UNDERSTANDING THE PHYSICAL AND CHEMICAL PROPERTIES OF CARBON-BASED GRANULAR FUELS

A Dissertation in
Chemical Engineering

by

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ABSTRACT

Coal and oil have been used as fuel sources for centuries, but the way they have been used has not fundamentally changed: coal is ground into pieces then burned, and oil is distilled into various liquid fractions that are then burned. This dissertation explores newer methods of utilizing those fuel sources.

Coal gasification is the process where coal is heated in a low oxygen environment so that the solid carbon is converted into a mixture of gaseous products. But some aspects of gasification, such as the role of catalysts and the structural evolution of coal particles throughout the reaction, remain unclear. These aspects were studied by analyzing, *ex situ*, the physical and chemical changes of coal feedstock samples extracted from a fluidized bed gasifier at various times throughout gasification. The changes in feed particle composition and size distribution composition showed that the gasification reaction rate was slower than the gas diffusion rates inside the coal particle at a typical catalytic gasification temperature of 800°C. Detailed composition analysis of samples with and without added catalyst showed that the catalyst increased the overall reaction rate by promoting the dissociative oxidation of the coal by gas phase oxidants, which provided more active sites for carbon-carbon bond breakage. The conclusions drawn from studying the feedstock can be combined with the data from *in situ* analysis of the gasification reactor to provide a fuller picture of the gasification process.

Petroleum coke, or petcoke, is a carbonaceous solid produced during oil distillation. Though petcoke could be an important energy source, its use is hindered by practical and environmental concerns. Producing a slurry with petcoke and water has been studied as an alternative method for utilizing petcoke, but the effective use of petcoke slurries requires that they have low viscosity while remaining stable against settling of the particles due to gravity. These rheological properties of petcoke-water slurries were examined and modified using various
additives. Polyvinyl alcohol (PVA) was found to dramatically reduce the viscosity of the slurry by adsorbing to the petcoke particle surfaces and modifying the particle-particle interactions. PVA was as effective at reducing the viscosity as naphthalene sulfonate – the most widely used additive for reducing the viscosity of coal-water slurry fuels – without adding to the slurry the inorganic sulfur which is present in naphthalene sulfonate. The slurries with low viscosity exhibited poor stability against settling due to gravity. The addition of xanthan gum imparted shear-thinning behavior on the slurries, which allowed much improved stability. The combination of PVA and xanthan gum provides an inexpensive, effective, and environmentally-friendly method of modifying the rheological properties of petcoke-water slurries.
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When I started graduate school, I felt like I knew nothing and that I had an impossible magnitude of learning ahead of me. Five years later, with all the wisdom (and degrees) I’ve gathered, I can now see the truth – I was totally correct then, and nothing has changed since.

But these last five years have been quite a journey nonetheless. I could not have made it to this point without the help of a staggering number of incredible people along the way. Though I had to condense most of my graduate research into this dissertation, condensing my gratitude to all of those people into a few short paragraphs seems improper and impossible. So I will leave only a simple message.

To my advisor. To my committee members and to the professors who taught all the classes I took. To my parents, my sisters, my newborn niece, and to the best labradoodle a boy could ever hope for. To the friendships that lasted only a few seasons in this absurdly itinerant town, and to the friendships that may yet last a lifetime. To everyone, everywhere, who has touched my life in some way, I can say only one thing:

Thank you.
Chapter 1

Overview

1.1 Overview and scope of work

This dissertation deals with newer uses of some old fuels. Coal and oil have been around for centuries, but the way they have been used has not fundamentally changed: coal is ground into pieces then burned, and oil is distilled into various liquid fractions that are then burned. With worsening climate change and ever-shifting energy markets, opportunity exists for alternative uses of those fuels. The rest of this chapter gives a brief overview of the research presented in this dissertation concerning those alternative uses, and the background to place that research in the much larger context of world energy markets.

Geologically young coal (or low rank coal) has lower fuel content and higher moisture content than the more commonly used anthracite or bituminous coals, so burning it is inefficient, and these low rank coals tend to be underutilized, even though they represent a majority of the worldwide coal deposits. One way to better utilize low rank coals is by gasification, the process where coal is heated in an environment with a controlled amount of oxygen, so solid carbon is converted to a mixture of useful gaseous products. Low rank coals are better for gasification because the moisture and ash content are an asset to gasification, whereas they are disadvantageous for burning. Chapter 2 gives some detailed background information on coal and the gasification process. Chapter 3 presents original research on characterizing coal and the changes it goes through during gasification. Some information about the reaction mechanisms taking place in the gasifier can be deduced by examining the coal particles taken from various points during the gasification reaction using a variety of analytical techniques. The reaction was
shown to be limited by the surface reaction rate rather than transport processes, and the added catalyst was shown to increase the overall reaction rate by promoting oxidation of the coal, all without taking any direct measurements from the reactor.

Though distillates of oil are the basis of almost all forms of transportation, the effective use of the heaviest fraction has been almost completely ignored. This fraction is called petroleum coke, or petcoke, and though it contains a significant amount of carbon, its low burning rate and high sulfur content means it is difficult to use as a fuel source. Chapter 4 outlines a new way to use petcoke by producing a slurry from petcoke powder and water. The slurry can then be burned in a manner similar to heavy oils, and it can even be gasified. Petcoke slurries are much more practical as a fuel source than raw petcoke, because SO\textsubscript{x} emissions can be reduced, and transportation of the liquid fuel is more convenient than the solid. Chapter 5 presents original research about the preparation of petcoke slurries with special regard to modifying their rheological properties. The combination of two polymers, one to decrease the slurry viscosity and one to increase the slurry storage stability, produces a slurry that fulfills the rheological properties required for industrial applicability.

The final chapter of this dissertation gives some perspective on the result from Chapters 3 and 5. The most important conclusions, their importance, and the further questions produced by those conclusions will all be addressed. Finally, three published articles from other projects are reproduced in the appendices. The articles are “Non-contact AFM imaging in water using electrically driven cantilever vibration”, “Effects of vapor environment and counter-surface chemistry on tribochemical wear of silicon wafers”, and “Atmospheric rf plasma deposition of superhydrophobic coatings using tetramethylsilane precursor”.

1.2 A brief overview of the world energy market

The world energy market goes through constant shifts and occasional revolutions. The usefulness of petcoke slurries or low rank coal gasification is not absolute; it depends on the context in which those technologies exist. The research presented in this dissertation might be immediately applicable for industrial-scale energy production, or the energy markets might shift in a way to render both slurries and gasification obsolete. This section attempts to put those technologies in the context of modern energy markets.

1.2.1 Trends in global energy demand

Any discussion about energy should start with the data in Figure 1-1, which show the growth in global energy over the past 25 years. The primary message is clear: the amount of energy required by humanity is inexorably increasing, and likely will continue on that path for decades to come. Interestingly, the energy consumption by “developed” countries (defined here as members of the Organization for Economic Co-operation and Development, OECD) has been flat since 2007, and the growth in energy consumption since then has been due to “developing” (non-OECD) countries.
Figure 1-1. Total global energy consumption by energy source for 1988-2013, from ref. [1].

The total energy used by non-OECD countries also overtook that of OECD countries in 2007. This development has affected the mix of fuels used because developed countries can invest in renewable energy sources, while developing countries must use more readily available sources. Coal is the most common fuel in developing countries, because it can be mined and burned cheaply and easily with very few additional processing steps. Figure 1-2 shows the share of global energy provided by each source, and confirms that the share of coal as a global energy source has increased significantly as it has kept pace with the energy consumption of developing countries. In fact, coal currently controls the highest share of the energy market over the past 40 years. Oil is also at its 40 year low, though as Figure 1-1 showed the total amount of oil used is still increasing, just at a much slower rate than coal.
1.2.2 The effect of fuel prices on research

While the demand for all energy sources has been increasing consistently over the last few decades, the actual prices of those sources have been much less stable. The price of oil in particular is very prone to dramatic swings dependent on the political situation in the Middle East. Since coal gasification and slurry fuels can supplement fuel needs, it follows that interest in those technologies would increase when oil prices increase. Figure 1-3 demonstrates the link between the price of oil and research about coal gasification. The price of a barrel of oil is plotted since 1970 and compared to the number of publications indexed with the term “coal gasification” in the title. One of the most dramatic features of the graph is the sudden and dramatic increase in oil price due to the 1973 oil crisis, which happened when rising political tensions prompted the Organization of Arab Petroleum Exporting Countries (OAPEC) to declare an oil embargo. In the decade that passed, the scientific community responded to the fuel shortage by investigating coal gasification as a new fuel source. There was not a single paper about coal gasification published in 1970, but in 1980 there were almost 100. The number of papers increased dramatically again.
between 1990 and 1993, likely due to the brief oil price shock that occurred after Iraq invaded Kuwait in 1990. The price of oil has also been steadily rising since the year 2000 due to increasing production costs as easily accessible sources are depleted, and the amount of gasification research has likewise increase steadily.

![Figure 1-3. The number of publications indexed by the Thomas Reuters (TM) Web of Science (TM) in a given year for the search term “coal gasification” and the price of a barrel of crude oil in that year.](image-url)
1.2.3 Future outlook

Gasification is not just a fringe topic for scientists seeking funding. It is a major source of energy, especially in China, where the energy economy is dominated by coal. Of all the energy consumed in China—the world’s largest energy consumer and a non-OECD country—67% comes from coal, with 17% of that from gasification. China also leads the world in research into coal-water slurry fuels as a supplement for oil, and the first coal slurry pipeline was built in that country in 2011 to efficiently transport coal almost 800 km. This focus on coal is due to China’s extremely rich coal sources, but relatively little domestic oil. Thus it seems likely that coal gasification will remain an important technology in China, and in other developing countries with abundant coal resources, for years to come.

Though low rank coal gasification could expand on the energy profile for developing economies, it will likely not affect developed countries. But the United States, the world’s largest economy, is on the verge of its own energy revolution due to the advent of shale oil and gas. Figure 1-4 shows the increase in oil production by the U.S. from the beginning of 2011 until the beginning of 2014, as well as the decrease in production in Libya and Iran that occurred due to political upheaval (the Arab Spring). The increase in U.S. oil production capacity in 2013 was one of the largest jumps in production ever; only Saudi Arabia has had larger increases in a single year. What lasting effects will come about due to this sudden and drastic development remains unknown. The price of oil in the U.S. will probably drop significantly. In that case, petcoke slurries—which are a useful supplement when oil is expensive—may become economically redundant. The opposite is also possible: the sudden increase in the supply of raw petcoke could motivate the industry to find a use for it. No matter the fate of slurry and gasification technologies, energy demands are increasing relentlessly and global energy reserves are at their lowest level in a decade, so having options for other fuel sources can only be helpful.
Figure 1-4. Quarterly oil supply disruptions and growth for Libya, Iran, and the U.S., from 2011 until 2014, compared to 4th quarter of 2010, from ref. [1].
1.3 References

Chapter 2

Coal Gasification

2.1 Summary

Though the world is switching to renewable energy sources, coal remains the most abundant fossil fuel on the planet [1], and its use will continue in much of the world over the coming decades [2]. Catalytic coal gasification is an attractive method for extracting energy from coal while reducing the environmental impacts compared to directly burning the coal. In the gasification process, coal is heated in an environment with a controlled amount of oxygen, so the solid carbon is converted to syngas—a useful, gaseous mixture of hydrogen, methane, and carbon monoxide. Geologically young coals, called low rank coals, such as lignite are especially attractive for gasification because their high moisture and impurity content can increase gasification efficiency compared to anthracite or bituminous coal. In fact, low rank coals that will be gasified are usually treated with catalytically active additives to further increase the gasification rate. The high impurity and relatively low carbon content of low rank coals also means that they are underutilized, even though they represent a majority of the worldwide coal deposits. Overall, catalytic coal gasification allows the efficient use of low rank coals which would otherwise be too costly and inconvenient to utilize [3-9].

This chapter will provide background information on coal gasification. It will begin with details about coal formation and properties in section 4.2, followed by a discussion of the coal gasification process and the thermodynamics and kinetics of gasification reactions in section 4.3. Section 4.4 will complete the chapter by describing the role of catalysis in gasification. The
following chapter will present original research on better understanding a gasification process by analyzing the coal that was gasified with various characterization techniques.

2.2 Coal Formation and Properties

Coal is formed by the fossilization of peat. Peat is formed from layers of partially decayed vegetation, usually in a waterlogged environment such as a bog or swamp. In those environments, the rate of decay of organic matter under the surface is low, because the aerobic bacteria responsible for decay deplete the water of oxygen and die off. The rate of accumulation of organic matter exceeds the rate of decay, and a layer of peat is formed over the course of thousands or millions of years. Coal is formed when that peat is buried by sediment. As heat and pressure build in the buried peat, the complex hydrocarbon structures in the peat begin to break down. Water and decomposition products are driven out of the peat bed, so it becomes more concentrated in carbon, and gradually becomes coal. Figure 2-1 illustrates this process, which is known as coalification or carbonization.

Figure 2-1. The coalification process, from ref. [10].
Figure 2-1 shows that the conversion from peat to coal is gradual, and different terms are used for coal depending on its extent of coalification, or its rank. Table 1 lists the different coal ranks, along with their typical composition and heating values. Lignite, or brown coal, is the first step past peat. Lignite is high in moisture, oxygen, and impurities. Further along the coalification process are bituminous coal and anthracite, which are the most common types found in the northwestern United States. At the limit of total carbonization is graphite, which can be considered the highest rank coal.

Table 2-1. Coal properties by rank.

<table>
<thead>
<tr>
<th>Coal rank</th>
<th>Carbon content (wt%)</th>
<th>Oxygen content (wt%)</th>
<th>Volatiles content (wt%)</th>
<th>Heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>40 – 75</td>
<td>15 – 35</td>
<td>45 – 65</td>
<td>0 – 20</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>70 – 90</td>
<td>3 – 10</td>
<td>10 – 45</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Anthracite</td>
<td>&gt; 90</td>
<td>&lt; 2.5</td>
<td>&lt; 10</td>
<td>&gt; 30</td>
</tr>
<tr>
<td>Graphite</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>32.8</td>
</tr>
</tbody>
</table>

Since coal is complex organic matter, it follows that coal is chemically and physically complex, and differs widely depending on its rank and place of origin. Figure 2-2 shows a schematic of that complexity. At the atomic level, aromatic and non-aromatic carbon ring structures, aliphatic carbon chains, and a variety of carbon functional groups with oxygen, sulfur, and nitrogen are all present in an impossibly complex network. The macroscopic physical structure is no simpler: organic and inorganic components are distributed heterogeneously, the individual components have their own unique structure, and the whole solid is permeated by a complex pore structure.
2.3 Gasification fundamentals

2.3.1 History and current use of gasification

Coal has been burned as a fuel source in Europe since Roman times, and in China for a thousand years before that. Coal gasification is a much newer method for utilizing coal via partial oxidation at high temperature to produce syngas—a mixture of useful gases like hydrogen, carbon monoxide, and methane. The basic method of coal gasification was originally developed in England in the eighteenth century and used for production of “town gas,” a fuel for home cooking and lighting. This process was successfully used until it was phased out due to the advent of cheap natural gas. Development of gasification technology began again in the 1920s-1940s after commercial level cryogenic separation of air allowed oxygen feed streams for higher production efficiencies, but was discontinued again when cheap oil became available. Another decade-long surge of research into the topic came after the 1973 oil crisis, but interest quickly subsided as...
cheap oil supplies again became assured [12]. Two gasification plants were funded by the Department of Energy in 1991 as part of the Clean Coal Technology Program [13]. These plants, one in Tiko, Texas, and one in Wabash, Indiana, have remained operational, but gasification research in this country has stagnated in the intervening years. Recently, the price of crude oil has been quickly and steadily increasing due to the falling supply of readily-accessible reserves, and coal gasification is now, once again, economically viable.

Gasification is not appropriate for use with all coals; the rank of coal determines how it can be used. Higher rank coals can be burned directly as a pulverized fuel (PF) for electricity production, and this method is responsible for about 40% of world electricity generation. But the low energy density of low-rank coals like lignite means that they cannot be directly burned with the same level of efficiency, and even transporting them is too expensive to be practical. So even though the majority of global coal reserves are low-rank coals, they are utilized only in plants very close to the mining operation, and even those are usually contentious due to their high pollution rates. Another problem with directly burning low-rank coals is that their high impurity content produces very high levels of ash in the furnace, which can cause expensive and time-consuming maintenance issues. Though these impurities in lignite may be a problem for direct burning, a significant portion of them—the alkali and alkaline earth metallic (AAEM) species in particular—actually act as catalysts in gasification reactions. So in contrast to direct burning, gasification is faster for lower rather than higher-rank coals [14, 15]. Table 2-2 summarizes the different types of modern gasifiers and their uses.
Table 2-2. The different types of modern gasifiers and their operational parameters [16].

<table>
<thead>
<tr>
<th>Fluidization regime</th>
<th>Moving bed</th>
<th>Fluidized bed</th>
<th>Entrained flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example gasifiers</td>
<td>Lurgi gasifier</td>
<td>Winkler process; KBR transport gasifier</td>
<td>GE Texaco gasifier</td>
</tr>
<tr>
<td>Coal rank</td>
<td>High</td>
<td>Low</td>
<td>Any</td>
</tr>
<tr>
<td>Feed size</td>
<td>5-60 mm</td>
<td>0.5-10 mm</td>
<td>&lt; 100 µm</td>
</tr>
<tr>
<td>Amount of oxidant</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Misc. information</td>
<td>Hydrocarbons in product gas</td>
<td>Lower carbon conversion</td>
<td>Purer product gas; high conversion</td>
</tr>
</tbody>
</table>

2.3.2 Gasification reaction thermodynamics

Fundamentally, gasification is the incomplete combustion of a carbonaceous solid. Practically, gasification is a complicated mixture of many simultaneous reactions and processes. The first process to take place is devolatilization of the feedstock, also referred to as pyrolysis or charring:

\[ \text{Coal} \rightarrow \text{Char} + \text{volatiles} \]  

(Reaction 2-1)

The charcoal bought in stores for fueling a backyard grill is simply devolatilized wood. Modern gasifiers typically use coal that has not been pyrolyzed, so the coal undergoes pyrolysis simultaneously with the gasification reactions. The next set of reactions to consider is the combustion reactions [16]:

\[ C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H_{\text{rxn}}^0 = -111 \text{ kJ/mol} \]  

(Reaction 2-2)

\[ C(s) + O_2(g) \leftrightarrow CO_2(g) \quad \Delta H_{\text{rxn}}^0 = -394 \text{ kJ/mol} \]  

(Reaction 2-3)

\[ CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H_{\text{rxn}}^0 = -283 \text{ kJ/mol} \]  

(Reaction 2-4)

\[ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H_{\text{rxn}}^0 = -242 \text{ kJ/mol} \]  

(Reaction 2-5)
The combustion reactions produce the intense heat in the gasifier that allows the gasification reactions to occur; typically, an external heat source is used only for starting up a gasifier. However, the goal of gasification is not to produce very hot gas, it is to produce syngas – a useful mixture of CO and H\(_2\) – with appreciable energy content. So the amount of oxygen must be carefully controlled to balance the reactor temperature with the product composition.

There are a few other gas-phase reactions that are important to consider for gasification:

\[ C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad \Delta H^0_{\text{rxn}} = +131 \text{ kJ/mol} \]  \hspace{1cm} \text{(Reaction 2-7)}

\[ C(s) + CO_2(g) \leftrightarrow 2CO(g) \quad \Delta H^0_{\text{rxn}} = +86 \text{ kJ/mol} \]  \hspace{1cm} \text{(Reaction 2-8)}

\[ C(s) + H_2(g) \rightarrow CH_4(g) \quad \Delta H^0_{\text{rxn}} = -37 \text{ kJ/mol} \]  \hspace{1cm} \text{(Reaction 2-9)}

\[ CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H^0_{\text{rxn}} = -41 \text{ kJ/mol} \]  \hspace{1cm} \text{(Reaction 2-10)}

\[ CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^0_{\text{rxn}} = +206 \text{ kJ/mol} \]  \hspace{1cm} \text{(Reaction 2-11)}

Reactions 2-7, 2-8, and 2-9 are known as the \textit{steam gasification} reaction, \textit{CO\(_2\) gasification} or \textit{Boudouard} reaction, and the \textit{methanation} reaction, respectively. These three reactions, along with Reactions 2-2 and 2-3, are the only reactions that convert solid carbon into a gaseous product that are commonly found in typical gasification processes. Reactions 2-10 and 2-11 are known as the \textit{water-gas shift} and the \textit{steam methane reforming} reaction, respectively, and they are reversible under typical gasification conditions. They allow another degree of control over the product gas composition, since the amount of water/steam added to the gasifier can be independently controlled [17]. In this way, the feed rates of steam, O\(_2\), and coal are controlled to optimize gasifier operation. Steam methane reforming and the water-gas shift can also be used
downstream to produce more H\textsubscript{2} from syngas. Finally, the *Fischer-Tropsch* process can be used to convert syngas into liquid hydrocarbons [16]:

\[
(2n + 1) H_2(g) + n CO(g) \rightarrow C_nH_{n+2}(g) + n H_2O(g)
\]  

(Reaction 2-12)

**2.3.3 Gasification reaction kinetics**

Gasification is a heterogeneous reaction between a carbonaceous solid particle and a reactant gas stream. For the entrained flow and fluidized bed type gasifiers, there is turbulent flow of the gas and the solid particles, and the temperature and concentrations vary throughout the reactor. For these reasons, modeling the kinetics of an industrial scale gasifier, even with the aid of a laboratory scale reactor, is nearly impossible, and new industrial gasifiers take decades of research to optimize. The complexity of gasification makes an exact kinetic analysis extremely difficult [16], so this section will discuss the effects of reaction rate and mass transfer in general.

The gasification process can be broken down into a sequence of discrete steps, which are illustrated in Figure 2-3.

