
</tr>
<tr>
<td>30</td>
<td>1.804</td>
<td>0.072</td>
</tr>
<tr>
<td>40</td>
<td>2.196</td>
<td>0.077</td>
</tr>
<tr>
<td>50</td>
<td>2.532</td>
<td>0.058</td>
</tr>
<tr>
<td>60</td>
<td>2.868</td>
<td>0.060</td>
</tr>
<tr>
<td>70</td>
<td>3.142</td>
<td>0.053</td>
</tr>
<tr>
<td>80</td>
<td>3.397</td>
<td>0.056</td>
</tr>
<tr>
<td>90</td>
<td>3.669</td>
<td>0.066</td>
</tr>
<tr>
<td>100</td>
<td>3.932</td>
<td>0.062</td>
</tr>
<tr>
<td>125</td>
<td>4.477</td>
<td>0.056</td>
</tr>
<tr>
<td>150</td>
<td>4.960</td>
<td>0.055</td>
</tr>
<tr>
<td>175</td>
<td>5.396</td>
<td>0.045</td>
</tr>
<tr>
<td>200</td>
<td>5.809</td>
<td>0.115</td>
</tr>
<tr>
<td>225</td>
<td>6.229</td>
<td>0.071</td>
</tr>
<tr>
<td>250</td>
<td>6.589</td>
<td>0.076</td>
</tr>
<tr>
<td>275</td>
<td>6.939</td>
<td>0.061</td>
</tr>
<tr>
<td>300</td>
<td>7.254</td>
<td>0.084</td>
</tr>
</tbody>
</table>
Figure 4.8: Column flow results for the 5 g/L filtered guar gum solution with standard deviation error bars

solutions. Moreover, the difference in pressure drop between the three solutions increased as flow rate increased. At a flow rate of 5 mL/hr the difference in pressure drop between the 5 g/L solution and the 3 g/L solution was only 0.313 psi, while the difference at 300 mL/hr was 4.651 psi.

Additionally, the graphs of apparent viscosity versus flow rate for all three guar gum solutions can be seen in Figure 4.10. This graph shows that the 3 and 5 g/L solutions experience a large decline in apparent viscosity as flow rate increases, which is consistent with shear thinning behavior. The 0.5 g/L solution also decreases in apparent viscosity as flow rate increases, but has a much smaller range of viscosities compared to the higher concentration solutions.
Figure 4.9: Column flow results

Figure 4.10: Viscosity calculated from Darcy’s law and column flow data
4.2 Rheometer

The complete results from the rheometer testing and subsequent line fitting are shown in Figure 4.11. These results show that apparent viscosity increases with concentration. Additionally, the results also show that for a single concentration, apparent viscosity decreases with shear rate. This is as expected, since guar gum is a shear thinning fluid. Figure 4.12 shows that there was no significant difference between the filtered and unfiltered 5 g/L guar gum solutions. This was true for all concentrations.

All concentrations showed the same general trend, beginning with a relatively constant or slowly decreasing apparent viscosity at low shear rates. As shear rates increased, the apparent viscosities began to decrease more rapidly in a linear trend. This pattern was more pronounced in the higher concentration solutions. In the 1 and 0.5 g/L solutions, this trend is greatly diminished, making their apparent viscosities versus shear rates seem almost entirely linear.

![Figure 4.11: Rheometer results with lines fit](image-url)
4.2.1 Rheometer data fitting results

As previously stated, the Cross model equation (2.6) was used to fit lines to the rheometer data. The values found for each parameter, as well as the $R^2$ value for each fit, are shown in Table 4.6.