1. Reactant diffusion from the gas stream through a stagnant boundary layer to the particle surface
2. Reactant diffusion through the pore structure of the particle
3. Adsorption of reactant
4. Surface reaction
5. Desorption of products
6. Product diffusion through pore
7. Product diffusion through the stagnant boundary layer to the gas stream

Note that the process is mirrored at the surface reaction: all steps for the reactant must happen in reverse for the product.
If one of the steps is substantially slower than another step, it becomes the rate-limiting step. Steps 3-5 are related to the reaction rate, while steps 1, 2, 6, and 7 are related to mass transfer. The reactor conditions determine whether the reaction rate or the mass transfer rate dominates the overall rate [18]. Figure 2-4a shows the three zones of overall reaction rate as a function of the temperature. In zone I, the temperature is low and the overall rate is low, but the rate strongly depends on the temperature. In that region, the surface reaction rate, step 4, is the limiting step, and increasing the temperature increases the reaction rate according to the Arrhenius law. In the high temperature zone III, the surface reaction rate is fast and no longer the limiting step. Instead, the rate that reactants and products can diffuse through the stagnant boundary layer outside of the particle is the slowest step. That rate is only a weak function of temperature, though it can be strongly influenced by changing the gas velocity. Zone II is the intermediate stage where the diffusion rate through the internal pore structure becomes important. Figure 2-4b shows actual data of these processes from ref. [12]. Below 700°C the overall rate follows the rate of the surface reaction, and above 1100°C the overall rate is controlled by the mass transfer rate, with a transition region between the two regimes.
Figure 2-4. The effect of temperature on the overall gasification reaction rate, from ref. [12].

The reaction regime leaves its fingerprint on the particles as they react in the gasifier. Figure 2-5 shows generalized reaction schemes for porous, solid particles reacting in a gas, either with (c, e) or without ash species present (a, b, d). If the reaction rate is very high, the reaction occurs mostly at the surface (b,c); if the reaction rate is low, then the reactive gas will have enough time to diffuse into the particle before reacting (a) [19-21]. When the reaction and diffusion rates are similar, there may be a more complex structure that develops (d, e). The difference between the reaction models at relatively high or low reaction rates can be seen from the change in the particle structure as the solid mass decreases. In the random pore model (a), the gasification reaction occurs throughout the network of pores in the solid particle. As gasification proceeds, the pores become larger and the mass of the particle decreases, but the diameter of the particle remains unchanged [22]. In the shrinking core model (b), the particle porosity is constant, and the particle diameter decreases until only ash remains [16]. Knowing the proper reaction model is useful for producing more accurate kinetic and computational fluid dynamic models for a gasifier [21, 23-26], and also gives insight into how to improve the reactor design and
operation, since different modifications would be needed depending on whether the diffusion or the surface reaction is the limiting step.

Figure 2-5. Reaction models for solid reactant particles consumed in a gasification reaction, adapted from ref. [21].
2.5 References

Chapter 3

Physical and Chemical Changes of Low-Rank Coal During Catalytic Fluidized Bed Gasification *


3.1 Summary

Though the world is switching to renewable energy sources, coal remains the most abundant fossil fuel on the planet, and its use will continue in much of the world over the coming decades. Catalytic coal gasification is an attractive method for extracting energy from coal while reducing the environmental impacts compared to directly burning the coal. This chapter presents a post mortem study about coal gasification performed by analyzing samples of feedstock extracted from a fluidized bed gasifier at various times throughout the gasification process.

Section 3.2 describes the materials and the gasification process used to create the samples, as well as the analytical techniques used to study those samples. The analysis techniques include energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy for elemental concentrations in the bulk and at the surface, respectively; acidimetric titrations to quantify the concentration of certain oxygen functional groups; and the BET method to determine surface area and porosity.

In section 3.3 the particle sizes, compositions, and surface areas are used to show that the overall reaction rate was limited by the surface reaction rate rather than transport processes. Section 3.4 gives detailed analysis of the composition and oxygen functional groups to show how the catalyst was bound to the coal, as well as shed some light on the catalytic mechanism. As the
gasification reaction proceeded, the oxidized carbon content increased in the coal loaded with catalyst, but decreased in the coal without catalyst. That result supports the idea that the catalyst increases the reaction rate by helping to oxidize the carbon and increasing the number of reactive sites, rather than by decreasing the energy barrier for carbon-carbon bond breakage.

3.2 Materials and methods

3.2.1 Coal samples and gasification procedure

All data presented here used a low-rank coal (lignite) from Inner Mongolia, China that was pre-ground. The proximate analysis showed that the coal contained 44.2% fixed carbon, 39.6% volatile matter, and 16.2% ash on a dry basis. The ultimate analysis showed that the coal consisted of 77.7% C, 15.9% O, 5.5% H, 0.4% S, and 0.4% N on a dry, ash-free basis. K$_2$CO$_3$ (purchased from Sigma-Aldrich) was chosen as the catalyst since it has the best combination of reactivity and low price, and is widely studied in the literature [1]. The K$_2$CO$_3$ catalyst was loaded into the coal via wet impregnation. The reacted (pyrolysed or gasified) samples were produced in a lab scale gasification reaction system shown in Figure 2-1a. It consisted of a bubbling type fluidized bed reactor three inches in internal diameter heated by an electric furnace. Before starting the reaction, 1kg of coal ground to an average size of ~200 µm was placed on the distributor which was placed at the bottom of the reactor, and the coal was fluidized by 300 sccm N$_2$ and 700 sccm He. The reactor was heated to 650°C for pyrolysis in the inert environment. For the gasification reaction, the reactor was heated to 800°C and oxidants were added to the inert flow. The oxidants added were CO$_2$ at 250 sccm, and liquid water at 0.23 cm$^3$/min., which corresponds to 290 sccm of steam at the reaction conditions.
Fig. 3-1 shows the temperature and gas mixture to which coal particles were subjected, along with carbon conversion measured at various time points. The two sets of data are for lignite and lignite with 10% K₂CO₃ catalyst. The catalyst-loaded coal was completely reacted after about 2.5 hours of gasification, while the coal without catalyst reached only 40% carbon conversion after four hours. The carbon conversion was calculated from the mass of the coal feed left in the gasifier at each time point, the initial mass added, and the initial concentration of carbon in the coal known from the ultimate analysis. This calculation assumes that no ash species are consumed during the reaction. In reality, a fraction of those species will leave the gasifier due to entrainment of small particles of ash (fly ash) with the product gas outflow.
3.2.2 Characterization techniques

Characterization data for this project comes from a variety of instruments and techniques.

- Chemical bonding information was obtained using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) with a Bruker Vertex V70 FT-IR and a Harrick Praying Mantis attachment for diffuse reflectance. DRIFTS is simply an IR spectroscopy method that can be used with powdered samples [2].

- Environmental scanning electron microscopy/x-ray dispersive spectroscopy (ESEM/EDX) using an FEI Quanta 200 Environmental SEM. SEM uses a beam of electrons to image the sample, while EDX analyzes the x-rays that are generated in and emitted from the sample due to that electron beam [3]. The x-ray energy is characteristic of the element from which it was generated, so EDX gives an elemental map of the sample. Environmental mode was needed to prevent charging of the insulating coal particles by the electron beam, so all SEM imaging and EDX analysis was done using a low vacuum of 100 mTorr H₂O vapor.

- X-ray photoelectron spectroscopy (XPS) using a Kratos Ultra XPS system. XPS is essentially the opposite of EDX: a beam of x-rays is used to generate electrons with an energy characteristic of the element from which they originate [4]. But the mean free path of an x-ray in a solid is much longer than for an electron, so the elemental information from EDX comes from a depth of ~3 µm, whereas XPS gives similar information but from a depth of only ~10 nm. Thus the comparison of EDX and XPS data allows some clues about the distribution of elements and their relative concentration at the surface (XPS) and in the bulk (EDX).
• Specific surface area and pore size distribution were measured using the BET method with a physi/chemi-sorption analyzer (Gemini VII 2390t, Micrometritics) that used N₂ as the sorbent.

• The size distribution of the ground coal was measured by laser scattering with a Malvern Mastersizer S.

• The acidimetric titrations were performed using the procedure originally developed by Boehm [5, 6] to give the concentration of surface acidic species. Three 5g samples of coal were mixed with an excess of three bases of increasing strength—\( \text{Na}_2\text{CO}_3 \), \( \text{NaHCO}_3 \), or \( \text{NaOH} \)—so that the surface acidic species were neutralized the H in acidic groups were ion exchanged with Na. The neutralized coal was then mixed with a solution containing 0.5 mmol HCl so that the Na in the surface acidic species ion exchanged back with H and the acidity of the solution decreased. The HCl solution was then titrated with NaOH to determine the amount acidic sites on the surface. The \( \text{Na}_2\text{CO}_3 \) neutralized only the strongest acidic groups, i.e., carboxylic acid sites; the \( \text{NaHCO}_3 \) neutralized both carboxylic and lactonic sites; and the \( \text{NaOH} \) neutralized all acidic sites, including carboxylic, lactonic, and hydroxyl groups. The concentration of each of those species on the surface could then be calculated from the results of the three titrations.
3.3 Identifying the proper reaction model

Figure 2-5 showed various possible reaction models for a solid particle undergoing gasification reactions. In order to determine which of these is valid, a few pieces of information are required. First, the models can be narrowed down to a shrinking particle model or a constant particle size merely by knowing the size of the particles throughout the reaction. Figure 3-2a shows the average size of the lignite particles as the carbon conversion proceeds due to gasification reactions. An SEM image of the particles at low conversion is shown in figure 3-2b. The particle size remains essentially constant for the majority of the reaction. However, when the carbon conversion exceeds 80% some of the particles begin to collapse into larger ash particles. Figure 3-2c shows an SEM image of the coal particles after two hours of gasification. The bulk of the particles are small and carbonaceous, but the larger particles (marked with arrows) are ash. EDX analysis gave the approximate composition of the two types of particles (in weight %): carbonaceous particles: C – 50%, O – 30%, K – 10%, Si – 5%, Al – 2%; ash particles: C – 0%, O – 50%, K – 22%, Si – 17%, Al – 6%, with the remainder for each a combination of Fe, Ca, and other trace minerals. At 97% conversion (2.5 hours gasification with catalyst loaded lignite), no carbonaceous particles remain; the SEM image of this sample in Figure 3-2d shows only the large, glassy ash particles are left, and the sample resembles a coarse sand.

In Figure 3-2a, the sizes were calculated from the SEM images so that EDX maps could be used to differentiate between carbonaceous and ash particles, and average particle size could be calculated once for only carbon particles (solid points) and again when including the ash particles (empty symbols). The particle size distributions were also measured by laser scattering for the samples without the large ash particles (which are too large for that technique), which confirmed the sizes calculated from SEM within <10%. The data shows that the carbon particles do not shrink much during the first 75% of carbon conversion (~10% decrease in average size
from 15% to 75% carbon conversion), but then collapse into large ash particles in the last 25% of carbon conversion. Thus, the correct models to use from Figure 2-5 will be those with constant particle sizes.

Figure 3-2. (a) The average size for K<sub>2</sub>CO<sub>3</sub> loaded lignite throughout the reaction. The inset shows the particle size distribution for particles at 15% conversion. (b-d) SEM images of the samples at (b) 15% carbon conversion, (c) 78% conversion, and (d) 98% conversion. The arrows in (c) point to ash particles. The scale bars in (b-d) are 1 mm.

Once the models of shrinking particles are eliminated, the possible reaction models can be differentiated by the relative magnitudes of the reaction rate and the diffusion rate of reactants. If the reaction rate is high compared to the diffusion rate inside the coal particle, then the gasification reactions will occur mainly at the outer surface of the particles. If the reaction rate is
low compared to the diffusion rate, then the reactants will have time to diffuse through the particle structure before reacting. In the latter case, the particle composition should be similar throughout the entire particle, while in the case of faster reaction the carbon would be depleted preferentially at the surface. And of course, if the reaction and diffusion occur at similar rates, the behavior will be somewhere between those two extremes [7]. If the reaction rate is fast enough, then there is an additional factor to consider: the diffusion time for oxidant from the gas stream to travel to the surface of the particle through a stagnant layer surrounding the particle [8]. The external diffusion only becomes rate limiting when the gasification temperature exceeds about 1200°C [9], so for the case of the fluidized bed at 800°C used in this study the influence of external diffusion is negligible.

Considering the differences for the two cases—the reaction rate dominates the diffusion rate or vice versa—the only information needed to determine which of these two extremes is dominant is the composition of the particles at various depths throughout gasification. Figure 3-3 shows the compositions obtained by XPS and SEM-EDX analysis of the coal particles over large areas. The information depth for EDX is on the order of 3 µm, while that of XPS is only ~10 nm. Therefore, comparing the data from these two techniques gives a rudimentary depth profile of the particles. As shown in Figure 3-3, the compositions detected by XPS and EDX are quite similar, so the carbon concentration in the outer skin of the particles is not significantly different than in the interior. EDX and XPS of the particles after thorough grinding, which exposed the core of the particles for analysis, produced nearly identical results. The gasification reaction must have occurred almost uniformly throughout the particle, indicating that diffusion of reactive species is much faster than the reaction itself at these conditions. Therefore, model (a) in Figure 2-5 is the most plausible or dominant mechanism for the gasifier that produced these samples. This process of pore expansion at constant diameter is illustrated in Figure 3-4.
Figure 3-3. Detected carbon signal from EDX (boxes) and XPS (circles) for lignite with 10 wt% K₂CO₃ throughout gasification reaction. EDX was performed after grinding the samples as well to get the internal concentration (triangles).

Figure 3-4. The expanding pores of carbon particles reacting at constant diameter.
3.4 Evolution of coal and catalyst structure

The physical and chemical structures of the coal change drastically as the primary component, carbon, disappears during the gasification reaction. This section will investigate those changes and their effects on the catalyst status and distribution. Figure 3-2 showed that the size of the coal particles does not change much during the gasification reaction until almost all of the carbon has reacted away. Figure 3-5 shows the size changes again (this time ignoring the large ash particles that form after 75% carbon conversion), and also includes data for the lignite without catalyst, which only reaches about 40% carbon conversion in the time it takes the lignite with catalyst to reach 97%.

Figure 3-5 also shows the surface area of the particles measured by BET. The surface area of the particles is initially very low, but increases dramatically soon after being subjected to gasification conditions. This could be due to pyrolysis and volatilization processes, which drive off reactive species, and may create internal pores throughout the coal structure; this process of physical activation of chars has been documented before [10]. The speed of this process is better illustrated in the coal without catalyst, since there are more samples at low carbon conversion, though it is likely that the pore creation occurs similarly in the catalyst-loaded samples, outlined by the dotted line in Figure 3-5. As gasification proceeds, the measured surface area decreases. Since the previous section showed that the reaction proceeds throughout the bulk of the particles (diffusion >> reaction), the reaction must be occurring at internal pore surfaces. There are micropores throughout the structure of the coal, leading to that high surface area, so the decrease in surface area must be due to the walls of the pores being consumed during gasification. Then, the volume of the pores would increase, but the total internal surface area would steadily decrease. These results are consistent with the random pore model for fluid-solid reactions [11].
Figure 3-5. (a) Average particle size and (b) BET surface area for coal particles at varying levels of carbon conversion from gasification.

In addition to the structural changes – particle size, surface area, pore volume – there are significant changes to the chemical composition of the coal, some of which are demonstrated by Figures 3-6 and 3-7. Figure 3-6 shows XPS spectra for lignite and lignite with 10 wt% K$_2$CO$_3$. For lignite before pyrolysis, the carbon peak at 285 eV is broad and has a long tail in the oxidized carbon region (286-290 eV). The carbon peak for lignite without catalyst becomes sharper as the gasification reaction proceeds, showing a concentration of C-C bonded carbons and a depletion of oxidized carbons. For lignite with catalyst, however, this trend is not seen; the carbon peak becomes broader until it disappears. The carbon peak disappears, of course, because after 2.5 hours of gasification nearly all of the carbon is depleted and the samples are mostly ash. The XPS spectra also show that the carbon in catalyst-loaded lignite becomes more oxidized throughout the reaction. Others have speculated that the role of the catalyst is to aid in dissociative adsorption of oxidant molecules and increase the number of sites where gasification can occur, rather than to decrease the activation energy of the gasification reaction (C-C bond breakage) [12]. The XPS
data support this hypothesis: the catalyst seems to continually increase the proportion of oxidized carbon, which could then lead to the faster overall reaction rate seen for catalyst-loaded lignite.

Figure 3-6. XPS spectra showing the 1s region for carbon (C-C: 285eV, C-O: 286eV, C=O: ~288eV, CO$_3^{2-}$: 289.5eV) and the 2p region for potassium (K: 293.5 and 296 eV) as gasification proceeds for (a) lignite and (b) lignite with 10 wt% K$_2$CO$_3$ added. The inset figures show the percent of carbon centered at the 285eV peak, i.e., the carbon that is not oxidized, compared to the sum of all carbon components (285-288eV), ignoring the carbonate component from K$_2$CO$_3$ at 289.5eV. The lines for lignite show an example of the XPS curve fitting used to calculate the amount of oxidized vs. not oxidized carbon.

While the elemental information from XPS can show the relative amounts of oxidized and not oxidized carbon, acidimetric titrations like those invented by Boehm can give quantitative concentrations of various oxygen functional groups. Figure 3-7 shows the results of Boehm titrations with lignite (without catalyst) before and after pyrolysis, which includes the concentration of phenolic, carboxylic, and lactonic groups. These functional groups are shown in Figure 3-7 as being attached to ring structures, an arbitrary representation of the complex coal structure which contains a high fraction of aromatic species. The quantity of all the detectible oxygen functional groups decreased significantly, even below the detection limit for carboxyl and lactone after the initial pyrolysis. Like the disappearance of the broad oxidized tail in XPS (Figure
3-6a), the Boehm titration data shows that the oxidized carbon groups are more susceptible to volatilization and gasification.

![Figure 3-7. Boehm titration results for the concentration of hydroxyl (COH), carboxylic acid (COOH), and lactonic (C=O-COH).](image)

It has been shown before that the acidic sites (phenol, carboxyl) on a coal or carbon surface can ion exchange with alkali species to form phenolate or carboxylate groups. These sites can serve as the primary source of alkali species in the coal matrix, or can serve as attachment points for catalyst particles. Since we now know that the oxygen functional groups change during the reaction, it is important to know if the oxygen functional groups play a role for catalyst dispersion. Figure 3-8a shows the concentration of K in the K$_2$CO$_3$–impregnated samples as detected by EDX and XPS as a function of the actual concentration of K added during sample preparation. The dashed line shows the amount of K that should be detected in the bulk for a given amount of K$_2$CO$_3$ added. The EDX data falls close to that line, showing that it indeed detects the expected bulk concentration. The XPS data for low amounts of loading also follow this line very closely, indicating the same concentration of catalyst in the surface region as in the
bulk. At catalyst loading above 15 wt%, however, XPS detects a significantly higher concentration of catalyst in the surface region than in the bulk. The propensity for catalyst to concentrate at the surface may be an indication that the coal surface (both external and internal) is saturated with catalyst in the bulk, so any additional catalyst beyond that point will precipitate onto the coal surface as the water from the impregnation solution evaporates.

![Figure 3-8. (a) Elemental concentrations of K-loaded lignite detected by EDX and XPS and (b) DRIFTS spectra of the same sample set.](image)

The IR spectra in Figure 3-8b correspond to the same sample set. DRIFTS can show the chemical form of the catalyst whereas XPS and EDX provide mostly elemental concentration data. The shoulder at 1710 cm$^{-1}$ is due to the carboxylic acid (COOH) asymmetric stretch [13]. Its continuous disappearance with increasing the loading of K$_2$CO$_3$ indicates that the COOH groups are ion exchanged to carboxylates (COOK$^+$), evidenced by the growth at 1380 cm$^{-1}$, as the amount of catalyst increases [13]. The peak at 875 cm$^{-1}$ is due to the out-of-plane deformation of the carbonate in K$_2$CO$_3$ [14], so its appearance and growth above 10 wt% loading indicates the appearance of crystalline K$_2$CO$_3$. 
The combination of data from EDX, XPS, and IR spectroscopy allows a few conclusions about the catalyst form and dispersion. Most of the loading is through ion exchange of COOH groups. This exchange occurs evenly through the structure of the particle: there is no preference for the outer surface. But whether the COOH groups are dispersed through the bulk or are on the pore surfaces through the particle cannot be concluded from these data. At 10 wt% K$_2$CO$_3$, particles of crystalline K$_2$CO$_3$ begin to form, though the ion exchange of K$^+$ with COOH is still dominant throughout the particles. Once the concentration of K$_2$CO$_3$ exceeds about 10 wt%, the K$_2$CO$_3$ particles seem to concentrate more at the surface. This may be due to the internal structure of the coal particles becoming saturated with catalyst. The maximum amount of catalyst that the coal can hold depends on the type of coal, its porosity, and its chemical makeup; these properties will change drastically during the gasification reaction.
3.5 References


Chapter 4

Introduction to Petroleum Coke-Water Slurries

4.1 Summary

Petroleum coke, or petcoke, is a solid byproduct of petroleum distillation. Petcoke is inconvenient to use as a fuel source for a variety of reasons, such as high SO\textsubscript{x} emissions, low reactivity, and difficulty transporting the solid material. One idea to more efficiently use petcoke is to produce a slurry from powdered petcoke and water and then burn it like a heavy oil. But some fundamental issues hinder the creation of useful petcoke slurries:

- Petcoke is hydrophobic, so dispersing it in water requires either a surfactant or some surface treatment to render them hydrophilic
- The petcoke particles in the slurry can be up to 100 µm in diameter, so some stabilizing agents are required to prevent settling due to gravity
- The viscosity of the slurry must be low to facilitate pumping through a power plant like an oil, but the low viscosity also facilitates settling due to gravity
- The solids loading must be quite high (ideal composition is >65 wt% petcoke and <35 wt% water) so that it has an appreciable heating value, but the high loading leads to a high viscosity

These goals are, in part, mutually exclusive, so designing the proper combination of additives to achieve the optimum properties is difficult. This chapter will begin with some background about petroleum coke and the creation of slurry fuels in section 4.2. Once the main issues are demonstrated, section 4.3 will present some fundamentals about slurry rheology. There
have been almost no studies about the creation of pet coke-water slurries, but coal-water slurries have been researched for decades. Section 4.4 will give a literature review about coal-water slurry fuels, paying special attention to the characterization and modification of their rheological properties. Chapter 5 will follow to present original research about modifying the rheological properties of pet coke slurries.

### 4.2 Petroleum coke and the need for slurry fuels

The idea of creating a fuel by mixing a powdered carbonaceous material into a liquid was first patented in 1879 [1], but did not find an economical use for many decades. Interest in coal slurry fuels has peaked during times when the oil supply was in doubt, notably during the 1970s and 1980s in response to the 1973 and 1979 oil crises [2], during which the nominal price (not adjusted for inflation) of a barrel of crude oil in the United States rose from $3 to nearly $12 [3]. While the earliest research focused on coal-oil slurries, coal-water slurries (CWS) are by far the most commonly studied slurry fuels of the past few decades [2]. Various other slurry fuels have been investigated, including biomass for the solid component [4], and methanol or municipal waste sludge as the liquid phase [5].

Recently, interest in petroleum coke-water slurries (PWS) has increased as well, though the literature on that material is not as well developed as coal-water slurries. Petroleum coke (pet coke) is a solid byproduct of petroleum refining [6]. Thermal cracking is used to produce various useful fractions from oil, such as hydrocarbon gases or fuel oils, and the excess carbon from this process forms pet coke. The properties and composition of a given pet coke are therefore dependent on the composition of the oil and the coking conditions used to produce it. A fraction of pet coke is produced with very low impurity content, and it can be used as a carbon source or carbon anode for a variety of industrial processes, especially in aluminum and steel production.
But since petroleum tends to be rich in sulfur and metals, the majority of petcoke produced also contains high levels of those impurities. The majority of petcoke is used as a fuel due to its high energy content, but the impurities cause substantial problems: SO$_x$ formation is a major environmental issue which must be addressed with expensive sulfur scrubbing. In addition, the ash species produced by the metal impurities cause abrasion and other costly maintenance issues in the boiler [7]. These same metal impurities were a primary barrier preventing the commercialization of coal-water slurry fuels, so the lower mineral content in petcoke gives it an advantage compared to coal. As a result of the problems associated with burning petcoke, petcoke-water slurries are beginning to be investigated as a cleaner, more efficient way to utilize petcoke [8].

The most common use of a slurry fuel is as a feed for a boiler or furnace to produce heat to be converted into electricity. A few practical design requirements are common to any fuel that will be used in this way [9, 10]:

1) High solids concentration for an appreciable heating value
2) Low viscosity at high shear rates ($5,000 - 30,000$ s$^{-1}$) corresponding to the atomization process as the fuel is sprayed into the boiler
3) Low viscosity at moderate shear rates ($10 - 200$ s$^{-1}$) characteristic of pumping
4) High viscosity at very low shear rates to prevent settling of the solid particles

Many factors affect the flow characteristics of slurries/concentrated suspensions [10, 11]:

- The physical and chemical properties of the solid particles
- The volume fraction of the suspension
- The particle size distribution
- The interparticle interactions
Practical slurries are generally prepared by carefully controlling the volume fraction, the particle size distribution, and with the use of various additives to change the interparticle interactions. Dispersants are added to decrease the slurry viscosity, while stabilizers are added to increase its stability. Each of these factors will be investigated in depth in the following sections.

4.3 Solids in Liquids: Rheology of Concentrated Suspensions

4.3.1 Basic principles of rheology

The flow properties of a Newtonian fluid can be described by the linear relationship

$$\tau = \mu \dot{\gamma}$$  \hspace{1cm} (Eq. 4-1)

where $\tau$ is the shear stress imposed on the fluid, $\dot{\gamma}$ is the shear rate, and the proportionality constant relating the two is the viscosity $\mu$. For non-Newtonian fluids, however, the viscosity is not a constant—it changes as a function of the shear rate [12]:

$$\mu = f(\dot{\gamma})$$  \hspace{1cm} (Eq. 4-2)

Figure 4-1 summarizes the different types of behavior for fluids [12]. The plots in Figure 4-1a show the shear stress $\tau$ as a function of the shear rate $\dot{\gamma}$ for the various types of behavior. Dividing those curves by the shear rate gives the plot of viscosity vs. shear rate in Figure 4-1b:

$$\mu = \frac{\tau}{\dot{\gamma}}$$  \hspace{1cm} (Eq. 4-3)
Figure 4-1. The types of rheological behavior displayed on plots of (a) shear stress vs. shear rate and (b) viscosity vs. shear rate.

Shear thinning, or pseudoplastic, fluids are commonly experienced in everyday life. Ketchup is the classic example of shear thinning behavior: when a bottle of ketchup is tilted towards a plate, the ketchup inside barely moves under the influence of gravity only. But if the bottle is shaken, smacked, or squeezed, the imposed shear on the ketchup allows it to flow quite liberally. Toothpaste behaves similarly. Shear thickening, or dilatant, fluids are less common, though that type of behavior is commonly demonstrated for general audiences using a concentrated corn starch solution [13]. A small pool is filled with the corn starch solution, a demonstrator steps into the pool, and he slowly sinks to the bottom. While he is sinking through the viscous liquid at a low shear rate, another demonstrator imposes high shear by quickly running across the surface of the pool, and she does not sink. The behavior of the liquid is different depending on the rate at which something interacts with it.

In the same way that gases deviate from the ideal gas law when their individual atoms or molecules interact, liquids deviate from ideal Newtonian behavior when there are species in the liquid that interact. The shear-dependent behaviors of ketchup and corn starch solution arise due to the interacting polymer species in the continuous aqueous phase [14]. Corn starch is a long-
chain, highly branched polymer, which forms an intertwined network in water. Under shear, the fluid will try to move and those polymer molecules will try to move past each other. At high shear rate (running), the molecules are interlocked and cannot move past each other, so the bulk fluid is very viscous. At low shear rate (standing), there is enough time for the polymer chains to relax and slide past each other, so the fluid is less viscous. In the case of ketchup, and indeed with most polymer solutions, the imposed shear causes the polymer chains to elongate and slide past each other. That same behavior can be seen at the macroscale when cooking long, thin noodles: when quiescent, the noodles are intertwined and resist motion. But stirring them rapidly causes the noodles to align with the motion, and they behave more like a fluid.

4.3.2 Solid suspensions

The corn starch experiment shows that Newtonian fluids with an added component can show non-Newtonian behavior. The same is true for a suspension of solid particles in a Newtonian liquid. Albert Einstein gave the first theoretical description of the non-Newtonian behavior of a suspension of solid particles in a Newtonian fluid in 1906 [15]. He produced an analytical solution for the hydrodynamics around a single hard sphere to find the viscosity of the suspension follows

$$\eta = 1 + 2.5 \phi$$

(Eq. 4-4)

where $\eta$ is the apparent viscosity of the suspension, $\phi$ is the volume fraction of solids, the coefficient 2.5 is a constant which he referred to as the intrinsic viscosity, though it is now often called the Einstein coefficient. This equation assumes that the suspension is extremely dilute (i.e., $\phi < 0.01$) so that the flow fields that form around the particles do not interact with each other.
Seven decades later, Bachelor [16] expanded on Einstein’s treatment by allowing the flow field created around one particle to interact with another particle and found

\[ \eta = 1 + 2.5 \phi + 6.2 \phi^2 + O(\phi^3). \]  
(Eq. 4-5)

This relationship is valid for \( \phi < 0.25 \), so the 3rd order term for \( \phi \) becomes quite small.

While the Einstein and Bachelor models are helpful for understanding dilute suspensions, they completely break down for concentrated suspensions \( (\phi > 0.25) \). This is apparent even from a mathematical standpoint: as \( \phi \to 1 \), the viscosity approaches a finite value, but the viscosity of a solid \( (\phi = 1) \) is infinite. Physically, the assumptions in these models become invalid in the concentrated regime because the interactions between particles become significant, and the flow fields around the particles overlap considerably [17]. To avoid this problem, Krieger and Dougherty expanded on Einstein’s model to account for a maximum packing fraction [18]:

\[ \eta = \eta_0 (1 - \phi/\phi_{max})^{-B} \phi_{max} \]  
(Eq. 4-6)

where \( \phi_{max} \) is the maximum packing fraction, \( \eta_0 \) is the viscosity of the liquid medium, and \( B \) is the Einstein coefficient. The parameter \( B \) is not automatically set equal to 2.5 in this equation because it changes when the particles are not perfect spheres [19]. Many other models exist to describe the behavior of concentrated suspensions – such as the ones developed by Mooney [20] and by Eilers [21] – though none of these semi-empirical models can capture all of the complex behaviors exhibited by concentrated suspensions [22].

### 4.3.3 Importance of size distribution

When a suspension becomes concentrated, the particle-particle interactions become significant. In fact, when the volume fraction of solids becomes high enough, the particle interactions dominate the bulk rheological behavior [23]. First, the physical presence of particles
will change the behavior of the suspension. The theoretical maximum packing fraction of perfect spheres is $\varphi_{\text{max}} \approx 0.74$, and since the particles need room to flow past each other, the maximum solids fraction for a suspension under shear is $\varphi_{\text{max}} \approx 0.68$ [24]. (Interestingly, the maximum packing fraction for a quiescent suspension is $\varphi_{\text{max}} \approx 0.64$ lower than the $\varphi_{\text{max}}$ under shear, because the shear imposes some order on the solid particles [24].) But these values all correspond to a suspension with monodisperse spheres; if the particle sizes fall in a distribution, the maximum packing fraction will increase. Figure 4-2 shows the value in having a distribution of particle sizes. The gray particles are monodisperse and close packed. The smaller black particles can fill in the voids that are left between the particles, while the shaded region shows the space that would be completely filled by a larger particle in place of multiple gray particles.

Figure 4-2. The amount of excess solids compared to monodisperse spheres (solid gray) that can be added when there is a size distribution of larger (shaded black) and smaller (solid black) particles.

Figure 4-3 shows experimental data from ref. [24] demonstrating the effects of size distribution on suspension viscosity. In all cases, the viscosity of the suspension steadily increases as the volume fraction of solids increases, then increases much more rapidly as the volume
fraction approaches $\varphi_{\text{max}}$. But the $\varphi_{\text{max}}$ is pushed to a higher and higher value as the distribution of particle sizes increases, i.e., having more differently sized particles allows a higher degree of packing or a lower viscosity at a given solids fraction.

![Suspension Viscosities](image.png)

Figure 4-3. Viscosity vs. solids fraction for suspensions with spheres of one or more sizes, from ref. [24].

### 4.3.4 Interparticle interactions and their effects on slurry rheology

The above discussions all assume that the particles in the suspension are “hard spheres”—they are non-porous, non-adsorbing, and non-interacting. But most solids in water do interact with the liquid medium or themselves in some way. In dilute suspensions, the particles do not interact with each other much, so particle-particle interactions are not very important. But as the suspension concentration increases, the total surface area of particles increases, and the average distances between those particles decreases. The number and strength of interactions increases, and can then affect or even dominate the suspension properties. Some particle-particle interactions come about due to the material properties, such as ionization of surface species
leading to surface charge. Other interactions are purposely introduced by adding some modifying species to the suspension. This section will briefly review the types of interactions that are experienced by solid particles in an aqueous suspension. For a more in-depth review about interparticle interactions and their effects on the rheology of concentrated suspensions, the reader is referred to the work of T. Tadros [23, 24].

**The van der Waals force**

Particles are always attracted to each other over short distances due to the van der Waals force, which comprises three different forces [23, 25]:

- Dipole-dipole interactions (Keesom force)
- Dipole-induced dipole interactions (Debye force)
- Induced dipole-induced dipole interactions (London dispersion force)

Since the London dispersion force is due to fluctuations in electron density distributions, it is present for both polar and non-polar materials, so it contributes the most to the total van der Waals force for non-polar particles.

The van der Waals force is important for slurry rheology because it is almost always attractive under normal conditions. (It is repulsive only in the special case when the van der Waals interaction between two particles is less than that between one particle and the medium, which generally requires particles of very different composition [26].) In the absence of repulsive forces, particles in a slurry flocculate due to van der Waals forces. A suspension of flocculated particles will have very different properties than the same suspension of dispersed particles. The viscosity can be several orders of magnitude larger [27], and the flocs will settle due to gravity at a much higher rate. To create a slurry with good rheological properties, the particles must be
prevented from flocculating, which requires the use of surface modification or additives that induce electrostatic or steric repulsion.

**Electrostatic forces and the electrical double layer**

Whenever there is a charged interface in an aqueous solution an electrical double layer (EDL) forms [28]. A surface can become charged either due to ionization of surface groups such as oxides, or by adsorption of ionic surfactants. In either case, co-ions and counter-ions present in the solution (having the same and the opposite charge as the surface, respectively) will tend to structure at the surface in response to the charge. Figure 4-4 shows a simple model of the EDL and the electrical potential in the EDL. The surface (1) is negatively charged with a potential of $\phi_0$. There is a layer of cations bound very close to the surface called the Stern layer (2), which results in a sharp decrease in the potential. The diffuse layer or Gouy-Chapman layer (3) encompasses everything between the Stern layer and the bulk solution. The excess concentration of counterions (and the potential) decays exponentially, following a Boltzmann distribution, until the concentration of ions is equal and the electrical potential is zero [28].
Figure 4-4. A simple model of the electrical double layer showing the ion distribution (top) and electrical potential (bottom) near a charged plate. (1) The charged surface, (2) the Stern layer of bound counterions, (3) the diffuse Gouy-Chapman layer of ions, (4) bulk solution.

The distance required for the potential to drop by $1/e$ is called the Debye length [28],

$$\kappa^{-1} = \frac{\varepsilon_0 \varepsilon_r k_B T}{\sqrt{2N_A e^2 I}}$$  \hspace{1cm} (Eq. 4-7)

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the dielectric constant of the solution, $k_B$ is the Boltzmann constant, $T$ is the temperature, $N_A$ is the Avagadro constant, $e_c$ is the elementary charge, and $I$ is the ionic strength in the solution in units of mole/m$^3$. Electrostatic forces are almost completely screened out at distances greater than a few times the Debye length. The screening effect is strongest when there are electrolytes in solution ($\kappa^{-1} \approx 10$ nm in 1 mM monovalent salt), but even in pure water the hydronium and hydroxide ions eventually screen the
charges ($\kappa^{-1} \approx 1 \text{ m}$ water at pH 7). Deionized water will absorb CO$_2$ from the atmosphere to have an equilibrium pH = ~ 5.5, corresponding to $\kappa^{-1} \approx 200$ nm.

When the distance between two charged particles in a dispersion decreases to the order of the Debye length, the electrical double layers overlap. The double layers cannot fully develop, and the electrical potential cannot fully decay. The particles will repel each other due to the electrostatic repulsion as well as the increased osmotic pressure from the higher concentration of ions in the diffuse layer. Inducing a charge on the surface of particles is one of the most common and effective ways of preventing particle agglomeration [24, 29]. Combining the double layer repulsion and the van der Waals attraction gives the well-known DLVO (Derjaguin and Landau, Verwey and Overbeek) theory, which describes the behavior of many systems quite well. However, there are some other non-DLVO forces that are also important to consider for dispersions.

**Steric hindrance**

Particles can also be made to repel each other using neutral polymers adsorbed to their surfaces [30]. If one region of the polymer has a high affinity to the surface, it will stay strongly adsorbed, whereas another region of the polymer that is highly soluble in the medium will prefer to stay solvated and stick out into the solution. When two particles approach each other, the dangling parts of the polymer chains begin to overlap. This results in a local increase in osmotic pressure, since the concentration of polymer has increased, as well as a reduction in configurational entropy, since some of the volume that could be occupied by one of the chains is now occupied by the other [28]. These two effects cause the close proximity of two particles to be thermodynamically disfavored, so the polymer chains act like a shell around the particles which reduces the interparticle interaction strength and thereby reduces the slurry viscosity [29, 30].
Hydrophobic interactions

Another type of interaction important to dispersions that is less understood is the hydrophobic interaction. The hydrophobic interaction is a long-range attraction (up to a few hundred nanometers) between hydrophobic surfaces or particles in aqueous solutions, which cannot be explained by DLVO theory, by the presence of polymers, or by local structuring of the solvent [31, 32]. The mechanism underlying this elusive force was unknown as recently as the 1990s. However, recent experiments have shown the hydrophobic interaction to be a result of nanobubbles that form on the surface [33, 34]. The hydrophobic interaction can cause strong agglomeration of hydrophobic particles in water, so it could act to increase the slurry viscosity, though separating the effects of van der Waals forces and hydrophobic forces is difficult [35].

4.3.5 Estimation of the forces acting on particles

Three of the most important forces acting on particles dispersed in aqueous solutions are the gravitational pull on individual particles, and the van der Waals attraction and electrostatic repulsion between two particles. These three forces are illustrated in Figure 4-5. Their magnitudes can be roughly estimated using Newton’s law and the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [24, 29, 30]. These approximations can be helpful in guiding the understanding of a given system.
Figure 4-5. An illustration of the electrostatic, van der Waals, and gravitational forces acting on a system of two particles. Note that the electrostatic force is repulsive and the van der Waals force is attractive.

These three forces can be calculated using [24, 29, 30]:

\[ F_{Gravity} = \Delta \rho \, V \, g \]  
(Eq. 4-8)

\[ F_{vdw} = -\frac{A_H \, r}{12 \, d^2} \]  
(Eq. 4-9)

\[ F_{Electrostatic} = -2 \pi \varepsilon \, r \, \kappa \, \psi^2 \, e^{-\kappa \, d} \]  
(Eq. 4-10)

- \( \Delta \rho \) is the difference between the particle and medium densities. For pet coke in water, 
  \[ \Delta \rho = \rho_{particle} - \rho_{medium} = 0.4 \, \frac{g}{cm^3} \] .

- \( V \) is the volume of the particle, calculated as \( V = \frac{4}{3} \pi \, r^3 \) for spherical particles.

- \( r \) is the radius of the particle.

- \( g \) is the gravitational constant, \( g = 9.8 \, \frac{m}{s^2} \).

- \( A_H \) is the Hamaker constant for the particles, which describes the strength of the van der Waals interaction for a given material. For carbonaceous particles, \( A_H = 10^{-20} \, J \) is reasonable [36].

- \( d \) is the particle-particle separation distance.
• $\varepsilon$ is the permittivity of the solution phase, which for water is $\varepsilon = \varepsilon_0\varepsilon_r = 80 \times 8.85 \times 10^{-12} \frac{F}{m} = 7.1 \times 10^{-10} \frac{F}{m}$.

• $\kappa$ is the inverse of the Debye length. For a 10 mM solution phase, $\kappa^{-1} = 3 \text{ nm}$ [36].

• $\psi$ is the surface potential of the particles. $\psi = -25 \text{ mV}$ is a typical value from zeta potential measurements of petcoke particles in water.

Fig. 4-6 shows the result of calculating these three forces while varying the particle size and particle-particle separation distances. The other variables were set at the typical values listed above, which were chosen to be relevant for the petcoke samples studied in Chapter 5. The plots in fig. 4-6 offer some insight into the behavior of the slurry, since the sum of all the microscopic interactions between particles results in the rheology of the slurry as a whole.

Figure 4-6. The magnitude of the electrostatic, van der Waals, and gravitational forces acting on particles in water. (a) The particle radius is varied at a constant separation distance of 3 nm. (b) The particle separation distance is varied at constant particle size of 10 µm.

Fig. 4-6 shows that the van der Waals force is always higher than the electrostatic force at the given conditions relevant to petcoke slurry. Since $F_{Electrostatic}$ is repulsive and $F_{vdw}$ is attractive, the condition of $F_{Electrostatic} < F_{vdw}$ will lead to net attraction between particles, which causes
particle flocculation and high slurry viscosity. $F_{\text{Electrostatic}}$ could be increased – i.e., the entire curve could be shifted up – by increasing the surface charge or by decreasing the ionic concentration of the solution. The curves for $F_{\text{vdw}}$, on the other hand, cannot be significantly changed because the Hamaker constant is determined by the materials of which the system is comprised. Modifying the surface charge of the particles is, therefore, one of the primary ways to reduce the viscosity of the slurry. This is the approach that has been favored in the coal slurry literature, where naphthalene sulfonates are used to impart a negative charge on the surface of the coal. The other way to nullify the van der Waals attraction is by introducing a different repulsive force, such as steric hindrance from adsorbed polymers. This is the approach used for the petcoke slurry study in Chapter 5. Both of these methods will be discussed in detail in the last section of this chapter.

Fig. 4-6 also shows that gravity begins to dominate as the particle size increases beyond a few microns. When the gravitational force is dominant, the particles will not be stable in the slurry and they will settle. For the petcoke used in the research covered in chapter 5, the majority of the particles were well above the size where gravity becomes dominant. Since the suspension of particles in a typical slurry is thermodynamically unstable, one way to prevent settling (besides reducing the force of gravity) is by changing the kinetics of settling so that the slurry is stable for “long enough”. The kinetics of settling for small particles can be approximated by Stokes’ law [36]:

$$F_{\text{drag}} = 6 \pi \mu r U$$  \hspace{1cm} (Eq. 4-11)

where $\mu$ is the dynamic viscosity of the solution phase, and $U$ is the settling velocity of the particle. For a particle settling due to gravity, $F_{\text{drag}} = F_{\text{gravity}}$, or

$$6 \pi \mu r U = \Delta \rho V g$$  \hspace{1cm} (Eq. 4-12)

which can be rearranged as
\[ U = \frac{\Delta \rho V g}{6 \pi \mu r} \]  
(Eq. 4-13)

For a given particle, every term in the equation for its settling speed is determined, except for the viscosity of the solution. Thus the problem of settling can be solved kinetically by increasing the solution viscosity \( \mu \). But high viscosity is undesirable for transport of slurry through a pipe. Note that the setting process is a very low-shear process, occurring at static storage conditions. So it is important to obtain a very high shear thinning behavior – i.e., high viscosity at low shear rates and low viscosity at high shear rates. The last section of this chapter will describe how stabilizer molecules increase the slurry viscosity at low shear rates where particle settling occurs, while maintaining the low viscosity at higher shear rates which is needed for practical use. The stabilizer molecules sandwiched between solid particles could also act as a softener allowing the settled solid pack to be disturbed easily upon shaking or mixing.