Table 4.6: Cross model parameters for rheometer data

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>$\eta_0$</th>
<th>$\tau^*$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.004823</td>
<td>4.2</td>
<td>0.9177</td>
<td>0.9649</td>
</tr>
<tr>
<td>1</td>
<td>0.007517</td>
<td>4.542</td>
<td>0.785</td>
<td>0.9108</td>
</tr>
<tr>
<td>2</td>
<td>0.03422</td>
<td>3.402</td>
<td>0.5035</td>
<td>0.9413</td>
</tr>
<tr>
<td>3</td>
<td>0.1606</td>
<td>3.447</td>
<td>0.3803</td>
<td>0.9946</td>
</tr>
<tr>
<td>4</td>
<td>0.399</td>
<td>4.1</td>
<td>0.3465</td>
<td>0.9969</td>
</tr>
<tr>
<td>5</td>
<td>1.362</td>
<td>3.766</td>
<td>0.345</td>
<td>0.9763</td>
</tr>
</tbody>
</table>

Comparing each of these parameter results to concentration shows that $\eta_0$ is exponentially related to concentration (Figure 4.13a), while $n$ is quadratically related to concentration.
The relationship between $\tau^*$ and concentration is less distinct, as $\tau^*$ appears to be almost independent of concentration as seen in Figure 4.13c. The relationships found between each parameter and solution concentration were used to obtain a Cross model curve for each concentration shown in figure 4.11.

Figure 4.13: Cross model parameters fit to rheometer data
CHAPTER 5: DISCUSSION

5.1 Viscosity model choice

Many studies examining the flow of non-Newtonian fluids through porous media assume that the fluid is a power law fluid [4, 16, 17, 19, 26, 31, 39]. The power law is a popular choice for modeling non-Newtonian fluids due to its simplicity, as it contains only two parameters. Figure 5.14 shows the general rheology of power law fluids in log-log scale. Despite its appeal, the simplicity of the power law can lead to a failure to capture important rheological properties of the fluid, especially at low and high shear rates. For instance, as shown in Figure 4.11, guar gum solutions have a period of relatively constant apparent viscosities at low shear rates. This property can not be captured by the power law, and for this reason, the power law is a poor choice to use as a model for these solutions.

![Rheology of a power law fluid in log-log scale](image)

Figure 5.14: Rheology of a power law fluid in log-log scale [28]

More recently, other models have been used to model non-Newtonian shear thinning
fluids, including the Carreau, Ellis, and Cross models [23, 28, 29, 33]. The Ellis model is a three-parameter model that describes shear-thinning fluids. It has intermediate complexity, being more complex than the power law but less complex than the Carreau and Cross models. Ellis fluids exhibit a viscosity plateau at low shear rates, however they do not display a plateau at high shear rates, as shown in Figure 5.15. The Ellis model is better than the power law at matching experimental data, and is given by the relation

\[ \eta = \frac{\eta_0}{1 + \left( \frac{\tau}{\tau_{1/2}} \right)^{\alpha - 1}} \]  

(5.10)

where \( \eta \) is the fluid viscosity, \( \eta_0 \) is the low shear rate viscosity, \( \tau \) is the shear stress, \( \tau_{1/2} \) is the shear stress at which \( \eta = \eta_0/2 \), and \( \alpha \) is a parameter related to the power law index by \( \alpha = 1/n \). The Ellis model is good for non-Newtonian fluids that only deviate significantly from power law behavior at low shear rates [21, 29]. An advantage of this model is its relative simplicity which allows for easy calculation of velocity profiles given a known stress distribution [21]. However, the reverse calculation is unwieldy using the Ellis model.

![Figure 5.15: Rheology of an Ellis fluid in log-log scale [28]](image-url)
The Carreau model is the most complex of this group and includes four parameters:

\[
\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda \dot{\gamma})^{n-1}},
\]  

(5.11)

where \(\eta_\infty\) is the viscosity at infinite shear rate and \(\lambda\) is a characteristic time. Figure 5.16 shows the general rheology of Carreau fluids in log-log scale. Carreau fluids display viscosity plateaus in low and high shear regions and is able to describe shear thinning behavior over a wide range of shear rates [21, 24]. The inclusion of a fourth parameter allows for more accurate fluid behavior descriptions over a wider range of shear rates, but at the cost of added complexity.