4.4 Coal-water slurry literature review

Due to its abundance, coal has been more thoroughly studied than pet coke as a base for slurry fuels. This is especially the case in China, where coal is abundant but oil is scarce. While the origins of coal and pet coke are quite different, their compositions are similar enough that conclusions and trends learned from coal-water slurry (CWS) research can be used to inform research directions for pet coke-water slurries. This section will review some of the main conclusions that have been found in the CWS research.
4.4.1 Effect of particle hydrophobicity

The ‘slurryability’ (amount of solids that can be added while maintaining a reasonable viscosity) of coal is strongly dependent on its hydrophilic/hydrophobic properties. Hydrophilic particles are less effective because water can partially fill their internal pore structure. In this case, since water is inside the particles, it does not contribute to the fluid phase of the slurry. Hydrophobic particles cannot be easily penetrated by water, so the viscosity of a slurry should be lower for more hydrophobic particles under otherwise identical conditions. This trend was shown by Roh et al. [10], who tested seven different coals which, due to their specific compositions, had equilibrium moisture contents varying from 1.5 – 14 wt%. They found that the concentration of coal required to make a slurry with fixed viscosity was inversely related to the moisture content of the coal. Figure 4-7 shows that a slurry with apparent viscosity = 2 Pa-s required about 60 wt% of the coal with 1.5 wt% moisture, but only 55 wt% of coal with 14% moisture. So the viscosity of the slurry increases with the hydrophilicity of the coal used. This conclusion agreed with the same one from Fu et al. [37], and was later supported in 2004 by Boylu et al. [38], and in 2012 by Gao et al. [8] and by Yu et al. [39]. Gao et al. saw a similar trend between the inherent moisture content in the coal and the slurryability of that coal. Yu et al. took a systematic approach and used hydrothermal dewatering to increase the hydrophobicity of the coal they were studying. That process led to a drastic increase in the amount of solids loading at a given viscosity, from 54% to 62% for one type of coal and from 46% to 59% for another type.
4.4.2 Effect of solids loading

The Einstein and Bachelor models, eqns. 4-4 and 4-5, showed that the viscosity should increase with the amount of solids loading. This result has been shown in a wide array of studies on coal-water slurries [8, 38, 40-42]. Roh et al. [10] also investigated the effect of the coal loading, and their results are shown in Figure 4-8. The viscosity did increase with the coal loading, as expected. They fitted their raw rheology data with the Oswald-de Waele relationship, or power law:

\[ \tau = K \dot{\gamma}^n \]  

(Eq. 4-7)

where \( \tau \) is the shear stress, \( \dot{\gamma} \) is the shear rate, and \( K \) and \( n \) are the rheological constants called the consistency factor and flow index, respectively. When \( n = 1 \), the equation reduces to Newton’s
law of viscosity, and $K$ is the viscosity. The value of $n$ is then a measure of the non-Newtonian behavior of the fluid: $n < 1$ is a shear-thinning fluid, and $n > 1$ is a shear-thickening fluid. The fitting parameters are also plotted in Figure 4-8, and they show that the slurry transitioned from Newtonian to shear-thinning behavior as the solids loading increased [10]. This probably happened because of the increasing number of coal particle-particle interactions. At low concentration, the particles do not interact much, so there is not much deviation from the Newtonian behavior of the fluid phase. But as the concentration increases, the particles are pushed closer together, and the number and strength of particle-particle interactions increase, leading to non-Newtonian behavior. This same conclusion was reached in many other studies, including those by Gurses et al. [40] and Boylu et al. [38].

Figure 4-8. Viscosity and power law fitting parameters for coal as a function of the solids loading, from Roh et al. [10].
4.4.3 Effect of size distribution

Section 4.3.3 explained the importance of the particle size distribution (PSD) on slurry rheology. This effect was best demonstrated, once again, in the paper by Roh et al. [10]. They measured the viscosity of 60 wt% slurries prepared with varying ratios of solids with two size distributions. Their data, reproduced in Figure 4-9, shows that a mixture of two sizes gives a slurry with lower viscosity than with only one of the two sizes. In this case, the best mixture was 2/3 larger particles with 1/3 smaller particles. Furthermore, the effect was magnified as the size disparity increased, since a wider size distribution allows more efficient packing of the particles. Gao et al. [8] and Logos et al. [43] also showed that a wider size distribution gives CWS with lower viscosity.

Figure 4-9. Viscosity of coal slurries with a given ratio of fine to coarse particles added. Mean particle sizes, \( d_{\text{fine}}/d_{\text{course}} \) (µm): \( \blacktriangle - 25/48; \quad \blacksquare - 12/48; \quad \blacklozenge - 12/75; \quad \blackstar - 12/114 \). From Roh et al. [10].
4.4.4 Rheological modifiers for coal-water slurries

Figure 4-9 showed that particle-particle interactions are not very important in slurries with low solids loading, but those interactions became much more important as the loading increases. Since practical slurry fuels need to have a very high solids loading, the interparticle interactions are one of the most important factors in controlling the slurry rheology. Various dispersants have been investigated to reduce the slurry viscosity by changing the interparticle interactions. Stabilizers have also been researched which prevent particle settling by inducing a gel or network structure in the fluid phase. This section reviews some of the work on additives for coal-water slurries.

Dispersants – reducing the slurry viscosity

The review of interparticle interactions in section 4.3.4 showed that van der Waals forces are always present and always attractive, which leads to particle agglomeration and higher slurry viscosity. The van der Waals forces can be mitigated by preventing particles from approaching each other, which can be accomplished by steric hindrance or by electrostatic repulsion. So the dispersants that are used to reduce slurry viscosity are molecules that adsorb to the particle surface and induce either steric hindrance, or electrostatic repulsion, or both.

Some of the earliest and most commonly used dispersants are naphthalene sulfonate and its derivatives [44, 45]. The naphthalene ring is believed to bind to the hydrophobic coal surface, while the sulfonate group dissociates to create a negative charge. Though the chemistry of naphthalene sulfonate is unremarkable, it has received widespread attention in the slurry community because of its extremely low price, owing to its extensive use as a dispersant for the cement industry. Overall, naphthalene sulfonates have been shown to work as an effective
dispersant for coal-water slurries by many studies using all sorts of different coals and procedures [11, 41, 44-46]. For this reason, naphthalene sulfonate will be tested for its effectiveness with petcoke slurries in the following chapter.

Various polymers have also been tested as possible dispersants. Pawlik [9] examined three anionic polymers and three non-ionic polymers. He showed that the anionic dispersants tended to be more effective than the non-ionic ones, since the combination of electrostatic and steric effects is usually stronger than the steric effects alone. However, the best non-ionic dispersant was still more effective than the worst anionic one in his research [9], which shows that the relative strengths of the dispersion mechanisms are important in addition to which mechanisms are present.

Rather than using commonly available dispersants and stabilizers, some researchers have attempted to custom design polymers to suit their needs. Xu et al. [47] synthesized a polymer with alternating groups of carboxylates, sulfonates, and PEO side chains on a polyethylene backbone. By synthesizing the polymer with varying conditions or precursor concentrations, they could effectively control the concentration of each of those groups, as well as the length of the PEO side chains and the overall molecular weight of the polymer. They showed that there were optimum values for the molecular weight of the polymer (about $M_w = 60,000$) and for the PEO side chain length (about 20 units) which gave the lowest slurry viscosity. The effects of changing those parameters were also slightly different when tested with different coals. Overall, this work showed that there is no perfect dispersant that works for all coal samples; there are only dispersants that work best for a given system. Zhou et al. [48] conducted a similar study with their own custom-synthesized dispersant and explained some of the same effects. According to their data, the molecular weight of the dispersant mattered because if it was too small, then the steric hindrance effect was not strong enough, but if it was too large, then the inherent viscosity of the polymer began to affect the viscosity of the solution phase.
**Stabilizers – preventing particle settling**

The preceding paragraphs discussed the various ways to reduce the viscosity of the slurry, but increasing the slurry stability by preventing particle stability is another critical problem that needs to be addressed. To solve that problem, a separate stabilizer molecule must be introduced to the slurry to impose shear thinning behavior. Section 4.4.2 discussed how the attractive interactions between hydrophobic particles lead to shear thinning behavior. Stabilizers work on a similar principle: they form a weak gel network which increases the viscosity at no shear or low shear conditions, but that network is disturbed at higher shear rates so the viscosity decreases.

Unlike the ongoing search for effective dispersants, the issue of finding the additives that give the best stability by inducing shear thickening has already been studied thoroughly by other industries. A huge number of prepared foods and consumer products rely heavily on thickeners to improve their consistency or increase their shelf life. A quick survey of the average household will show these chemicals on the ingredients lists of soaps, shampoo, toothpaste, salad dressings, sauces, and even some ice creams. As a result of their ubiquity, there is a wealth of information about the various thickeners that are commonly used in those products. Figure 4-10 shows a comparison of some common thickeners, including xanthan gum, arabic gum, and cellulose gum (carboxymethyl cellulose, CMC). Since it is a log-log plot of viscosity vs. shear rate, shear thinning is represented by a negative slope. Clearly, xanthan produces the highest degree of shear thinning over the greatest range of shear rates.
XG and other gums thicken by forming a network of chains which are transiently cross-linked by non-covalent bonds [50]. The structure of XG, a branched polysaccharide produced by the bacteria *Xanthomonas campestris*, is shown in Figure 4-11. The molecular weight of xanthan chains range from $2 \times 10^6$ - $2 \times 10^7$, depending on the conditions in which its parent bacteria is fermented [51]. The chain takes on a helical conformation at room temperature [52], though that structure transitions to a random coil when temperatures exceed 50-100°C, depending on the ionic concentration of the solution [50]. Since XG is anionic, ions in solution can act to stabilize the more closely-packed helical conformation. The helical conformation is much more rigid than the extended, random-coil conformation [53].
Success for stabilizing coal-water slurries has been reported with both XG [55-57] and CMC [47, 58]. But there has not been a systematic review of the effectiveness of various stabilizers for coal-water slurries. In the absence of that information, it seems more prudent to use XG than CMC, since the shear thinning ability of XG is much greater. As a result, XG was chosen as the stabilizer for the research presented in the following chapter.

Figure 4-11. The chemical structure of xanthan gum [54].
4.5 References

6. Oxbow-Corporation, Petroleum Coke.


5.1 Summary

The dwindling supply of easily accessible oil has led to the exploration of carbon slurry fuels—highly loaded suspensions of solid carbonaceous particles in liquid media—as a means to supplement liquid fuels. Petroleum coke, or petcoke, is a solid byproduct of petroleum distillation. Petcoke is inconvenient to use directly as a fuel source for a variety of reasons, such as high SO_x emissions, low reactivity, and difficulty of transporting the solid material. Utilizing fuels in slurry form helps to solve those issues, so petcoke is an ideal candidate to be used as the solid component of a slurry.

This chapter discusses research about the creation of a petcoke slurry and the modification of its rheological properties. The goals of this line of research are to create a slurry with high solids loading ( > 60 wt%), low viscosity ( < 1 Pa-s), and good storage stability (no hard pack formation after ~1 month). Since many factors affect the rheological properties of a slurry, a single petcoke source and size distribution was chosen.

Section 5.2 gives some characterization data about the petcoke used in this study. The additives used to modify the slurry rheology and the characterization techniques to understand that process are also described. Section 5.3 outlines the use of dispersants to reduce the slurry viscosity. Naphthalene sulfonate (NS), which has been studied thoroughly in the coal-water slurry literature, is shown to be an effective dispersant for petcoke-water slurries. But the sulfur in NS could lead to an increase of SO_x emissions, and the sodium leads to the formation of more ash,
species that can degrade the boiler in which the slurry is being burned. Polyvinyl alcohol (PVA), a polymer containing only carbon, oxygen, and hydrogen, is shown to be as effective as NS without those drawbacks. Adsorption isotherms show that PVA and NS must be adsorbed to the particle surface to be effective – the viscosity cannot be reduced further once the particle surface is saturated. But decreasing the slurry viscosity also causes very poor stability against settling due to gravity. Adding xanthan gum (XG) to PVA-treated slurries gives strong shear-thinning behavior, which allows for excellent stability. PVA and XG are practical and effective additives for producing petcoke-water slurries with good rheological behavior.

5.2 Materials and methods

5.2.1 Petroleum coke and additives

Petcoke was provided pre-ground by SK Innovation Global Technology, Korea, and is sourced from India. Figure 5-1a shows the size distribution of the ground petcoke, for which the volume median diameter is D[v,0.5] = 31.7 µm. Figure 5-1b shows the XPS spectrum obtained from as-received petcoke. Table 1 gives the bulk elemental concentration obtained from ultimate analysis (elemental analysis of combustion products) of the petcoke, as well as the surface concentration obtained from XPS. The two techniques show that the surface and bulk compositions are similar. The oxygen concentration is higher at the surface, probably due to oxidation from the environment [1], and the sulfur content is slightly lower, perhaps due to the surface oxidation.
Figure 5-1. (a) The particle size distribution of ground petroleum coke, and (b) the XPS spectrum of that sample.

Table 5-1. Elemental concentration for untreated petcoke found by ultimate analysis, for bulk concentration, and by X-ray photoelectron spectroscopy, for surface concentration. ** - XPS cannot detect H, and the concentration of individual ash species was below the detection limit.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bulk Concentration</th>
<th>Surface Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>86.3</td>
<td>93.4</td>
</tr>
<tr>
<td>O</td>
<td>0.6</td>
<td>2.4</td>
</tr>
<tr>
<td>N</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>S</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>H</td>
<td>3.9</td>
<td>**</td>
</tr>
<tr>
<td>Ash</td>
<td>1.1</td>
<td>**</td>
</tr>
</tbody>
</table>

The rheological modifiers were purchased from Sigma Aldrich. These included: polyvinyl alcohol, 80% hydrolyzed, $M_w = 9,000-10,000$ (cat. # 360627); sodium 2-naphthalene sulfonate (cat. # N6885); and xanthan gum (cat. # G1253). Polyvinyl alcohols with different molecular weights and degrees of hydrolysis were tested, but they all gave similar results.

**Preparation of petcoke slurries:** The necessary masses of petcoke, water, and any additives were measured on a scale. The concentrations of additives in the slurry are reported as weight percent based on the dry mass of petcoke, i.e., ignoring the mass of water. The additives
were mixed into the water first, and the solution was mixed until no visible solids remained. The solution was allowed to settle until any bubbles produced during mixing disappeared, then the petcoke was added to the solution, and the slurry was vigorously mixed. Rheological measurements of the slurries were inconsistent in the first few hours after mixing due to the effects of bubbles, so all slurries were allowed to settle for at least 24 hours before any measurements.

5.2.2 Characterization techniques

Rheological measurements were performed using a Rheometric Scientific RM180 rheometer, a rotational, concentric cylinder rheometer that covers shear rates from 6.5 to 1290 s\(^{-1}\) and can detect torques from 0.25 to 7.5 mNm.

The particle size distribution was obtained using a Malvern Mastersizer S laser diffraction system. Particle zeta potentials were measured with a Malvern Zetasizer ZS. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical Axis Ultra.

**Adsorption isotherms:** Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR) was used to measure adsorption isotherms via solution concentrations. A Thermo Scientific Nexus 670 FT-IR with a ZnSe ATR crystal was used for these measurements. The adsorption measurements were performed using ATR-IR instead of the simpler transmittance mode because the broad water absorption region obscured the PVA spectra in transmittance mode. The experimental procedure to create the adsorption isotherms is as follows:

- Create solutions of PVA in deionized water; measure IR absorption intensity of those solutions; plot the absorption peak area vs. PVA concentration. Figure 5-2a shows the spectra from these solutions, and Figure 5-2b shows the resulting calibration curve. The adsorption isotherms could be calculated using any of the peaks shown in Figure 5-2a, but the C-O
stretching (in –C-OH) region in 1150-1000 cm\(^{-1}\) was chosen because it had the most clear baseline and gave the least error in peak area calculation.

- Create samples with known concentration of PVA and petcoke; wait at least 24 hours for full adsorption; filter petcoke particles from solution phase; measure IR absorption intensity of PVA that is not adsorbed on the petcoke surface and left in the solution.

- Using the calibration curve from step (1), determine the concentration of PVA in the filtered solution. Subtract the amount of PVA remaining in solution from the amount initially added to get the amount of PVA adsorbed to petcoke particles.

![Figure 5-2. (a) ATR-IR adsorption spectra for PVA in water. The dashed lines show the fingerprint peaks in the range 1150-1000 cm\(^{-1}\) that were used to calculate the adsorption isotherm. (b) Calibration curve for ATR-IR peak area vs. PVA concentration in water using the peak at 1150-1000 cm\(^{-1}\). Peak assignments were found in ref. [2].](image)

5.3 Reducing the slurry viscosity

The primary function of the additive is to reduce the slurry viscosity. Figure 5-3 shows the viscosity of petcoke slurries vs. the amount of polyvinyl alcohol (PVA) or naphthalene sulfonate (NS) added to the slurry. The viscosity shown was measured at a shear rate of 100
second\(^1\), which is common practice in industry [3, 4]. NS is a common additive for reducing the viscosity of coal-water slurries [5-7], and Figure 5-3 shows that it is quite effective at lowering the viscosity of petcoke-water slurries as well. Adding only 0.1 wt% NS caused the viscosity to drop by over half, from 0.33 Pa-s to 0.16 Pa-s. Adding 1.0 wt% NS further reduces the viscosity to 0.07 Pa-s, and not much benefit is seen beyond that concentration. While the first 0.1 wt% of PVA only decreases the viscosity by \(\sim\) 1/3 to 0.21 Pa-s, 0.5 wt% PVA is enough for significant viscosity reduction to 0.05 Pa-s. Overall, PVA and NS behave quite similarly, and both are very effective at reducing the slurry viscosity.

![Viscosity Graph](image)

**Figure 5-3.** The viscosity of 55 wt% petcoke slurries with naphthalene sulfonate or polyvinyl alcohol added measured at a shear rate of 100 1/sec. The points are the average of four experiments and the error bars are one standard deviation in the measurement.

Figure 5-4 shows the relationship between the adsorption and viscosity behaviors for PWS with PVA and NS. The viscosity data for both are the same as that shown in Figure 5-3. The NS adsorption data was measured as the zeta potential of the NS-coated petcoke particles. The zeta potential is a measure of the surface charge at the fluid slip plane. Since NS is negatively charged, any change in the charge of the petcoke particles would be due to adsorption of NS.
Since PVA is non-ionic, it would not affect the zeta potential. So the adsorption isotherm for PVA had to be measured indirectly using ATR-IR to detect the amount of PVA remaining in solution after adsorption.

The same trend is apparent for both NS and PVA: the viscosity reduction in the slurry is directly related to the amount adsorbed. All PVA that was added to the slurry is adsorbed to the petcoke particles up to 0.5 wt%, and the viscosity continually decreases until that point. Any more PVA added beyond that amount does not adsorb to the particles, and does not affect the slurry viscosity. The same behavior occurs for NS, though some of the NS added beyond 0.5 wt% does adsorb, and it does decrease the viscosity slightly. The initial negative charge on the petcoke without NS was –23 mV, which probably results from the acidic surface oxygen functional groups and surface thiols [8]. The particle surfaces must be saturated with PVA at 0.5 wt% loading, and nearly saturated with NS at the same loading. The inset in Figure 5-4b shows the XPS spectra of petcoke with and without NS adsorbed. When NS is added, an additional S2p peak appears 5 eV higher than the original sulfur peaks of petcoke in XPS. This is the highly oxidized sulfur from the sulfonate of NS.

The mechanism by which NS reduces the slurry viscosity is well known. The naphthalene ring structure in NS is believed to adsorb to hydrophobic regions of the particle surface, while the sodium that is initially attached to the sulfonate group dissociates in water, leaving the sulfonate group with a negative charge. The zeta potential is then directly related to the amount of negatively charged sulfonate groups in NS adsorbed on the petcoke. However, the layer of negative charges on the surface attracts cations in the solution phase to form an electrical double layer, which partially screens out the surface charge, so the zeta potential is smaller in magnitude than the actual surface charge. These effects are described by the well-known DLVO theory [9, 10]. When two particles approach each other, their electrical double layers overlap and repel; this repulsion negates the attractive interactions that would exist between bare particles, thereby
preventing particle agglomeration and lowering the viscosity [11]. Since NS in the solution phase does not affect the surface charge on the particles, it does not directly affect the slurry viscosity.

The mechanism of non-ionic polymer dispersion has also been studied in depth. In contrast to the electrostatic dispersion from the small molecules of NS, large and non-ionic polymer chains prevent particle aggregation via steric hindrance, which occurs between shells of polymers adsorbed to the particle surface. When two particles approach each other, the polymer chains on the two surfaces begin to overlap. This results in a local increase in osmotic pressure, since the concentration of polymer has increased, as well as a reduction in configurational entropy, since some of the volume that could be occupied by one of the chains is now occupied by the other. These two effects cause the proximity of two particles to be thermodynamically disfavored, so the polymer chains act like a shell around the particles, which reduces the interparticle interaction strength and thereby reduces the slurry viscosity.

Figure 5-4. (a) Slurry viscosity and amount of PVA adsorbed from solution (measured by IR adsorption isotherm) vs. amount of PVA added to solution. (b) Slurry viscosity and zeta potential of petcoke particles vs. amount of NS added to solution. The dashed line in (a) has slope=1 for PVA added vs. PVA adsorbed, i.e., 100% adsorption of PVA. The inset in (b) shows overlaid XPS high resolution scans the S 2p region for petcoke with and without NS added.
Though PVA is a hydrophilic polymer, it still adsorbs to a hydrophobic surface. Kozlov et al. [12, 13] tested the adsorption of various PVAs on hydrophobic surfaces. They showed that the adsorption is favored because it reduces the interfacial energy between the surface and the water – the surface-polymer-water interface is lower energy than the surface-water interface – and the adsorbed chains stabilize themselves by crystallizing through inter-chain hydrogen bonding. The thickness of the PVA film increased when the molecular weight decreased, which they attributed to enhanced crystallization of the smaller PVA chains. They also showed that the thickness increased as the proportion of hydrophobic acetate groups in the chain increased, i.e. fewer hydrophilic hydroxyl groups leads to the less hydrophilic PVA chains being able to adsorb more strongly.

The data in Figure 5-5 show the there is no difference in the viscosity of slurries prepared with PVAs of different molecular weights or different degrees of hydrolysis. This result implies that the adsorbed PVA layer on the petcoke particles only needs to be thick enough to prevent particle agglomeration. Any additional PVA below the outermost layer – the layer that interacts with the solution and other particles – is redundant. Finding the PVA parameters that create the smallest layer while remaining effective as a dispersant will allow for the most cost effective use of PVA.
For practical use, a petcoke slurry must have a high solids loading to give an appreciable heating value. Figures 5-3 and 5-4 showed that PVA reduces viscosity, while Figure 5-6 shows that PVA allows much higher slurry loadings at a given viscosity range. In the slurry without PVA (only water and petcoke), the viscosity was 0.45 Pa-s at a slurry loading of 60 wt%. This viscosity was measured at a shear rate of 100 second$^{-1}$, and approached the upper limit of torque detectible by the concentric cylinder rheometer. Using the conclusion from fig. 5-3 that 0.5 wt% PVA is enough to cause the maximum viscosity reduction, that much PVA was added to slurries at varying loadings. With 0.5 wt% PVA added the viscosity at 60 wt% dropped 4-fold. Combining the results from figs. 5-3 and 5-6 shows that PVA is a good additive to reduce the viscosity and increase the loading for petcoke slurries. The viscosity for slurries with PVA at loadings > 62 wt% could not be measured reliably because the rapid settling of particles led to the formation of hard pack, which clogged the rheometer. The critical need to increase the stability of the slurries is addressed in the next section.
Figure 5-6. The viscosity of slurries at varying loading levels either with no additives or with 0.5 wt% PVA (on dry mass of pet coke basis).

Krieger-Dougherty Calculations

Several semi-empirical models have been developed to describe the flow behavior of concentrated suspensions. One of the most widely used models is the one developed by Krieger and Dougherty [14]:

$$\eta = \eta_0 (1 - \phi/\phi_{\text{max}})^{-B \phi_{\text{max}}}$$

where $\eta$ is the suspension viscosity, $\eta_0$ is the viscosity of the fluid phase, $\phi$ is the volume fraction of solids, $\phi_{\text{max}}$ is the maximum solids fraction (the liquid-solid transition), and $B$ is the Einstein coefficient. In Einstein’s original model, the coefficient $B$, which characterizes the flow field around a suspended particle, was equal to 2.5. But that value is valid only for suspensions of perfect spheres that freely rotate. For model suspensions with particles of a well-defined aspect ratio, the exact value of $B$ can be calculated [15]. In real slurries, however, the particles are all different shapes and sizes, and adjacent particles can partially constrain movement; more energy is lost to maintaining flow fields in these slurries, which increases the value of $B$ [16]. In the
Krieger-Dougherty (K-D) model, $B$ is therefore a fitting parameter that captures the combination of these effects.

Fig. 5-7 shows the predicted viscosity from the K-D model compared to the experimental viscosity obtained from slurries with and without PVA at varying solids loadings, as was shown in fig. 5-6. The solids loading was converted from weight fraction $X$ to volume fraction $\phi$ using

$$\phi_{\text{petcoke}} = \frac{X_{\text{petcoke}}}{\rho_{\text{petcoke}} + X_{\text{water}}/\rho_{\text{water}}}.$$  

The density of petcoke was measured using a simple Archimedes displacement experiment, which yielded $\rho_{\text{petcoke}} = 1.4 \text{ g/cm}^3$. The density of petcoke is usually reported to be higher in the literature, around $\rho_{\text{petcoke}} = 2 \text{ g/cm}^3$, but the presence of inaccessible, air-filled pores in the interior of the petcoke particles reduces the effective density. A reasonable value for the maximum packing fraction was chosen as $\phi_{\text{max}} = 0.70$ [17]; the exact value of $\phi_{\text{max}}$ is a function of the particle size distribution, and could be measured for a given sample to give a more precise fit, though an approximated value is enough to illustrate the most important conclusions from the K-D model. Similarly, a value of $B = 5$ was chosen as the Einstein coefficient because it yielded a satisfactory fit and is a typical value used for K-D fitting in similar systems [18]; a more exact measurement of $\phi_{\text{max}}$ would also result in a more accurate value for $B$. 
Figure 5-7. The viscosity vs. solids loading data from fig. 5-6 re-plotted and compared to the predicted value from the Krieger-Dougherty model.

Figure 5-7 clearly shows that the solid volume fraction dependence of the measured viscosity indeed follows the K-D model for the slurry with PVA added as a dispersant, but the model wildly underestimates the viscosity for neat slurry. An important assumption in the K-D model is that the particles are isolated and do not directly interact with each other (the only interaction is through the overlap of flow fields around those particles). In the case of slurry with PVA added, the petcoke particles are insulated from each other by the adsorbed PVA, so that assumption is reasonable. But the strong hydrophobic interactions between bare petcoke particles lead to aggregations of particles forming large clusters, which results in a much higher viscosity that cannot be predicted by the K-D model.
5.4 Increasing the slurry stability

In addition to low viscosity and high loading, a petcoke slurry must also be stable against settling due to gravity. The best way to prevent settling due to gravity is to modify the slurry so that it has shear thinning behavior [10, 17]: the high viscosity when no shear is applied prevents particle settling, but the low viscosity at high shear rates allows the slurry to be pumped through pipes and sprayed into boilers for practical use. Figure 5-8 shows the detailed behavior of the slurries with PVA added in concentrations from 0 to 0.5 wt%. The data in Figure 5-8 shows that adding PVA does decrease the viscosity, but it also reduces the amount of shear thinning.

The dashed lines in Figure 5-8a are the results of fitting the data with the Ostwald-de Waele relationship, or power law [10, 17]:

\[ \tau = K \dot{\gamma}^n \]

where \( \tau \) is the shear stress, \( \dot{\gamma} \) is the shear rate, and \( K \) and \( n \) are the rheological constants called the consistency factor and flow index, respectively. When \( n = 1 \), the equation reduces to Newton’s law of viscosity, and \( K \) is the viscosity. The value of \( n \) is then a measure of the non-Newtonian behavior of the fluid: \( n < 1 \) is a shear thinning fluid, and \( n > 1 \) is a shear thickening fluid. Since the flow curves in Figure 5-8a approach the origin of \( \tau = 0 \) at \( \dot{\gamma} = 0 \), fitting with the Herschel-Bulkley model [10, 17],

\[ \tau = \tau_0 + K \dot{\gamma}^n \]

where \( \tau_0 \) is the yield stress, gave values of \( \tau_0 \) very close to 0. The lack of any yield behavior was probably due to a limitation of the experimental method – the rheometer used could not provide reliable data at shear rates low enough (< 10 s\(^{-1}\)) to measure yield behavior [17].

The parameters from the power law fits in Figure 5-8a are plotted in Figure 5-8b. The consistency factor decreased markedly as the PVA concentration increased up to 0.5 wt%. The only difference between the consistency factor and the viscosity changes from Figure 5-3 is that
the consistency factor characterizes the slurry across all shear rates, while the viscosity reported in Figure 5-3 was measured at a shear rate of 100 seconds\(^{-1}\). The flow index in Figure 5-8b, however, shows something not immediately apparent from the viscosity data shown in Figure 5-3: the slurry changes from initially shear thinning behavior \((n = 0.75)\) to Newtonian or even slightly shear thickening \((n = 1.07)\) behavior at higher concentrations of PVA.

This shift from shear thinning to slightly shear thickening is due to the modification of the interaction between petcoke particles from the adsorption of PVA. The interactions between bare petcoke particles, which are hydrophobic, are net attractive due to van der Waals forces. The attractive interactions result in a network structure that causes high viscosity at static or low shear conditions, but at high shear the hydrodynamic forces applied to the system overwhelm the interparticle attractive forces, causing dissociation of aggregates which results in a lower viscosity. So the natural tendency of the hydrophobic petcoke particles is to produce a shear thinning slurry. The adsorption of PVA causes steric hindrance which negates the attractive forces between the particles. The non- or weakly-interacting particles increase the viscosity, but do not otherwise affect the slurry properties, so the slurry with PVA behaves more like a Newtonian fluid.

The slight shear thickening behavior at high PVA concentration could be due to the interaction between PVA chains on adjacent particles. At high slurry concentrations, the particles are forced into close contact, so the polymer chains of a steric dispersant are forced together. If those chains become slightly entangled, then they will have some difficulty being separated, and the amount of energy dissipated by pulling the chains apart will increase as the shear rate increases [19, 20]. Though this shear thickening transition was not explored further, the chain entanglement hypothesis could be tested by experimenting with different PVA molecular weights and slurry solids loadings, since the degree of entanglement should increase with increasing chain length and increasing particle packing.
Figure 5-8. Detailed rheological behavior of slurries with PVA. (a) Flow curves for slurries (symbols) and the power law fitting of that data (lines). (b) The rheological constants from the power law fits vs. concentration of PVA.

The ideal slurry should be strongly shear thinning to give both high storage stability and low pumping viscosity, but Figure 5-8 showed that shear thinning behavior disappears when PVA is added to reduce the viscosity. As a result, the slurries with PVA added tended to settle much faster. Figure 5-9 shows a picture and a schematic of the slurries with PVA from 0 to 1.0 wt% after one hour of settling time. With only 0 or 0.1 wt% PVA added, the slurry viscosity was still high, but the petcoke particles did not settle much, because the hydrophobic interactions between particles create a network structure that increases the viscosity and prevents settling. When 0.25–1.0 wt% PVA was added, the slurry viscosity dropped significantly—as shown by Figures 5-3, 5-4, and 5-8—which resulted in the particles settling out of suspension. At 0.25 wt% PVA, there was a layer of water on top of a loosely packed layer of petcoke particles resting at the bottom. At 0.5 and 1.0 wt% PVA, all of the petcoke settled into an extremely dense layer that expelled most of the water. So the PVA did reduce the slurry viscosity, but that viscosity reduction led directly to the severe settling behavior.
Since PVA disrupts shear thinning behavior and leads to severe settling, another additive is needed to recreate a network structure that will give shear thinning. Xanthan gum (XG) is a common and effective additive used to fulfill that role in many industries, including for coal-water slurries [21, 22]. Figure 5-10 shows the effect of adding 0–1.0 wt% XG to petcoke slurries, including the flow curves of viscosity vs. shear rate on a log-log scale, and the rheological parameters from the power law fitting of those curves. Figures 5-10a and d show that, when PVA was present, the addition of XG did cause the expected increase in the slurry viscosity. But the
behavior is a little more complicated when there is no PVA and only XG is added to the slurry. Figures 5-10b and d show that the viscosity initially decreased with the first 0.03 wt% XG added then increased as further XG was added. In the absence of other additives, the low concentration of XG behaved like a dispersant. In fact, the XG is an even more effective dispersant than PVA at that concentration. The larger chains and stiffer backbone of XG compared to PVA must be more effective at preventing adjacent petcoke particles from touching each other. That may have happened by adsorption of XG to the particle surface to create steric hindrance, or the XG might have remained in solution as hydrocolloid particles which acted as springs or spacers between adjacent particles [23]. Whether or not XG adsorbed to the particle surfaces could be determined by adsorption isotherms. We attempted using the same ATR-IR procedure as was used for the PVA adsorption isotherms, however, the ATR-IR spectral features were very insensitive to the concentration of XG in calibration solutions. That is likely due to the negatively charged surface of the ZnSe ATR crystal repelling the negatively charged XG chains, since the information depth of ATR-IR is similar to the Debye length in deionized water.

Figure 5-10c shows that XG did indeed impart shear thinning behavior on the slurry. The flow index continuously decreased as more XG was added, with the exception of low concentration XG without PVA, which acted like a dispersant and decreased shear thinning in a similar way as the addition of PVA in Figure 5-8. Comparing the viscosities measured at different shear rates shows the effect of shear thinning more clearly. For example, comparing the PVA-containing samples with no XG and with 0.3 wt% XG added, from Figure 5-8a, shows that the viscosity measured at 100 s\(^{-1}\) increased by a factor of 15, while the viscosity measured at 1000 s\(^{-1}\) increased by only a factor of 5. It is clear that XG is an effective stabilizer for the slurries, but whether the combination of PVA and XG is the best way to reduce the viscosity while increasing the stability is not so clear.
Comparing the slurries with and without PVA in Figure 5-10d shows that the consistency factor is actually higher for the slurries with PVA when the XG concentration exceeds 0.1 wt%. Figure 5-10c also shows that the increased viscosity does not even come with the benefit of significantly enhanced shear thinning behavior. That effect could indicate some increased interaction between the particles and the XG gel structure due to the adsorbed PVA, i.e., entanglement between the dangling PVA chains and the XG chains permeating the fluid phase. Like the shear thickening transition seen in Figure 5-8, that interaction could be verified by testing PVA with different chain lengths and by changing the slurry solids loading. If there is an adverse interaction between the PVA and XG, the use of another dispersant or a shorter chain of PVA could mitigate that interaction. Overall, PVA is an effective dispersant for petcoke-water slurries, and XG is an effective stabilizer, but whether the combination of those two additives gives petcoke-water slurries with optimum rheological properties requires some further study. Figure 5-11 shows a phase diagram constructed from some of the data in Figure 5-10 to show the effects of PVA and XG on the viscosity and stability of the slurry. Note that the “good stability” region at low XG and PVA concentrations is due to the network structure created by the hydrophobic interactions between particles. Though the diagram is necessarily vague due to the small amount of available, it demonstrates how further research into slurry additives could allow the selection of the optimal combination of additives for a given application.
Figure 5-10. Rheological behavior of slurries with varying concentrations of XG. (a) 0.5 wt% PVA in addition to XG. (b) Only XG added. (c) Flow index and (d) consistency factor from power law fitting of the data in (a) and (b).
Figure 5-11. A phase diagram summarizing the combined effects of PVA and XG on the viscosity and stability of petcoke slurries. It is intentionally vague; much more data would be required to produce a quantitatively accurate diagram.
5.5 References


Chapter 6

Conclusion

6.1 Perspectives

Fossil fuels power modern society. But dwindling supplies of those fuels and the looming threat of catastrophic climate change behoove us to explore alternate options for clean, efficient, and abundant energy. Alternative energy sources such as wind and solar power will certainly power the world of the future, but coal and oil will remain as the dominant fuel sources during the transition period.

Sections 6.2 and 6.3 summarize the most important conclusions about the coal gasification research from Chapter 3 and the petcoke-water slurry research from Chapter 5, respectively. The importance of those conclusions for their respective fields and the new questions generated from that research will be addressed. The two projects may seem like separate lines of research, but they both seek to answer one fundamental and extremely important question: how can we better use solid carbon fuel sources? Coal and petcoke are similar enough to each other that their uses overlap somewhat; there has also been considerable research into coal-water slurries and petcoke gasification. The research in Chapters 3 and 5, therefore, could be useful for the wider audience of slurry preparation and gasification in general.
6.2 Understanding coal gasification by analysis of feedstock

Chapter 3 showed that a substantial amount of information can be learned about the reaction dynamics during catalytic coal gasification by analyzing the coal particles taken out from the reactor during various stages of the reaction. The average coal particle size and the elemental composition profile did not change much until >75% conversion, and the surface area steadily decreased (after an initial increase during an activation period). Those results fall in line with random pore models for solid-gas reactions: the reaction takes place throughout the pore structure of the particles, rather than at the exterior surface.

Analysis of the chemical composition of the particles gave some insight into how the catalyst functions. There was a significant amount of oxidized carbon in the as-received coal, mostly in the form of phenolic and carboxylic acid groups. In coal without added catalyst, the oxidized species were driven off during pyrolysis and gasification leaving only a small fraction of oxidized carbon. But in coal with K$_2$CO$_3$ catalyst, the proportion of oxidized carbon increased throughout the reaction. The accumulation of oxidized species supports the hypothesis that the role of the catalyst is to increase the rate of dissociative adsorption of oxidant molecules from the gas phase, thereby increasing the concentration of active sites available for gasification, rather than to increase the gasification rate by reducing the carbon-carbon bond strength.

Gasification is a complicated process, and coal is a complicated substrate, so these results may not necessarily apply to other systems or conditions. But the method of learning about a gasification process by analyzing the changes in the physical and chemical structure of the coal throughout the reaction could be utilized for gasification systems of any type or scale. It would be a useful and interesting extension to apply this method to study other catalysts, carbon sources, and gasifiers.
6.3 The behavior of rheological modifiers in petroleum coke-water slurries

Chapter 5 presented research about finding the proper additives to produce a viable slurry from petroleum coke (petcoke) and water. Coal-water slurries have been studied since the oil crises in the 1970s, but petcoke-water slurries have received much less attention. Drawing on past successes from the coal-water slurry literature, naphthalene sulfonate (NS) was chosen as a model dispersant for reducing the petcoke slurry viscosity. NS was an effective dispersant, but the sodium and sulfur content makes it undesirable for use with petcoke slurries. Polyvinyl alcohol (PVA) was identified as a candidate dispersant that does not have the same drawbacks as NS, and PVA was shown to be similarly effective as NS. The adsorption behavior of these dispersant molecules was examined to show that they are both effective only when adsorbed to the particle surface. Knowing that adsorption is a crucial part of the effectiveness of a dispersant opens up many possibilities for improving on those dispersants. For example, the PVA properties could be tuned to minimize the thickness of the adsorbed layer and allow more efficient and economical use of that dispersant.

Besides reducing the viscosity, the other major issue with slurry formulation that must be addressed is the settling of the solid particles. There are a huge variety of industrially available additives for stabilizing suspensions. They generally work by forming a network structure or a weak gel so that the movement of particles—a very low-shear process—is hindered enough to prevent settling. As the influence of hydrodynamic forces grows, the network structure collapses and the viscosity of the solution decreases. Though this shear thinning behavior is highly desirable for slurries, there is a dearth of information about the effectiveness of those stabilizers as applied to coal- or petcoke-water slurries. Xanthan gum (XG) was chosen based on the consumer products and food additives industries, since it produces the most pronounced shear
thinning effect. XG was shown to be effective at inducing shear thinning in pet coke-water slurries and, as a result, greatly increased the stability of those slurries.

It is now clear that PVA is an effective dispersant and XG is an effective stabilizer for pet coke-water slurries. But whether the combination of those two additives produces a slurry with the optimum properties of both low viscosity and prominent shear thinning will require further study. Once the most effective formulation of additives is identified, the production of slurries with ideal rheological properties becomes an engineering exercise of optimizing the additive concentrations and the size distribution of the pet coke particles to suit the particular application. The use of slurry fuels is growing, and many other solids are commonly transported through pipes as slurries. Understanding the adsorption and interaction of various additives at liquid-solid interfaces is an interesting and complex problem, and in the case of slurry preparation it is a problem that must be addressed.
Appendix A

Non-Contact AFM Imaging in Water Using Electrically Driven Cantilever Vibration

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A.1 Update to the original paper

In its originally published form, the paper reproduced here explained most aspects of how the applied electrical voltage produced a mechanical vibration in the cantilever. In Figure A-2b, the frequency dependence of the vibration amplitude, the vibration amplitude in water decreases continuously as the driving frequency increases. While the two resonance peaks in those same curves are easily explained as mechanical resonance, the origin of the continuous decrease of the cantilever vibration amplitude in water remained unclear at the time of publication.

Since then, Umeda et al. have published a series of papers about a similar AFM system under development in their lab [1-3]. Their system had the same type of frequency-dependent behavior, which they explained using the concept of electrochemically induced surface stress. The following paragraphs will explain the origin of the surface stress and how it completes the theoretical framework used to describe the AFM system described in our original publication.

A.1.1 Origin of surface stress

If the two sides of a beam are under different amounts of stress, that beam will bend. In the simplest case of a thin, uniform beam of thickness \( t \) with differing surface stress of \( \Delta \sigma \), the radius of curvature \( R \) imparted on the beam will be

\[
\frac{1}{R} = \frac{6}{E} \frac{1 - \nu}{t^2} \Delta \sigma
\]

where \( E \) is the Young’s modulus and \( \nu \) is the Poisson ratio for the beam [4]. The surface stress can be calculated from the surface energy using the Shuttleworth equation:

\[
\sigma = \gamma + \frac{dy}{d\varepsilon}
\]
where $\varepsilon$ is the surface strain. Raiteri and Butt were the first to use this method with an AFM cantilever to measure electrochemically induced surface stress in gold and platinum [4]. For that system, they estimated $\frac{dy}{d\varepsilon} \approx 10^{-4} \text{ N/m}$ and $\gamma \approx 10^{-1} \text{ N/m}$ so that $\sigma \approx \gamma$. The surface energy $\gamma$ is proportional to the surface charge [5], and the surface charge is, in turn, proportional to the applied potential. So combining these equations shows that the amount of bending in a cantilever is a function of the voltage applied to the cantilever.

A.1.2 Surface stress voltage biased AFM imaging

Umeda et al. developed an AFM system with a similar setup as the one reported here [1-3]. They applied an oscillating bias voltage between the cantilever and a counter electrode above the cantilever, whereas our system uses the sample as the counter electrode. The result of the two different setups is the same: the oscillating electrical voltage applied to the cantilever drives a mechanical vibration, and the characteristics of that vibration are similar for both systems. The system used by Umeda et al. demonstrated the same type of low frequency amplitude enhancement shown in Figure A-2. Their results are reproduced as Figure A-0. The dashed lines in the figure are theoretical curves that were created by combining the contributions from the mechanical response and surface stress. Whereas our models fail to predict any low frequency amplitude enhancement, the models used by Umeda et al.—which included the surface stress component—accurately predict the amplitude of the vibration across the full range of frequencies tested. Thus the effect of the surface stress is likely the component that was missing from our original models.
Figure A-0. Frequency response curves from the AFM system developed by Umeda et al. [3]. The dashed lines are theoretical curves obtained by combining contributions from mechanical response and surface stress response.