![Rheology of a Carreau fluid in log-log scale](image)

Figure 5.16: Rheology of a Carreau fluid in log-log scale [28]

The full Cross model is very similar to the Carreau model in form. It is also a four-parameter model given by the relation

\[
\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\eta_0 \dot{\gamma}/\tau^*)^{1-n}},
\]  

(5.12)

A generic graph of a Cross fluid has the same shape and features as a generic graph of a
Carreau fluid, such as in Figure 5.16.

Both the Carreau and Cross models can be modified by excluding $\eta_\infty$. Modification of the models is often done when the magnitude of $\eta_\infty$ is very small and, therefore, difficult to determine experimentally. This is the case with many polymers derived from gums, such as guar gum [24]. For this reason, combined with the limitations of the rheometer used, Eqn (2.6), which neglects $\eta_\infty$, was used to fit the rheometer results from these experiments.

While the Ellis model and the modified Cross and Carreau models all have the ability to match the experimental data obtained for the guar gum solutions, the Cross model was chosen for multiple reasons. As previously stated, the Ellis model is initially appealing due to its relative simplicity, but ultimately was not the best choice because calculating shear rate distributions from velocity profiles is tedious using the Ellis model. Moreover, future experiments might extend the range of shear rates examined so that the lower viscosity limit $\eta_\infty$ is observed. The Ellis model does not include this parameter, so its ability to accurately describe the data would be limited. The Cross and Carreau models were both fit to the current data, and the modified Cross model provided the best fit, so it was chosen over the Carreau model.

5.2 Guar gum rheology

The column flow data combined with the rheometer data obtained from these experiments provide data for the rheology of guar gum at different scales. The porous medium system that makes up the column gives a megascale flow regime for the guar gum solutions. This provides insight as to how fracking solutions would behave when being pumped into wells. However, to have a complete understanding of the rheology of fracking fluids, microscale
information is needed as well. This is because the length scale of porous medium systems is large compared to the pore size made up by the medium [8]. In terms of fracking systems, in order to predict how fracking fluids would behave while in the fractures created by hydraulic fracturing or in the pore space of a porous media, it is necessary to have a microscale view of its flow properties. The rheometer data obtained from this study provide microscale measurements that can be used to formulate a model describing the flow properties. This model must then be averaged up to be meaningful at the megascale.

Much of the current understanding of fluid flow in porous media has been established for Newtonian fluids. The viscosities of Newtonian fluids are independent of shear rate and can be described using Darcy’s law. As shown in Figure 4.9, guar gum solutions in general do not have a linear flow profile and, therefore are non-Newtonian. This means that the viscosity of the solutions varies with shear stress, which is corroborated by the rheometer data obtained, shown in Figure 4.11. The variation of viscosity with shear stress means that each pore will have a different velocity profile.

Additionally, a common approach to modeling non-Newtonian flow through porous media has been to represent the medium as a bundle of capillary tubes [3, 4, 10, 26]. This method provides a simplified representation of the media, which can fail to consistently predict behavior of shear-thinning fluids at the macroscale given bulk properties of the fluid. Instead, microscale simulations could be used to more realistically model porous media systems. Microscale simulations provide a detailed analysis of these non-Newtonian systems without having to oversimplify the rheology of the fluid or the representation of the media. Preliminary collaborative work has been done to model the observed systems at the pore scale and compare the results to the column-scale observations made with relatively good
agreement observed.

5.3 Comparison to previous methods

There have been numerous studies whose aim is to predict single phase properties of shear thinning fluids in a porous medium from the bulk rheology of the fluid [3, 4, 10, 26, 39]. These studies derive expressions for an apparent shear rate ($\gamma_{\text{app}}$) felt by the fluid in the porous medium. Many of these studies begin from a bundle of capillary tubes approach to representing the porous medium, and they also assume that the non-Newtonian fluid can be represented by the power law. This is often a valid assumption, as many shear thinning fluids display a region of power law behavior with intermediate shear rates. However, this is not entirely satisfactory when looking at shear rates corresponding to fracking practices, since flow rates can vary widely.