A.1.3 References

A.2 Abstract

An atomic force microscopy (AFM) imaging mode is presented that can simultaneously record surface topography and local electrical properties in aqueous solutions without mechanical contact between the AFM tip and the sample. The interaction between the electrically biased tip and the grounded sample in aqueous medium causes the AFM cantilever to vibrate. This operation mode is based on the previously-developed SPFM technique, though using water as the medium instead of air introduces some important practical and theoretical differences, and also greatly extends the applicability of this technique. There are two vibration modes, one at the frequency of the applied voltage ($\omega$) and one at twice this frequency ($2\omega$). The surface topography can be imaged using feedback control of the $2\omega$ vibration amplitude, which is very sensitive to the tip-sample separation distance in the range of 1~10 nm. The amplitude and phase of the $1\omega$ vibration can be recorded simultaneously during imaging to obtain information on local surface charge or potential differences. Similar techniques exist for imaging in air or vacuum, but the addition of a polarizable medium such as water adds significant theoretical and practical complexities. This paper addresses those complexities, and demonstrates the effectiveness of the technique for surface imaging and analysis in aqueous environments.
A.3 Introduction

The atomic force microscope (AFM) has become one of the most versatile tools in small-scale imaging and investigation of surface properties since its invention. One of the reasons for the success of AFM is its applicability to a broad range of samples and environments, and the ability to detect many different types of properties. In addition to the simplest scanning modes, various techniques have been developed to probe soft or fragile surfaces without damaging them, such as non-contact mode[1] and intermittent-contact (tapping) mode.[2-4] Other techniques have been developed to identify local electrical properties such as surface charge or dielectric differences. These techniques include electrostatic force microscopy (EFM),[5, 6] magnetic AC (MAC) mode,[7, 8] Kelvin probe force microscopy (KFM),[9-12] and scanning polarization force microscopy (SPFM).[13-17] KFM and SPFM combine the detection of electrical properties with the advantages of intermittent- or non-contact imaging for simple and non-invasive simultaneous imaging of surface topography and local charge or potential differences in vacuum or air.[9-11] These techniques, however, have not been applied for imaging in aqueous environments.

The ability to map surface topography and local electrical properties in liquid, especially in aqueous environments, would benefit a wide range of fields.[18, 19] For example, surface charge plays an important role in many interfacial processes occurring in aqueous environments, such as DNA adhesion,[20-22] colloid adsorption and aggregation,[2, 3, 23] and polymer swelling.[4, 6] Solid-water interfaces naturally develop a surface charge in aqueous environment if the pH of water is different from the isoelectric point of the surface. These charges may not be uniform[24, 25] and can influence the mechanical, optical, and electrical properties of colloids and polymer films[2-4, 6, 15, 23, 26] and are believed to be a key factor in many bio-adhesion processes.[20-22]
In this paper, we demonstrate the oscillatory actuation of a conducting cantilever in water and other liquids upon application of sinusoidal electric fields, and the use of this electric-field-induced vibration for simultaneous non-contact imaging of topography and local electrical property differences. We present the set-up and operation of the technique with comparisons to the similar methods in air, along with the effectiveness, advantages, and disadvantages of the technique. This imaging mode does not require the two-scan method of first imaging topography then rescanning while following that topography to record an electrical signal, nor does it touch the surface like a contact scan that measures electrical potential. Thus this technique is suitable for soft surfaces that would be damaged by contact with the probe. We also discuss the theoretical complications brought about by the presence of liquids, especially water with its polarity, high dielectric constant, and dissolved ions.

A.4 Experimental

A.4.1 Experimental Setup

The experimental set-up and operation of this imaging technique is very similar to that of the previously-developed SPFM:[14] the main difference here is that the sample and AFM probe were immersed in water. Figure A-1a shows a schematic of the setup. The AFM system used for this study consisted of a Molecular Imaging Pico-SPM with an RHK controller. A position-sensitive detector sensed the AFM cantilever position via a laser reflected from the cantilever. When a sinusoidal time-variant voltage at frequency $\omega$ ($V(t) = V_{AC} \sin (\omega t)$) was applied to a conducting AFM tip, the cantilever vibrated at the frequency of the applied bias ($1\omega$) and at twice this frequency ($2\omega$). These frequencies are not related to the mechanical resonance of the AFM tip. In addition, there was a time-invariant ($0\omega$) deflection of the cantilever from its
neutral position. Figure A-1b illustrates an example of the sinusoidal voltage applied and the cantilever motion detected with an oscilloscope. Two lock-in amplifiers and the AFM’s built-in low-frequency voltage measurement unit were used to separate and analyze the three components ($0\omega$, $1\omega$, and $2\omega$), which were recorded by a computer; no higher-order components ($3\omega$ or $4\omega$) were detected. The $2\omega$ amplitude signal was used for the feedback control for topographical imaging. The reported cantilever vibration amplitudes were calculated by converting the root-mean-square voltage output of the lock-in amplifier to peak-to-peak voltage and multiplying by the deflection sensitivity of the detector.

Figure A-1. (a) A schematic of the system components. (b) A 1.0 V_{pk-pk}, 2.5 kHz AC driving voltage (top line, left axis) and the resultant tip position profile (bottom line, right axis).
A.4.2 Materials and Methods

Rectangular n-doped silicon AFM probes (Vista Probes) with spring constants of ~0.1 N/m and resonance frequencies of ~30 kHz were used for all experiments. That cantilever stiffness was chosen considering the balance between allowing a large vibration amplitude (softer cantilever) and a good signal-to-noise ratio (stiffer cantilever). In general, a stiffer cantilever is needed in water than in air due to the increased viscosity, which causes higher damping of the vibration. The media used for all experiments were either ambient air, Milli-Q deionized water (18 MΩ-cm), or n-decane (Sigma-Aldrich). The cantilevers were n-doped (conductivity ~50-100 S/cm) and electrical contact was made by scratching off the native oxide layer (a ~2 nm thick SiO₂ layer that forms on all Si surfaces exposed to air) at the back of the chip with a glass cutter and coating the area with conducting silver paste. The AFM probes were cleaned in a UV/Ozone chamber for 20 minutes prior to use and the silicon wafers were cleaned with the RCA-1 process (5:1:1 H₂O:NH₄OH:H₂O₂ at 70°C for 30 mins). Thermal oxide layers with varying thicknesses were grown on silicon wafers by heating in air at 800-1000°C, and the oxide thickness was measured using ellipsometry.

Thiol-based self-assembled monolayers (SAMs) on gold films were used as model charged surfaces that could be damaged by contact with the AFM probe. The gold substrates (Aldrich, 100 nm thick 99.999% Au layer on Ti adhesion layer on <100> Si wafer) were cleaned by O₂/Ar Plasma for 15 minutes. The SAMs were deposited on the gold by placing the gold substrate in a 20 mM solution of the SAM molecules in ethanol for 1 hour, then thoroughly rinsing with ethanol to ensure only a monolayer remained. Hexagonal etched pits were produced by wet etching (111) silicon wafers using reactive 520 nm amidine functionalized polystyrene latex colloidal particles.[27]
A.5 Results and Discussion

A.5.1 Vibration of Electrically-Biased Cantilever in Water

The AFM cantilever vibrates when a sinusoidal electrical voltage is applied to it in liquid. The electrical input to the cantilever/tip can be varied in either frequency or voltage; these two parameters are examined in Figure A-2. Figure A-2a shows the voltage dependence of the cantilever vibration amplitude at a driving frequency of $\omega = 4 \text{ kHz}$. Here, the amplitudes of both vibration frequencies – $1\omega$ and $2\omega$ – are monitored in addition to the time-independent ($0\omega$) deflection. The $1\omega$ amplitude shows a linear dependence to the applied driving voltage, while the $2\omega$ and $0\omega$ amplitudes both have second-order dependence. Figure A-2b shows the effect of changing the applied frequency in both air (SPFM) and water. In air, there is a distinct peak in each channel due to mechanical resonance: the $1\omega$ channel detects the mechanical resonance at $\omega = \omega_{\text{resonance}} = 30.3 \text{ kHz}$, while the $2\omega$ channel detects it at $\omega = \omega_{\text{resonance}}/2 = 15.2 \text{ kHz}$. The vibration amplitude in air is very small far away from the mechanical resonance peaks, though both channels show an appreciable signal at $\omega < 5 \text{ kHz}$. The origin of the low frequency vibration is unclear, and is not discussed in the literature about SPFM.[14, 16, 28]

For a purely mechanical system, using water as the medium instead of air would lead to the mechanical resonance peak becoming more broad and shifting to lower frequency due to viscous damping.[29] But the increased dielectric constant of water yields a much stronger electric field between the charged tip and the grounded sample, so the vibration amplitude should increase compared to operation in air. Figure A-2b shows both of these behaviors: the vibration at low frequencies seen in SPFM is greatly magnified in both the $1\omega$ channel and especially the $2\omega$ channel. The amplitude enhancement due to mechanical resonance is also present in each channel at $1\omega = \sim 3.5 \text{ kHz}$ and $2\omega = \sim 7 \text{ kHz}$, though the viscous damping renders these as bumps on the
low frequency vibration rather than dramatic peaks rising from a small background. The origin of the vibration at low frequencies may be central to understanding the nature of the interactions driving cantilever vibration in water.

Figure A-2. (a) Voltage sweep from 0 to 2.0 V\textsubscript{rms} in water at $\omega = 4$ kHz. (b) Frequency sweep from 0 to 40 kHz in air and in water at an applied bias of 1.0 V\textsubscript{rms}. The cantilever was positioned ~300 nm above a grounded silicon wafer substrate in both cases.

The equation describing the cantilever movement can be derived in order to facilitate the discussion about the cantilever vibration. This derivation begins with the basic equation of motion for a vibrating beam:[29, 30]

\[
\frac{d^2z}{dt^2} + \frac{\omega_0}{Q} \frac{dz}{dt} + \omega_0^2 z = \frac{F_{\text{applied}(t)}}{m} \tag{1}
\]

where $z$ is the cantilever displacement from the free-standing position, $t$ is time, $\omega_0$ is the mechanical resonance frequency of the cantilever, $Q$ is the quality factor (a constant that depends on the stiffness of the cantilever and the viscosity of the solution, which characterizes the viscous damping behavior), $m$ is the mass of the cantilever, and $F_{\text{applied}(t)}$ is the applied force. In the left-hand side of eq. (1), the first and third terms are the kinetic and potential energies, respectively, and the second term is the damping by the medium. When considering electrical interactions, the AFM system can be viewed as a capacitor, where the cantilever and the substrate are two
electrodes separated by a dielectric medium. The electrostatic (ES) force between the two electrodes can be expressed as

$$F_{ES} = -\frac{1}{2}\frac{\partial C}{\partial z} V^2 \quad (2)$$

where C is the capacitance of the system (which depends on the geometry and separation distance of the electrodes and dielectric properties of the medium), and V is the voltage difference. For a parallel plate capacitor with a dielectric medium, the $\frac{\partial C}{\partial z}$ term depends only on the electrode area, separation distance, and permittivity of the medium. In AFM, the substrate electrode is essentially infinite (cm-scale) while the tip/cantilever counter-electrode is quite small (μm-scale) and has complex shapes, producing varying field gradients depending on the location.[11, 13, 14, 31, 32] In addition, the polarization of ions in aqueous solution adds complexity via dielectric and charging responses of the medium.[33] In any case, the voltage term in eq. (2) is the sum of the applied alternating voltage and the natural surface potential differences of the electrodes $\phi$,

$$V = V_{AC} \sin(\omega t) - \phi \quad (3)$$

where $V_{AC}$ and $\omega$ are the magnitude and frequency of the applied voltage, respectively. Inserting eqs. (2) and (3) into eq. (1), and converting the sin$^2$(ωt) term into a cos(2ωt) term using a trigonometric identity, yields the governing equation for the motion of a cantilever due to an alternating voltage:

$$\frac{d^2z}{dt^2} + \frac{\omega_0}{Q} \frac{dz}{dt} + \omega_0^2 z = \frac{1}{4m} \frac{\partial C}{\partial z} [V_{AC}^2 \cos(2\omega t) + 4 \phi V_{AC} \sin(\omega t) - (2 \phi^2 + V_{AC}^2)] \quad (4)$$

With proper models for the $\frac{\partial C}{\partial z}$ term, eq. (4) can describe the cantilever vibration in air quite well.\textsuperscript{11-13, 26, 27} Even without considering the $\frac{\partial C}{\partial z}$ term, the right-hand side of eq. (4) illustrates the origin of the three features shown in Figure A-1b: the $2\omega$ and $1\omega$ vibrations originate from the first and second terms of the right hand side of eq. (4), respectively, and the time-invariant $0\omega$ deflection comes from the third term. Eq. (4) also explains the second-order dependence of the
2ω and 0ω amplitude and the first-order dependence of the 1ω amplitude on the applied voltage (V_{AC}), as shown in Figure A-2a.

A.5.2 Imaging

Scanning probe techniques require feedback control to properly follow the surface topography. The feedback controller uses the gradient of some detectible force with respect to the cantilever position (e.g., contact-mode uses the spring force from a mechanically deflected cantilever) to control the tip via piezoelectric actuators. In the case of SPFM, and our non-contact imaging technique in water, the vibration amplitudes depend on the tip-surface separation distance, so these amplitudes can be used for feedback control. There are significant differences in the amplitude-separation behaviors for air and water, as shown in Figure A-3 (only 2ω vibrations are shown, but the 1ω vibrations act similarly). In SPFM in air, the electrical forces act over a short range: the cantilever vibrates only when within a few hundred nm of the surface. In water, however, the vibration amplitude was essentially constant over this range, then it decreased suddenly but smoothly in the closest ~10 nm to the surface. At this range in air, the tip snapped-in to the surface because the attractive forces between the tip and surface became larger than the restorative spring force of the cantilever. There is no snap-in behavior in water because the attractive forces between clean (hydrophilic) surfaces in water are very small. If the tip and sample are hydrophobic and immersed in water, then there can be tip snap-in behavior due to hydrophobic interactions,[29] so without the use of surfactants this technique may be limited to hydrophilic samples.
Figure A-3. The distance dependence of the $2\omega$ cantilever vibration amplitudes in air at 15 kHz and in water at 4 kHz, respectively. In both cases the applied electrical bias was 4 kHz and 1.0 V$_{\text{rms}}$, and the cantilever was positioned ~ 300 nm above a grounded silicon wafer substrate. Inset: The $2\omega$ cantilever vibration in water over a distance of 100 µm.

The inset of Figure A-3 shows that the cantilever still vibrates in water even up to 100 µm away from the surface, a distance about three orders of magnitude greater than the maximum in air. Ion migration in solution would normally lead to electrical polarization – as often described by DLVO theory[34] – so one might expect the electrostatic force to be fully screened at a distance three times larger than the Debye length (or after $\kappa^{-1} \approx$ 1µm in deionized water). But this theory is only valid for static electrodes; the ions take time to migrate to the electrodes, so there is an instantaneous force upon switching the sign of the applied bias. Typical ion diffusivity is on the order of $D = 10^{-9}$ m$^2$/s, so the characteristic ion polarization frequency is approximately $\kappa^2 \times D = \sim 1000$ Hz. This is similar to the electrical bias switching frequency, so the ion polarization may influence the magnitude of the electrical interaction (especially at higher ion concentration, as shown in Figure A-8), but it will not be fully suppressed. Thus, the electrostatic force could be the dominating driving force for the cantilever vibration in water,
although other electrical phenomena may not be negligible.\[35\] In water, the instantaneous electrostatic force can be very large since the dielectric constant of water (\(\varepsilon_{\text{water}} = 80\)) is much larger than that of air (\(\varepsilon_{\text{air}} = 1\)).\[33\] In a simple control experiment, insulating silicon nitride cantilevers were substituted into the system. These did not vibrate at all when voltage was applied, verifying that the driving force originates directly from the electrical bias, and not a hydrodynamic effect. The amplitude-distance curves in water from Figure A-3 were simulated using various models found in the literature (including electrostatic and electrokinetic processes).\[9, 11, 14, 29, 35-39\] These models produced the \(2\omega\) vibration through the \(V(t)^2\) terms, and they demonstrated that the long-range interaction comes from the flat plate part of the cantilever while the tip/apex only become important very close to the surface,\[9\] though none of them worked satisfactorily over the range studied.

The dependence of vibration amplitude on the tip/sample separation distance shown in Figure A-3 can be used for feedback control and surface imaging. SPFM uses the negative slope region of the F-D curve above the tip snap-in distance, while our technique uses the positive slope region of the F-D curve. In other words, when the force error signal increases, the feedback control is set to retract the cantilever when imaging in air, but to approach the substrate when in water. The SPFM image in air had to be collected at an imaging distance of \(~30\) nm to avoid tip snap-in, while in water the tip was only \(~5\) nm from the surface. The effect of these imaging schemes is illustrated in Figure A-4 using hexagonal pits etched into silicon. The pits have sharp edges with a flat center, as can be seen in the SEM image in Figure A-4a.\[27\] Contact mode AFM (Figure A-4b) gives an accurate topographical reproduction of the surface; a superimposed line profile shows the flat center at a depth of \(~160\) nm. Figure A-4c shows the image of a hexagonal well collected with SPFM in air, while Figure A-4d shows the same pit imaged using the new non-contact imaging technique in water. Comparing Figures A-4c and A-4d demonstrates that imaging with the new technique in water can give a higher resolution image than SPFM. The tip
“feels” a much smaller region of the surface when imaging in water compared to air because of the decreased imaging distance, since the electric field emanating from the sharp tip broadens quickly. Due to this increased resolution, the image collected in water closely resembles that from the contact mode AFM image. The superimposed line profiles over each image also show the higher topographical sensitivity in water than in air. The detected topography may be cross-coupled with the dielectric constant or the local surface potential of the sample,[16] though the etched pits in Figure A-4 avoid this problem since the entire substrate is clean silicon. SPFM and KFM also experience the cross-coupling problem, but can ameliorate it by simultaneously imaging with a tapping mode through the application of an additional, mechanical vibration at higher frequency[28] or by using more complicated feedback schemes.[40]

Figure A-4. Images of a hexagonal etched well on silicon imaged by (a) SEM, (b) contact mode AFM, (c) SPFM in air, (d) electrically driven, non-contact imaging in water. These are not the same etched well in each image, but collected from a single sample containing many wells. The AFM images are all right-to-left scans. The contact mode image was collected with a 6.7 nN normal force. The SPFM image was collected with at a tip-sample separation distance of ~ 30 nm. The image using our technique was collected at ~ 5 nm separation, which corresponded to 50% damping of the $2\omega$ vibration amplitude feedback signal (6 Å, compared to 12 Å at a separation greater than 10 nm). The color scale on the right side corresponds to the feature height in (b), (c) and (d), while the depth scales to the left of each of these images correspond to the line scan depth profile superimposed on each as a red line.
The imaging technique using the electrically-driven cantilever vibration can also distinguish chemical heterogeneity of the surface during topographic imaging by recording the $1\omega$ amplitude and phase simultaneously. This ability was demonstrated with organic SAMs on Au, as shown in Figure A-5. A negatively-charged SAM (Au-SC$_{11}$H$_{22}$COOH; zeta potential = -20 mV; ellipsometry thickness = ~2 nm) and a positively-charged SAM (Au-SC$_{11}$H$_{22}$NH$_2$; zeta potential = +20 mV; ellipsometry thickness = ~2.2 nm) were prepared on polycrystalline gold films deposited on Si wafers. A 1 µm × 1 µm area was contact-scanned at a high load (applied load = ~300 nN; maximum Hertzian contact pressure = ~5.5 GPa) in water to remove or damage the SAM in the contact-scanned region. A 4 µm × 4 µm region centered on the contact area was then scanned with the same tip using our new imaging mode in water; the topography and $1\omega$ amplitude and phase images obtained are shown in Figure A-5 for the negatively charged (a) and positively charged (b) surfaces. The topography shows that both SAMs in the contact scanned regions are damaged and some debris is piled at the edge of the contact-scanned area, though the topography may not be completely accurate due to cross-coupling with the surface potential. The roughness of the SAM-covered surface arises from the sputter-deposited gold film. The $1\omega$ vibration signal image, recorded simultaneously during the topography imaging, shows some contrast between the inside and outside of the contact-scanned region. The amplitude and phase of the $1\omega$ vibration both change detectibly in the contact-scanned region of the negatively-charged SAM, while the same region of the positively-charged SAM exhibited only a change in the amplitude but not the phase of the $1\omega$ vibration.
Figure A-5. Electrically-driven, non-contact images of gold surfaces covered with self-assembled monolayers (SAMs) of Au-SC$_{11}$H$_{22}$COOH, top, and Au-SC$_{11}$H$_{22}$NH$_{2}$, bottom. A 1 µm × 1 µm area of the SAM was damaged by the AFM tip using a high load (~ 300 nN) contact scan. A 4 µm × 4 µm area centered on the damaged region was then imaged using the electrically-actuated vibrations in water, using the 2ω amplitude for feedback control while monitoring the 1ω amplitude and phase.

The 1ω phase changes observed in Figure A-5 are consistent with the correlation observed for the 1ω phase signal and the surface charge, which is shown in Figure A-6. The four surfaces tested have varying isoelectric points, so their surface charges are different when immersed in water. Polyallylamine hydrochloride (PAH) becomes positively charged, while gold, native silicon oxide, and polyacrylic acid (PAA) have increasingly negative charges. The 1ω phase is observed to decrease as the surface charge increases. The data shown in Figure A-5 and A-6 thus demonstrate the sensitivity of the electrically-actuated non-contact imaging technique to local surface charge or potential differences. When the conducting cantilever is grounded and the
alternating electrical voltage is applied to the substrate, the cantilever also vibrates with its phase being shifted by 180° from the case where the voltage is applied to the cantilever.

Figure A-6. The \(1\omega\) phase shift recorded for the vibration of the cantilever vs. the isoelectric point (pI) of the substrate. The surfaces are a bare silicon wafer (with a native SiO\(_2\) layer), or films of PAA, PAH, or gold. The phases were recorded in deionized water, at a tip-sample distance of 300 nm, and with an applied sine wave bias of 1.0 V at 4 kHz.