The shear rate model proposed by Christopher and Middleman [4] is shown in Eqns (5.13-5.15). This formulation is derived from the Hagen-Poiseuille equation for flow in a long, straight capillary. It also assumes that the permeability of the porous medium is the same for all identical packed bed configurations, independent of flow conditions in the bed.

$$\gamma_{\text{app}} = \left( \frac{3n + 1}{4n} \right) \frac{12G}{\rho \sqrt{150 \kappa \epsilon}}$$

(5.13)

where $G$ is mass velocity calculated from a pressure difference and is given by

$$G = \rho \left( \frac{\kappa \Delta P}{H L} \right)^{1/n}.$$  

(5.14)
In this equation, $\Delta P$ is the pressure drop, $\kappa$ is the permeability, $L$ is the unit length, $n$ is the flow behavior index determined by the power law, and $H$ is the non-Newtonian bed factor given by

$$H = \frac{K}{12} \left( \frac{9 + 3}{n} \right)^n (150\kappa\epsilon)^{\frac{1-n}{2}} \quad (5.15)$$

where $K$ is the power law parameter.

A second common shear rate model was proposed by Hirasaki and Pope [10], which is shown in equation Eqn (5.16). This model is also based on a bundle of capillary tubes representation for non-Newtonian fluid flow and applies to power law fluids. The Hirasaki and Pope model is derived from the Blake-Kozeny equation, whose starting point is the Hagen-Poiseuille equation. This model uses a bundle of capillary tubes approach.

$$\gamma_{app} = \left( \frac{3n + 1}{4n} \right) \frac{n}{n-1} \frac{12q}{\sqrt{150\kappa\epsilon}} \quad (5.16)$$

Chauveteau and Zaitoun [3] also proposed a model for shear rate at the wall of the pore, shown by equation Eqn (5.17). This formulation was determined both experimentally and using dimensional analysis and is given by

$$\gamma_{app} = \alpha \frac{4q}{r} \quad (5.17)$$

where $\alpha$ is a shape parameter of the pore structure. The value of $\alpha$ was determined experimentally, and was found to be $\alpha = 1.7$ for packs of large spheres with the same diameter. This value increases with increased pore structure heterogeneity. The average pore throat
radius, \( r \), is estimated from the bundle of capillary tubes model, given by

\[
    r = \left( \frac{8\kappa}{\epsilon} \right)^{1/2}.
\]  

(5.18)

The shear rate model proposed by Sabiri and Comiti [26] is shown in equation Eqn (5.19). It is formulated for a power law fluid and uses a modified capillary bundle representation for the porous medium, which takes into account structural parameters for the media.

\[
    \gamma_{app} = \left( \frac{3n + 1}{2n} \right) \frac{(q\mathcal{J})}{\epsilon^2} (1 - \epsilon) a
\]

(5.19)

Here, \( a \) is the dynamic specific surface area and \( \mathcal{J} \) is tortuosity.

The final model for shear rate estimation is taken from Valvatne et al. [39], shown in equation Eqn (5.20). This formulation is derived using dimensional analysis and experimental observation. Valvatne et al. determined that experimental results suggested that the overall shape of the apparent viscosity-Darcy velocity curve \( (\eta_{app}(q)) \) was similar to the shape of the bulk \( \eta(\gamma) \) curve, where \( \gamma \) is the shear rate. They then used dimensional analysis to relate Darcy velocity and shear rate, which resulted in equation Eqn (5.20).

\[
    \gamma_{app} = \frac{\alpha q}{\sqrt{\kappa\epsilon}}
\]

(5.20)

where \( \alpha \) is a parameter generally ranging from 1 to 15, which is determined experimentally. The parameter \( \alpha \) was included after noticing that the equation produced by dimensional analysis produced rheograms that were shifted from the bulk curve by a constant factor [39].
As stated previously, these methods were derived for power law fluids, which are represented by a simpler model than Cross model fluids. Additionally, these methods assume the media can be described by capillary tubes, which greatly simplifies the processes occurring. Following the methods used to derive an apparent shear rate model for power law fluids in capillary tubes described by Christopher and Middleman [4] and Hirasaki and Pope [10] does not work for cross model fluids due to the complexity of the system.

Instead, to get an analogous apparent shear rate from the bulk flow data obtained from the column flow experiments, the modified Cross model was solved for shear rate

$$\dot{\gamma} = \frac{\tau^*}{\eta_0} \left( \frac{\eta_0}{\eta} - 1 \right)^{\frac{1}{1-n}}.$$

(5.21)

The parameters $\tau^*$, $\eta_0$, and $n$ were taken from the fitted rheometer data, shown in Table 4.6. The viscosity $\eta$ was calculated using Darcy’s law and the pressure drop data obtained from the column flow experiments, shown in Tables 4.3-4.5. These values were then graphed against flow rate ($Q$) for each concentration used in the column flow experiments and compared to shear rates calculated using the previously formulated models.

The power law portion of the rheometer data was fit with the power law to find the parameters $n$ and $K$, which are used in shear rate estimations by Christopher and Middleman and Hirasaki and Pope. The results of these fits can be found in Table 5.7. The parameter $n$ relates to deviation from Newtonian behavior. As $n$ approaches 1, the fluid approaches Newtonian behavior. The power law index, $n$, determined by the rheometer data follows this pattern; $n$ increases as concentration increases, and its value for the 0.5 g/L solution is close to 1. This matches column flow pressure data shown in Figure 4.5, which displays
a linear relationship between pressure drop and flow rate and suggests that the 0.5 g/L solution is close to Newtonian.

Table 5.7: Power law parameters calculated from rheometer data

<table>
<thead>
<tr>
<th>Concentration</th>
<th>n</th>
<th>K</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 g/L</td>
<td>0.401</td>
<td>1.7914</td>
<td>0.9980</td>
</tr>
<tr>
<td>3 g/L</td>
<td>0.551</td>
<td>0.3271</td>
<td>0.9957</td>
</tr>
<tr>
<td>0.5 g/L</td>
<td>0.978</td>
<td>0.0026</td>
<td>0.3154</td>
</tr>
</tbody>
</table>

Figure 5.17: Shear rate comparison of experimental data vs. previously published methods for 5 g/L guar gum

Figures 5.17 and 5.18 show the comparison between shear rate calculations obtained using the Cross model and column flow data (labeled Tapscott) and calculations using previously published methods. The shear rate calculations for the 5 and 3 g/L guar gum solutions fall within the range of shear rate values calculated using previously published methods. Although some of these methods come close to the experimental data obtained,
they tend to deviate more towards the low shear rates. This could be because the previously published methods are formulated for power law fluids, and the power law is not meant to be used for low shear rates. This makes it impossible to know if those models accurately portray fluid properties at low shear. It is important to have reliable models that can cover a wide range of shear rates for guar gum if these models are intended to be applied fracking fluids, as fracking operations used a wide range of flow rates. Additionally, previously published methods are based on a bundle of capillary tubes representation of a porous medium. Real porous media are much more complex than the capillary tube model and therefore are not very well described by these models.

Figures 5.19 and 5.20 show the comparison between viscosity calculations obtained experimentally and calculations using previously published methods. The experimental viscosity data (labeled Tapscott) were found using Darcy’s law and pressure drop data from
the column flow experiments. The viscosity measurements using previously published measurements were found using the power law (Eqn (2.5)), and the power law parameters for each solution found in Table 5.7.