**A.5.3 Other factors affecting cantilever vibration**

The model presented with eq. (4) used only AC electrostatic interactions between the tip and sample. While this model was useful for explaining some of the essential features of the vibrating cantilever, it fails to provide quantitative predictions. Other forces could add to some of these features; dielectrophoresis, in particular, generates a second-order term that could account for essentially all of the behavior described so far. This section presents additional experimental data to better understand the physics controlling the cantilever vibration. Even if all other possible forces are ignored, the dissolved ions in water cause a finite resistance that complicates the theoretical understanding of the tip-water-sample interactions. Unlike in air, where the system can be described purely as a capacitor, the presence of water causes leaky behaviors of the capacitor. The analysis becomes much more complicated when some voltage is allowed to pass through the
medium to the other electrode – the system behaves as if it were a capacitor and resistor in parallel between the two electrodes, rather than a pure capacitor. The $\frac{aC}{\dot{z}}$ term in equations 2 and 4 cannot account for this change. According to classical electrostatics, the capacitance in air is a function of the system geometry, tip-sample separation, and permittivity of the medium. In water, the dielectric constant is frequency dependent, and the conductivity depends on the ion concentration.[43]

The model of eq. (4) must be extended from simple electrostatic interactions to account for any resistive behavior in the medium. The data shown so far (Figures A-1b and A-2) provide some clues for the other forces that could be acting. The detection of the $2\omega$ vibration mode necessitates the existence of a second-order response; at least one force (perhaps just electrostatics) must have a dependence on the square of the applied voltage to generate the $2\omega$ term. Other second-order effects exist, such as dielectrophoresis. Furthermore, many first-order effects, such as electrophoresis, electroosmosis, etc., could also be at play. The experiments presented in the following paragraphs reveal the complex nature of the cantilever vibration originating from the application of an electrical bias.

The effect of the dielectric properties of the medium between the cantilever and the substrate was investigated using a square wave response in Figure A-7.[14] Figures A-7a and A-7b show identical experiments except for the frequency of the applied square wave at 5 Hz and 50 Hz. Dielectric media of widely ranging dielectric constants were used: air ($\varepsilon_r = 1$), n-decane ($\varepsilon_r = 2$), and deionized water ($\varepsilon_r = 80$). The cantilever deflection responses in air and n-decane were very fast without any slow decay process; but the amplitude was very small. In contrast, the cantilever in water showed the fast attraction response whenever the electric bias polarity was switched, followed by the polarity-dependent relaxation response with a decay time constant of ~1 ms, and then a much slower decay to zero with a time constant of ~5 ms. In the non-polar
medium with no ions, the cantilever response seems to be governed by simple electrostatic responses. But many different phenomena seem to be at play when the medium is highly polarizable and contains ions.

![Figure A-7](image.png)

Figure A-7. Cantilever deflection (left axis) due to an applied +/- 0.5 V square wave (top line, right axis) for (a) $\omega = 5$ Hz and (b) $\omega = 50$ Hz. Air, decane, and water were used as the medium, with a gold coated silicon wafer substrate. The deflection in water was reduced by a factor of 5 for easier visualization.

The aqueous solution can have both capacitive (highly dielectric) and resistive (highly conductive) properties depending on ion concentration. Figure A-8 shows the effect of ion concentration on the actuation of the cantilever in an aqueous solution. KCl was added to deionized water to make solutions of 0.01, 0.1, 1, and 10 mM strength; these correspond to conductivities of roughly 1.5, 15, 150, and 1400 $\mu$S/cm. The $2\omega$ amplitude decreases continuously as the solution conductivity increases, while the $1\omega$ amplitude first increases slightly then decreases. Above 10 mM KCl, the $1\omega$ and $2\omega$ vibration amplitude becomes too small to be useful for feedback control in imaging. At this high concentration of salt, a significant portion of the applied voltage might be lost by electrical current through the solution, since the electrode attached at the back of the AFM cantilever chip is exposed to the solution. The monotonic decrease of the $2\omega$ amplitude could be explained by the leaky dielectric model: losing voltage to
the conductive solution reduces the amount of electrical energy that can produce cantilever vibration. For the $1\omega$ vibration, however, the lack of a consistent trend may imply that another process is acting as the ion concentration increases (e.g., electrophoresis or electroosmosis). Identical behaviors (and identical responses to square waves) were observed regardless of the ion type (HCl, LiCl, KCl, NaCl, CsCl, KBr, and K$_2$CO$_3$), so the ion mobility (and electrode polarization time) are not an important factor. The different dependences of the $1\omega$ and $2\omega$ vibrations on the ion concentration shows that the extra processes acting on $1\omega$ are not simply the result of electrode polarization due to the ions.

The $1\omega$ and $2\omega$ vibration amplitudes are also sensitive to the surface properties of the substrate such as the effective dielectric constant or conductivity. Figure A-9 shows the $1\omega$ and $2\omega$ vibration amplitudes for silicon wafers with thermal oxide layers ranging in thickness from 2 nm (the native oxide found on all silicon wafers exposed to air) to 350 nm. The $2\omega$ amplitude steadily decreased as the oxide thickness increased, but the $1\omega$ amplitude increased and then leveled off at the oxide thickness larger than $\sim$100 nm. The difference in behavior for the $1\omega$ and
2ω vibrations in Figure A-9 also indicates that the two vibration signals may originate from different mechanisms.

Figure A-9. The 1ω and 2ω vibration amplitudes on silicon surfaces with thermally grown oxides. The applied signal was 1 Vrms at 5.5 kHz, which was the 2ω resonance frequency, though the behavior was consistent at other applied frequencies. The tip was positioned 300 nm above the surfaces.

The transient response of the cantilever deflection upon sudden change in the polarity of the electrical bias voltage could provide additional information needed to understand the origin of the electro-active force. Figure A-10 shows the cantilever bending as a function of time in response to the application of a square wave bias of 500 Hz at 1.0 Vpk-pk to the cantilever in deionized water with substrates of silicon (2 nm native oxide layer), 50 nm and 100 nm thermally grown oxides on silicon, and a silica glass slide. For the native oxide layer, the cantilever was attracted every time the voltage was switched in both negative-to-positive and positive-to-negative directions. This behavior implies that there is an attractive force whenever the electrical bias voltage changes. The relaxation rate of the bent cantilever at the constant voltage bias (flat region of the square pulse) depends on the polarity of the applied voltage. The cantilever appears to recover from the downward bending quicker at the negative bias voltage. The Si wafers with 50 and 110 nm oxides exhibit attractive forces when the cantilever is switched to the positive
voltage bias and repulsive forces when the negative voltage is applied to the cantilever. These forces decay at the same rate while the applied voltage is kept constant for 1 ms. The response above the glass slide (essentially an infinitely thick insulator), however, has no apparent peak or relaxation: it looks like simple electrostatic attraction and repulsion to a negatively charged surface (silicon develops a negative charge in solution due to dissociation of surface hydroxyl groups). Because of this different behavior over the insulating (glass) substrate, our technique is limited to conducting or highly dielectric substrates.

Figure A-10. Cantilever deflection (left axis) due to an applied square wave voltage ($\omega = 500$ Hz, right axis) for a silicon tip in deionized water 300 nm above various substrates: silicon with a native oxide layer (blue line), 50 nm (red line) and 110 nm (purple line) thermally grown oxides on silicon, and a glass slide (green line).

There are many features that could not be explained with simple models such as eq (4): (i) the tip/sample distance dependence, (ii) the increase of the vibration amplitude as $\omega$ decreases, (iii) the difference in the $1\omega$ and $2\omega$ amplitude dependence on the oxide layer thickness of the substrate or the salt concentration of the solution, and (iv) the dependence of the $1\omega$ phase on the surface charge. The presence of water leads to these complications when applying the capacitor model. Mechanical complications also abound since the capacitor vibrates while experiencing
these forces. Some further studies are required to understand the underlying physics that controls these features.

A.6 Conclusions

Applying an AC voltage to an AFM cantilever in water causes it to vibrate at the frequency of the applied voltage ($1\omega$) and twice this frequency ($2\omega$). Multiple types of actuation mechanisms seem to be involved, though their determination and quantification is very difficult given the complex nature of the vibrating electrode in water. The $2\omega$ vibration amplitude could be used for feedback control and imaging of apparent topography, while monitoring the $1\omega$ simultaneously gave information on local surface properties in water. The practical effectiveness of this non-contact imaging technique was demonstrated. Imaging of model samples showed that the technique can discern apparent topographical features, as well as qualitative changes in the chemical nature of the surface, and the resolution is higher than in air (SPFM) due to a short tip-sample imaging distance. With some further development, this new technique for electrically-driven, non-contact imaging in water may be a useful tool for the characterization of myriad soft samples with charged domains, such as charged polymers or cells in biologically relevant conditions. The use of other liquid media, such as oils or alcohols, is another possibility that could further expand the applicability of this technique.

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A.7 References


43. Morgan, H. and N.G. Green, Ac Electrokinetics: Colloids and Nanoparticles 2003: Research Studies Press LTD.
Appendix B

Effects of vapor environment and counter-surface chemistry on tribochemical wear of silicon wafers

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B.1 Abstract

The effects of counter-surface chemistry and adsorption of water and alcohol from the environment on the tribological responses of silicon surfaces were investigated using atomic force microscopy (AFM). When scratching with a SiO$_2$ tip at contact pressures below the hardness of the materials, changing the environment yielded drastically different wear behaviors. In humid air, the adsorbed water molecules facilitated wear of the surface and material removal. In N$_2$ environment, there was subsurface deformation but no wear, so the surface protruded outward in the rubbing region. In the ethanol vapor condition, the adsorbed alcohol molecules acted as a lubricant and prevented any discernible changes to the surface even at contact pressures above 1 GPa. These results extend upon previous studies of vapor-phase alcohol lubrication using even more protective longer-chain alcohols where failure was observed at much lower contact pressures in macro-scale tests, probably due to high-pressure asperity contacts. Thus the chemical environment can govern the response of silicon to mechanical rubbing. Rubbing with a diamond tip, however, yielded protrusions in all three environments, showing that the chemistry of the counter-surface also contributes to the tribological response; in this case, diamond is not tribochemically reactive towards Si surface. The protrusion formed by the diamond tip in ethanol vapor was only ~20% the height of the one in humid air, even though the measured friction coefficients (and so the applied shear forces) were similar. These results clearly show that the surface chemistry at the tribological interface can substantially alter both the wear and subsurface damage processes.
B.2 Introduction

Friction and wear of sliding interfaces are important in all length scales from earthquakes [1] down to nano/microelectromechanical systems (NEMS / MEMS) [2-4]. When the dimensions of tribological interfaces shrink to the nanoscale, the surface forces, such as friction and adhesion, play a much more important role than the bulk forces because of the large surface-to-bulk ratio (a large fraction of atoms are exposed at the surface) [5, 6]. In NEMS/MEMS devices, Si and SiO$_2$ are especially important because they are the main materials used for device fabrication, but the types of movement and device lifetimes are restricted due to nano-tribological problems such as high friction and serious wear [2, 3, 7, 8]. Therefore, it is essential to address how to effectively lubricate silicon at the nanoscale.

Many previous studies about nanowear of silicon have resulted in various proposed mechanisms. Some indicated that the nanowear caused by scratching with a diamond tip was dominated by abrasive wear with plastic deformation [9-11], while others proposed that deformation via amorphous phase transitions and viscous flow played a more important role [12, 13]; which mechanism governs the behavior may depend on the applied load and contact geometry. It has been shown that rubbing can produce protrusions on silicon surfaces instead of removing material, at contact pressures below the hardness of silicon [14]. These protrusions were formed by mechanically disrupting the subsurface lattice structure in the rubbing region, which produced an amorphous region of lower density [15]. Under similar conditions, nanoindentation alone – deformation without shear – led to no discernible change in the surface. Therefore, shear is a critical element for the protrusion formation process, but the precise mechanism by which shear disrupts the lattice structure (and nanoindentation does not) remains unclear.
The tribological response is very well known to depend on materials properties such as elastic modulus, hardness, and structural dislocations [9-15]. For sliding interfaces in a gaseous environment, however, chemical reactions involving molecules impinging onto the sliding solid surfaces from the gas phase can also play a critical role [7, 16-21]. There are many examples in the literature showing the influence of this tribochemistry on the wear of silicon. Tribochemical wear has been studied for Si-MEMS devices [17, 18], and analysis of the wear product in a MEMS tribometer showed amorphous debris particles with high oxygen content [7], indicating tribochemical reactions with ambient oxygen. The importance of the environment was demonstrated at the macroscale for SiO$_2$ vs. Si [16], and at the nanoscale for both SiO$_2$ and diamond vs. silicon. The nanoscale experiments conducted with AFM showed that the wear behavior was dominated by tribochemical reactions: wear was much more severe when water molecules were available from humid air compared to dry or inert environments. Comparing the SiO$_2$ tip to the diamond tip also showed that the counter-surface chemistry is important to the tribochemical wear process: the SiO$_2$ tip was reactive for tribochemical wear, but the diamond tip was not [19-21].

Recent research has begun to show the effects of the environment on tribological responses. Strawhecker et al. [22] found that alcohol vapor could effectively prevent wear damage of silicon substrates and Asay et al. [23, 24] followed by applying this method to lubrication of MEMS devices. Barnette et al. [25] explained the efficacy of alcohol vapor lubrication using density functional theory calculations: the alkoxide termination from alcohol chemisorbed on the SiO$_2$ surface raises the energy barrier for cleaving the Si-O-Si bonds, as compared to the hydroxide termination of the pristine surface, so tribochemical wear is prevented. They also indicated that the alcohol vapor failed to protect the silicon substrate in a ball-on-flat tribotest when the apparent maximum Hertzian contact pressure was larger than ~500 MPa [26-28]. However, the actual contact pressure between the SiO$_2$ ball and Si substrate in the ball-on-
flat test must be far larger than this value due to the existence of nanoasperities at the contact interface. Therefore, it is interesting to verify whether alcohol vapor can still provide protection against tribochemical wear at contact pressures higher than 500 MPa at a single-asperity contact.

Yu et al. showed that the environment also plays an important role in protrusion formation. In dry air, a SiO$_2$ tip caused hillock formation on a Si surface. But as the relative humidity increased above 3%, there was a transition to nanowear [20]. A later study on the structure of the protrusions showed that, in oxygen-containing environments, oxidation of the Si surface lead to a small increase in the protrusion height over the amorphous expansion alone [15]. It is currently not known if alcohol vapor can prevent the formation of protrusions similarly to how it prevents nanowear [14, 15].

In this paper, we test the efficacy of using ethanol vapor to protect Si surfaces from damage using a single-asperity AFM tip as a model counter-surface, as well as and the effect of the vapor environment on the formation of protrusions due to subsurface damage. We show this lubrication scheme protects the Si surface from wearing due to rubbing by a SiO$_2$ tip even at single-asperity contact pressures above 1 GPa. The friction force remains constant during the entire process because the alkyl-terminated SiO$_2$ surface is more stable against tribochemical wear [25]. Whereas longer-chain alcohols (e.g. pentanol) were used in the past, this study shows that a much smaller molecule like ethanol is also sufficient to prevent wear even under higher contact pressures. We also compare and contrast the formation of protrusions due to subsurface deformation, which form only in dry N$_2$ environments when using SiO$_2$ tips, but in all environments when using diamond tips. The protrusions formed with the diamond tip were much smaller in ethanol vapor environment than in N$_2$, even though the friction forces were similar. These results show that tribochemistry plays an important role in both the material removal leading to wear, and the subsurface damage leading to surface protrusion.
B.3 Materials and Methods

Nanowear testing and imaging was performed with AFM (SPI3800N, Seiko, Japan) using an environmental chamber. The chamber could be filled with ambient air, dry N\textsubscript{2}, or ethanol vapor. The relative humidity (RH) of ambient (humid) air was measured during tests and is given with the corresponding results in the following section. The ethanol vapor environment was produced by a custom-made flow system, described as follows. A N\textsubscript{2} line passed through a bottle filled with ethanol and glass beads. The increased path-length of a bubble through the beads ensured that the stream was close to equilibrium. The flow rate through the ethanol bottle was matched by a stream of pure N\textsubscript{2}, so that the partial pressure of ethanol in the resulting stream was approximately 50\% of saturation, \(p_{\text{ethanol}}/p_{\text{sat, ethanol}} = 0.5\) [29]. This stream was used to fill the AFM imaging chamber, after it was evacuated by a vacuum pump.

The substrates used were p-doped Si(100) wafers purchased from MEMC Electronic Materials, Inc. The root-mean-square (RMS) roughness of these wafers was measured to be 0.05 nm over a 500 nm \(\times\) 500 nm area. The wafers were ultrasonically cleaned in methanol, ethanol, and deionized water for 10 minutes before testing; the native oxide layer was not removed. Nanowear testing in the AFM chamber was performed using either a SiO\textsubscript{2} microsphere tip or a diamond spherical tip, purchased from Novascan Technologies. The SiO\textsubscript{2} tips consisted of a 1.0 \(\mu\)m SiO\textsubscript{2} microsphere glued to a cantilever; these were calibrated to find the nominal spring constants in the range of 16.8\textendash19.7 N/m. The SiO\textsubscript{2} tips were cleaned after each test by rubbing against a fresh area of Si wafer until the friction force and adhesion force returned to the values obtained before the test. The diamond tip had a radius of 0.3 \(\mu\)m with a cantilever spring constant of \(\sim\)203 N/m. The nanowear tests were performed using a single-line reciprocating contact scan mode of AFM. After nanowear tests, the topography of the wear area was imaged with a silicon
nitride tip (MLCT, Veeco, USA), which had a radius of 20 nm and a nominal spring constant of 0.1 N/m.

### B.4 Results and Discussion

Figure B-1 summarizes the primary findings about the effects of surface chemistry and environment on the tribochemical wear of Si rubbed with SiO$_2$ and diamond tips at applied contact pressures in the range of ~1.0 – 4.7 GPa. For the SiO$_2$ tip, the wear behavior was controlled by the environment. In humid air (Figure B-1a), the tip removed material from the silicon in a wear track, as is intuitive for a frictional rubbing process. In the alcohol vapor environment (Figure B-1b), the lubricating effect of the alcohol molecules adsorbed on the surface prevented wear completely. And in dry nitrogen (Figure B-1c), a small protrusion was formed, as previously described by Yu et al. [14, 15]. Since these tests were done with the same materials under the same mechanical conditions, the differences observed in the three different environments – water vapor, alcohol vapor, and inert gas – indicated that the main wear process must be tribochemical, not purely mechanical. In contrast to the environmental sensitivity with a SiO$_2$ tip, a diamond tip produced a protrusion regardless of the type of environment (Figures B-1d, B-1e, and B-1f); the only noticeable difference is the reduction of the protruded feature in the alcohol vapor environment. The comparison between the scratch effects of the SiO$_2$ and diamond tips clearly revealed that the environment-induced tribochemical wear has a strong dependence on material chemistry of the counter-interface. Each of these behaviors will be examined in detail below.
Figure B-1. AFM images of the wear track after rubbing Si wafer with a SiO\(_2\) tip (a, b, c) or diamond tip (d, e, f) in environments of humid air at 50% RH (a, d), 50% P/P\(_{\text{sat}}\) ethanol vapor in N\(_2\) (b, e), or in pure N\(_2\) (c, f). In each case the surface was rubbed for 200 cycles at an applied load of 3 \(\mu\)N (calculated DMT contact pressures: 1.2 GPa for SiO\(_2\) tip and 4.7 GPa for diamond tip) and sliding speed of 800 nm/s. The scale bars are 100 nm, and the full Z scales are 20 nm for (a, b) and 5 nm for (c-f).

Figure B-2 compares the effects of humid air (55% RH) vs. alcohol vapor (50% P/P\(_{\text{sat}}\) ethanol vapor in N\(_2\)) for a SiO\(_2\) tip scratching a Si surface at three different loads. In humid air, a layer of water adsorbs to the surfaces which facilitates Si-Si or Si-O bond breakage, thereby leading to greater tribochemical wear [19, 25]. As the applied load during scratch tests increased in humid air (relative humidity = 55%), more mechanical energy is transferred to the surface causing a correspondingly larger amount of wear.
Figure B-2. AFM images showing the wear tracks after rubbing Si wafer with a SiO$_2$ tip, in humid air at 55% RH (a, b, c) and in 50% P/P$_{sat}$ ethanol vapor in N$_2$ (d, e, f). The applied load was varied from 1 µN (a, d), 3 µN (b, e), and 5 µN (c, f) at sliding speed 800 nm/s for 200 cycles. The calculated DMT contact pressures for these cases were: 1.0 GPa (1µN); 1.2 GPa (3µN); 1.3 GPa (5µN). The scale bars are 100 nm, and the full Z scale for each image is 20 nm.

A few facts can be gleaned from the fact that the adsorbed layer of ethanol protected the Si surface from damage. At least a monolayer of alcohol must have remained on either or both contacting surfaces, so the high contact pressure did not squeeze the molecules out from the contact region. The physisorbed molecules interacting with the substrate surface cannot readily flow in the lateral directions [30], and they would be replaced by equilibrium adsorption from the ambient if they were removed by shear. Furthermore, the ethanol layer must be able to protect the underlying surface even though the surface was elastically deformed by the probe [31].
Figure B-3. The friction force due to rubbing a SiO₂ AFM tip against Si in (a) humid air at 55% RH and (b) 50% P/P_{sat} ethanol vapor in N₂. The sliding speed was 800 nm/s and the applied load was varied at 1 μN (bottom, black line), 3 μN (middle, red line), and 5 μN (top, blue line). The calculated DMT contact pressures for these cases were: 1.0 GPa (1μN); 1.2 GPa (3μN); 1.3 GPa (5μN).