The viscosity calculations for the 5 and 3 g/L guar gum solutions fall within the range of shear rate values calculated using previously published methods. Both the 5 and 3 g/L viscosity data fall close to the results obtained using the method published by Valvatne et al. [39]. Despite the fact that some of these methods come close to the experimental data obtained, the general shape of the data curve is slightly different. Also, as with shear rates, the data show more apparent deviations at low flow rates. Again, this is could be because the previously published methods are based on capillary bundle models and are formulated for power law fluids, and the power law can not accurately describe shear thinning behavior at low shears. Having a model that can accurately predict viscosities of guar gum solutions from bulk rheology is crucial to being able to predict how fractures might form and how fracking fluids flow within the fractures.

The shear rate calculations for the 0.5 g/L guar gum solution, shown in Figure 5.21, do not provide a good match. Similarly to the shear rate calculations, the viscosity calculations for the 0.5 g/L guar gum solution, shown in Figure 5.22, also do not provide a good match. The rheometer data for the 0.5 g/L solution, shown in Figure 4.11, along with the flow behavior index $n$ calculated for both the power law and Cross model suggests that this solution is approaching Newtonian flow characteristics. However, the shear rate and viscosity calculations from the column flow data suggest that this solution has more non-Newtonian characteristics. This could be, in part, because the pressure drop data obtained for the 0.5 g/L solution has relatively large error values compared to the difference between the points
Figure 5.19: Viscosity comparison of experimental data vs. previously published methods for 5 g/L guar gum

Figure 5.20: Viscosity comparison of experimental data vs. previously published methods for 3 g/L guar gum
for each flow rate, which might indicate that these values were not accurate. This can be tested by using a pressure transducer with a smaller error tolerance, which could provide more accurate pressure readings at low pressures. Other potential sources of error for the 0.5 g/L solution could be that the pressures arising from low flow rates are not great enough to overcome the surface tension of the solution in the pore spaces of the column, in the plungers, or in the steel mesh filter, which could result in a higher pressure reading than would be expected.

![Shear rate comparison](image)

Figure 5.21: Shear rate comparison of experimental data vs. previously published methods for 0.5 g/L guar gum
Figure 5.22: Viscosity comparison of experimental data vs. previously published methods for 0.5 g/L guar gum
CHAPTER 6: CONCLUSIONS

Natural gas plays an important role in providing energy for the United States. The U.S. has vast reservoirs of natural gas trapped in shale formations, which have low permeability which limit the flow of gas through the formation. Recent advances in horizontal drilling and hydraulic fracturing have made these reservoirs economically viable. Hydraulic fracturing employs the use of a shear thinning fracturing fluid, made up of guar gum solutions, to fracture shale formations. The rheology of these fluids dictates, to a significant extent, the properties of fractures formed. Thus, it is important to have a good understanding of the rheology of these fluids, and to be able to predict rheological properties of these fluids from bulk phase properties.

Column flow experiments and rheometer data for various concentration guar gum solutions provide a combination of data, which can be used to formulate a model describing the rheology of guar gum solutions. Column flow results showed that pressure drop increases non-linearly with flow rate for higher concentration guar solutions, while it increases linearly for the lowest concentration solution, 0.5 g/L. Using Darcy’s law to calculate apparent viscosities from column flow data showed that viscosity decreases with flow rate for all three guar gum solutions. This is consistent with how shear thinning fluids should act. Rheometer data obtained for guar gum solutions showed that apparent viscosity decreases with shear rate. All concentrations of guar gum followed viscosity trends dictated by the modified Cross model, where there is a region which approaches Newtonian flow characteristics at
low shears and a region of power law behavior at higher shears. Comparison of the results from the column flow and rheometer experiments to published studies on non-Newtonian fluid flow through porous medium show reasonable agreement, though not exact. This is likely due to the fact that previous studies tend to use the power law and other derivative assumptions like bundle of capillary tubes to represent shear thinning fluids, but there is a limited range of shear rates for which the power law is appropriate for most shear thinning fluids. Further work is being done using microscale simulations to more realistically model these porous media systems, and initial results show good agreement between pore scale modeling and column-scale observations. These simulations will be able to provide a more precise shear rate model for fluids relevant to fracking.
BIBLIOGRAPHY


sentatives.