Figure B-3 shows a comparison of the friction force (lateral force on the AFM probe) from each image shown in Figure B-2, throughout the 200 rubbing cycles used to produce the wear tracks. In Figure B-3a the friction forces are compared for wear in humid air at three different loads. In each case, the friction force was very high for the first 5 cycles, decreased steadily until 50 cycles, then leveled off at less than half the original value. This behavior could be associated with the removal of the native oxide layer on the Si wafer during the run-in period [32]. The underlying Si that becomes exposed is hydrophobic and has a lower surface energy than the hydrophilic native oxide layer, so the tip-sample interaction is reduced, as is the friction coefficient. Although one might expect the presence of some dangling bonds at the exposed Si surface, they must be deactivated by reactions with water or oxygen and their reaction products must be less reactive than the wearing SiO₂ surfaces. Otherwise, they could have led to higher friction and faster wear. Indeed, the adhesion force measured between the surface and the SiO₂ probe was found to decrease from 1.6 ± 0.3 μN outside of the wear track to 0.24 ± 0.02 μN inside.
The same experiment conducted in ethanol vapor environment, Figure B-3b, showed that the friction force was essentially constant over all 200 rubbing cycles. Since the adsorbed ethanol layer prevented wear from occurring, there could not be a run-in process like the one observed in humid environment; the surface condition was constant. Furthermore, the lubricating adsorbed layer of ethanol could not be worn away over time, since it was continuously replenished through equilibrium adsorption process in the ethanol vapor environment. This replenishment is one of the key advantages of vapor-phase lubrication compared to one-time coatings like self-assembled monolayers. The adhesion force measurement corroborated the constancy of the surface condition; the adhesion forces outside and inside the rubbing region were within experimental error of each other, at $0.62 \pm 0.01 \, \mu\text{N}$ and $0.65 \pm 0.03 \, \mu\text{N}$, respectively. When the adhesion force was included in the normal load, then the friction coefficient was calculated to be around 0.2. This value is consistent with the previous reports for alcohol adsorption cases measured with AFM with sharp tips, MEMS devices, and macroscopic pin-on-disc tribometers [23-25, 33]. It is also noteworthy that this friction coefficient value is comparable with the values observed for diamond-like carbons in vapor phase lubrication with n-pentanol [34]. The fact that similar friction coefficients are observed for drastically different materials with alcohol vapor lubrication supports the hypothesis that the adsorbed alcohol layer dominates the tribochemical interaction and is not squeezed out from the interface; the adsorbed alcohol molecules remain in the compressed and elastically-deformed contact area and mitigate friction upon sliding. For sliding contact with contact pressures below the hardness of the materials, the environment and interfacial chemistry – not the mechanical properties of the contacting surfaces – dominate the interaction.
Figure B-4. (a) The friction force recorded while rubbing Si wafer with a diamond AFM tip in humid air at 55% RH (Figure B-1d) and in 50% P/P\text{sat} ethanol vapor in N\textsubscript{2} (Figure B-1e), and (b) the average AFM line profiles of the resulting protrusions for humid air and ethanol vapor. The sliding speed was 800 nm/s and the applied load was 3 µN (calculated DMT contact pressure: 4.7 GPa).

In addition to the wear prevention effect demonstrated in Figures B-2 and B-3, the adsorbed layer of ethanol from vapor environment can also inhibit the protrusion formation process. Figure B-4 compares the protrusions formed by rubbing Si wafer with a diamond tip in humid air and in ethanol vapor environments. Even though the mechanical conditions were identical (same tip, sample, applied load, and sliding speed) in both cases, the protrusion formed in humid air was ~3.2 nm tall, while the one formed in ethanol vapor was only ~0.6 nm tall (reduction by ~80%). Interestingly, though the protrusion formed in ethanol was significantly smaller than the one in humid air, the friction force in ethanol during the protrusion formation was only slightly smaller than in humid air. Therefore, the protrusion inhibiting effect cannot be completely attributed to the lubricating effect of the adsorbed ethanol layer; the interplay between chemical and mechanical interactions must be considered.

Yu et al. showed that the protrusion formation in inert environment was primarily the result of disrupting the lattice structure of the Si crystal in the rubbing region [15]. Since
nanindentation alone did not cause protrusions, they hypothesized that the protrusions formed by transferring energy to the surface through shear, but without the chemical interactions that elicit wear. The results shown in Figure B-4 suggest that this hypothesis should be modified, since the shear force (frictional force) alone cannot fully account for the protrusion formation without considering the interfacial chemistry. There are a few possible explanations about how the adsorbed layer of ethanol changes the protrusion formation process. The first possibility would be a chemical effect: as previously discussed, the adsorbed ethanol molecules increase the energy barrier for Si-Si or Si-O bond breakage, so the molecules may also increase the energy barrier for the amorphous phase transition of sub-surface Si that leads to the protrusion formation. Another possibility to explain the results in Figure B-4 is that, since the adsorbed ethanol molecules are not squeezed out of the contact region during rubbing [35], the shear plane between the surfaces is changed. The third-body ethanol molecules fundamentally change the frictional and power dissipation processes [36, 37], so the energy from sliding contact may be dissipated into the adsorbed alcohol molecules instead of the surface. In humid and inert environments the friction force detected by AFM causes the disruption of subsurface bonds and the amorphous phase transition; in ethanol environment, though the AFM detects a similar friction force, that energy may be diverted into the film, preventing the bond disruption. These complications mean that the precise reason why the adsorbed layer of ethanol inhibits the protrusion formation remains unclear.

The importance of the environment and surface chemistry for protrusion formation were also clearly demonstrated in Figure B-1. The protrusions occurred during rubbing with the diamond tip in all three environments (humid air, ethanol vapor, dry nitrogen), but with a SiO₂ tip they formed only in dry nitrogen environment. These results show that the counter-surface chemistry (SiO₂ is more chemically reactive for nanowear of Si than diamond) plays a role in the protrusion formation process, in addition to the environmental chemistry as previously
discovered. From these results, it becomes clear that mechanical properties alone are not sufficient to predict tribological responses; the presence of interfacial molecules (like ethanol or water), and the chemistry of the counter-surface that is interacting with those molecules, must be considered.

### B.5 Conclusions

We investigated the wear behavior of Si surfaces by single-asperity scratching with SiO$_2$ and diamond tips, in environments of humid air, dry nitrogen, and ethanol vapor. Both the counter-surface (tip) chemistry and the environment are critical to the tribological behavior of Si. With the SiO$_2$ tip, completely different behavior was observed for each environment. In humid air, the adsorbed water facilitates breakage of the Si-Si (bulk) and Si-O (native oxide layer) bonds at the surface, so scratching led to wear via material removal. In dry N$_2$, there is no chemical wear, but the mechanical energy disrupts the lattice structure below the surface and forms an amorphous region with lower density, which then protrudes from the surface. In ethanol vapor, the adsorbed alcohol layer prevents either type of surface damage. The short alkyl chain from the adsorbed ethanol layer is sufficient to prevent wear even at contact pressures exceeding 1 GPa, compared to previous macro-scale studies which used longer-chain alcohols (e.g., pentanol) that failed at ~700 MPa. For the case of a diamond tip, scratching resulted in surface protrusions in all three environments. But the protrusion formation process was still quantitatively affected by the environment: the protrusion formed in ethanol vapor was about 20% the size of the one formed in humid air, even though the applied (normal) forces were the same and the frictional (shear) forces were very similar. These results show that the environment surrounding surfaces in sliding contact is critically important to their tribological response.
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B.6 References


Appendix C

Atmospheric RF Plasma Deposition of Superhydrophobic Coatings Using Tetramethylsilane Precursor

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C.1 Abstract

Non-fluorine-based organic-inorganic-hybrid coatings exhibiting superhydrophobic properties were prepared using a single-step process of atmospheric rf glow discharge plasma deposition with a tetramethylsilane (TMS) precursor. The plasma was generated with He in air and the TMS precursor concentration was 0.01 – 0.04 volume% of the He carrier gas. The dissociation of TMS in the atmospheric plasma accompanied the formation of particulates through gas-phase condensation reactions, which lead to organic-inorganic-hybrid coatings with a root-mean-squared roughness in the ~ 30 – 80 nm range and a water contact angle of ~150 – 165° on a variety of substrates including flat wafers, papers, and cotton fabric without any sample pre-treatments. Due to the excitation and dissociation of ambient molecules (oxygen, nitrogen, and water) in the atmospheric plasma, the produced coatings contained oxygen and nitrogen, in addition to silicon and hydrocarbon groups. The oxygen species in the film appears to be a part of Si-O-Si networks similar to silicone compounds. The films produced with TMS exhibited an improved environmental durability compared to purely hydrocarbon-based films deposited with the same atmospheric plasma process.
C.2 Introduction

Superhydrophobicity is of great interest for its potential applications in various surface treatments. Superhydrophobic surfaces have a very high water contact angle (typically above 150°) and very low contact angle hysteresis (typically below 10°).[1, 2] On these surfaces, water drops tend to bead up and roll off very easily, and remove dirt and debris along their path.[3] These properties could be useful for a variety of consumer products and industrial uses, such as self-cleaning glass for windows, windshields and solar panels,[4] self-cleaning fabrics, friction reduction in microfluidic devices,[5] etc.

Superhydrophobicity requires a surface that is both hydrophobic and rough at the sub-microscale:[5, 6] this kind of structure naturally occurs in the lotus leaf, so superhydrophobicity is sometimes called the lotus effect.[7] Fabrication of these surfaces can be accomplished using one of three methods: (i) roughening hydrophobic materials, (ii) depositing hydrophobic coatings on roughened surfaces, or (iii) single-step application of a rough and hydrophobic coating.[8] For practical applications, the most desirable of these processes would be the simplest to implement and the most applicable to a wide variety of substrates. Plasma polymerization and deposition processes can be a single-step method that meets these requirements.[9]

A variety of plasma based methods have been developed for creating superhydrophobic coatings. In the past, these methods relied on etching a pre-deposited polymer film, and sometimes required an extra step to deposit a hydrophobic layer.[10-13] Single-step plasma polymerization and deposition processes have become increasingly common and more attractive due to their simplicity.[14, 15] In order to deposit superhydrophobic coatings on flat substrate surfaces, a single-step plasma process must create nanoscale topographic features that are hydrophobic.[8] These features could be obtained by forming solid, hydrophobic particulates that adhere to the surface.[16]
Glow discharge plasma can create solid particulates from a reactive gas via plasma polymerization reactions.[17] The high energy plasma polymerization reactions comprise a suite of atomic reactions, so they are much more complex and much less specific than typical chemical polymerization reactions. In the plasma, many reactive species are generated from the neutral precursor molecules: radicals, ions, excited molecules, photons, and electrons. These species react in many ways, and their products range from low molecular weight species to highly branched and cross-linked polymers.[17] Gas phase condensation reactions can occur when the density of reactive species is high enough, producing solid particles that can then adhere to a substrate.[18-20]

Among various plasma deposition processes, atmospheric plasma is attractive since it could allow for continuous in-line surface processing, without the need for batch process vacuum reactors.[21] Most studies for production of highly hydrophobic surfaces in plasmas have concentrated on fluorinated hydrocarbon precursors, because the fluorinated surfaces have very low surface energy.[12, 22, 23] However, using fluorinated precursors in atmospheric plasma is undesirable since their radicals and ions are highly toxic and corrosive. We previously reported that fluorinated precursors can be avoided by using benzene as the precursor for atmospheric plasma deposition of superhydrophobic coatings. Benzene produced coatings with a contact angle of >160°, while n-hexane, cyclohexane (aliphatic C6) and methane precursors all produced smooth, hydrophobic films with a contact angle of only ~95°.[24] However, the benzene-based coatings had a significant drawback, compared to the fluorine-containing ones, in that they were very powdery and the particle adhesion to the substrate was weak. The fragility of superhydrophobic coatings is an ongoing problem that limits their applicability.[25]

This paper demonstrates the construction of more durable superhydrophobic films using an organic-inorganic hybrid precursor. Tetramethylsilane (TMS) was chosen as the precursor
molecule for atmospheric rf plasma deposition since it is a stable and volatile organosilane compound with good reactivity in plasma,[14, 26, 27] and its relatively low health hazard means that it can be used in air as long as there is proper ventilation. Silane-based plasma polymerization techniques for producing superhydrophobic coatings have been attempted before. However, those processes have often required separate steps for roughening and hydrophobic layer deposition,[10-13] and used more complicated silanes with long chains, fluorinated groups, or disilanes.[28-30] The TMS-based method presented herein seeks to simplify these superhydrophobic coating processes and accomplish single-step deposition on various substrates at atmospheric conditions.

C.3 Experimental

An atmospheric radio-frequency (rf) glow-discharge plasma system was constructed with a custom-made plasma generator head with a 13.56 MHz rf power supply. A schematic of the system is shown in Figure C-1, and details of the system have been described previously.[16, 23] Helium (99.99% purity) was used as a plasma gas at flow rates of 2.5–4 L/min. A separate He gas stream was sent through a bubbler containing liquid TMS (>99.9%, purchased from Sigma-Aldrich) with a flow rate varied for the desired concentration (0.01-0.04 v%) of TMS in the plasma gas. The pure He gas stream (2.5-4 L/min) and the TMS-saturated stream (3-6 mL/min) were mixed prior to entering the plasma head. The plasma was operated in glow-discharge mode using an rf-powered cylindrical electrode and a quartz crystal dielectric barrier, with a moving sample stage as the grounded counter electrode positioned ~3mm below the head. The sample stage was made of aluminum and water-cooled to dissipate excess heat generated by the plasma. The plasma covered an area ~1 cm wide and ~10cm deep (into the plane of Figure C-1), with the stage moving back and forth at ~1cm/s. The substrates used were silicon (100) wafers and glass
slides, cleaned with $\text{O}_2$ atmospheric plasma (using the same system) prior to use, as well as white office paper (Boise® ASPEN® 30), low-lint cleaning wipes (KimTech Science Precision Wipers) and cotton (Texwipe® wiper, twill fabric), which were used as received.

![Figure C-1. A schematic diagram of the dielectric barrier discharge atmospheric plasma system.](image)

The static water contact angles were measured by calculating the slope of the tangent line of a water drop at the liquid-solid-vapor interface. The reported measurements were averages of the contact angle for water droplets with a volume of $\sim 10\ \mu\text{L}$ measured in at least three different spots on each sample. The advancing and receding contact angles were measured with an automated goniometer (First Ten Angstrom, Inc.) that used 20 $\mu\text{L}$ drops, and the contact angle hysteresis was calculated as the difference between these two measurements. Samples giving a static water contact angle higher than 150° and a contact angle hysteresis less than 10° will be called superhydrophobic in this paper.
The surfaces of deposited films were imaged using scanning electron microscopy (SEM; FEG-Nova 600 Nano SEM). Chemical analyses were performed with reflection-absorption infrared spectroscopy (RAIRS; Thermo Nicolet NEXUS 670) and X-ray photoelectron spectroscopy (XPS; VG Scientific/RHK Technology multi-chamber UHV surface science facility). Opacity measurements were achieved using an Ultraviolet-Visible spectrophotometer (UV-Vis; Agilent 8453).

The wicking rate of water into paper was measured by hanging a ~1 x 5 cm piece of paper vertically above a dish of water and submerging the bottom ~1 mm, then measuring the distance of water wicking in a given time. The wicking rate reported is the coefficient (k) relating the penetration distance (L) to the square root of time (t) as in the Lucas-Washburn equation, 

\[ L = k\sqrt{t}. \] [31, 32] The penetration distance was measured at 3, 10 and 30 minutes to ensure consistency in the measurement.

C.4 Results and Discussion

Various process variables were first analyzed to determine the optimum conditions and limitations for our system. Superhydrophobicity was not achieved with fewer than 10 plasma passes (~10 total seconds of exposure time), as shown in Figure C-2a, due to incomplete coverage of the substrate before that point. Above 10 passes the coating characteristics were fairly constant with increasing passes, since the interfacial properties of the coating do not change by increasing the thickness once the surface is fully covered. Changing the rf power affects the energy of the ions, radicals, and electrons in the plasma, which can affect the particle formation and deposition processes. Figure C-2b shows that the contact angle of the coatings increased slightly as the plasma power increased from 100 W to 200 W. However, at 200 W and above there was some
streaming between the two electrodes, so the system was run at 150 W in all following experiments.

The precursor concentration and residence time in the reaction volume can also affect the particulate formation and deposition processes. Figure C-2c shows the combined effects of both the He carrier gas and the concentration of TMS in the gas. The optimum conditions for the highest contact angle were found to be a flow rate of 2.5 L/min of He carrier with 0.03 v% TMS. An increase or decrease of either He flow rate or TMS concentration caused a slight decrease in the contact angle. The lower He flow rate might increase the residence time of the intermediate species in the gas phase, which could lead to some side reactions or agglomeration. At the higher He flow rate of 4.0 L/min the coatings produced were inhomogeneous; there were regions of higher and lower contact angles, leading to a lower measured average value. The inhomogeneity was probably due to instabilities of the plasma discharge at this higher flow rate. Figure C-2d shows a water droplet on a surface using these optimized settings. The static contact angle on this surface is about 158°. Advancing and receding angles were also measured at 162° and 156°, respectively; these values and the hysteresis of 6° conform to the requirements for labeling the surface as superhydrophobic.
Figure C-2. The effect of deposition time, plasma power, and TMS concentration on the contact angle of the deposited coatings for the glow discharge plasma deposition apparatus used in this study. (a) Number of plasma passes (1 pass ~ 1 second deposition time) at 150 W rf power, 2.5 L/min He and 0.02 v% TMS; (b) supplied rf power for 10 passes at 2.5 L/min He and 0.02 v% TMS; (c) TMS feed concentration for various carrier gas He flow for 10 passes at 150 W rf power; (d) a sessile droplet of water used to measure the static contact angle on a superhydrophobic surface created with optimized settings of 150 W, 10 passes, 2.5 L/min He and 0.02 v% TMS; the scale bar is 500 µm.

The dependence of contact angle on TMS concentration can be explained by the surface morphology observed with SEM. Figure C-3 shows the surface morphology of the coating applied at three TMS concentrations with the optimum conditions for the other parameters (10 passes, 150 W, 2.5 L/min He). At the low concentration of 0.01 v%, the particles were mostly small (< 100 nm) with a few larger ones (~ 200 nm) scattered about. The average particle
diameter was ~65 ± 25 nm (within one standard deviation). At the high concentration of 0.04 v% there were more particles of the ~200 nm size, so the size distribution shifted to an average diameter of ~130 ± 45 nm. In the middle concentration of 0.025 v% there is a diverse mix of small particles, large particles, some fusing/agglomeration, and some larger particles with smaller ones attached to them. This mix led to an average size between the two extremes of low and high TMS concentration, but with the widest size distribution of ~105 ± 55 nm. The size distribution as a function of precursor concentration can change depending on the dynamics of the gas phase condensation reactions that drive the particulate formation in the plasma.[18-20] This mix of smaller and larger hydrophobic particles is similar to the naturally occurring system in the lotus leaf, which has nanoscopic wax particles growing on microscopic papillae,[7] and is likely the reason for this concentration exhibiting the highest contact angle.

Figure C-3. SEM images showing morphology of the coatings deposited at TMS concentrations of 0.01 v% (a), (d); 0.025 v% (b), (e); and 0.04 v% (c), (f). Scale bars are 2 µm for (a), (b), and (c), and are 200 nm for (d), (e), and (f). All coatings were deposited at using 10 passes at 150 W and 2.5 L/min He.
While the SEM images are useful for visualizing the surface morphology, they do not allow measurements of the coating’s thickness. For this measurement, the superhydrophobic coatings were characterized using an atomic force microscope (AFM). Samples were prepared using the optimum conditions of 10 passes at 150 W and 2.5 L/min He, but with varied TMS concentrations. Figure C-4 show characteristic line scans from AFM images of these samples. The samples were scratched with a razor blade prior to imaging to locally remove the coating while not damaging the underlying Si wafer;[33] the line scans are centered around $x = 0$ (the vertical dashed line), so the part of the line in negative $x$ values are the Si substrate (with some debris) and the part in positive $x$ values are the undamaged coating. The horizontal dotted lines show the baseline thicknesses of the coatings, which were about 20 nm, 30 nm, and 50 nm for TMS concentrations of 0.01 v%, 0.02 v%, and 0.03 v%, respectively. The root-mean-squared roughness values for these three conditions were about 35 nm, 40 nm, and 80 nm, respectively. Comparing the data in Figures C-3 and C-4 to the contacts angles in Figure C-2 shows how the morphology of the coating affects its hydrophobicity.
Figure C-4. AFM line scans of superhydrophobic coatings that were scratched with a razor blade to form a flat area of Si wafer (negative values on X axis) to compare to the undamaged coating (positive values on X axis). The coatings were formed using 10 passes at 150 W, 2.5 L/min He flow. The TMS concentrations used were 0.01 v%, 0.02 v%, and 0.03 v%. The horizontal dotted lines show the baseline coating thicknesses of about 20 nm, 30 nm, and 50 nm, respectively. The root-mean-squared roughness values obtained from these scans were about 35, 40, and 80 nm, respectively.

XPS spectra were collected in order to discern the chemical difference between the particles formed at various TMS concentrations. Figure C-5a shows the XPS survey spectra for coatings formed in TMS concentrations ranging from 0.01 v% to 0.04 v%. The survey spectra showed carbon and silicon, the constituents of TMS, as well as oxygen and nitrogen. The O and N must have originated from the air enveloping the atmospheric plasma. While post-deposition oxidation is a possible source of the detected O,[34] it must not play a dominant role. Otherwise, the oxidized surface would become hydrophilic. Reactions with N\textsubscript{2} in air cannot take place under ambient conditions. The N\textsubscript{2} and O\textsubscript{2} diffused into the plasma gas during the deposition, where they become activated and dissociated, then reacted with the TMS species forming the plasma dust. With increasing TMS concentration, the C1s and Si2p peaks grow while the N1s and O1s peaks
decrease. These trends are summarized in Figure C-5b, where the atomic percentages are plotted as a function of the TMS concentration. As the TMS concentration increases, reactions between radicals generated from TMS dominate over those with the small amounts of O and N diffusing through the He process gas. The lower contact angle at 0.01 v% TMS in 2 L/min He flow rate (the lowest concentration and flow rate tested) might be due to the incorporation of a larger amount of oxygen and nitrogen species in the deposited film, since the diffusion of air into the plasma region can occur more readily at lower flow rates.

Figure C-5. (a) XPS spectra of deposited superhydrophobic coatings for varying TMS flow rates. (b) The atomic percentages of each element vs. TMS concentration in He, calculated from the XPS data in (a). The coating deposition conditions were the same as those used for the sample in Figure C-3.

The high resolution XPS spectra, shown in Figure C-6, were analyzed to find the chemical environment of each species. The roughness of the coatings made the use of an electron flood gun for charge compensation difficult, so the samples were allowed to electrically float and then the obtained spectra were shifted to position the C1s peak at 285.0 eV, shown in Figure C-6a. Within the C1s region, there were no discernible peaks in the 286.5–290 eV region, indicating that the concentration of oxygenated species bonded to carbon is low. As expected from the elemental survey information, the C1s peak intensity increases with increasing TMS
concentration. The N1s peak (Figure C-6b) was the largest for the low TMS concentration coating and it decreased as the TMS concentration increased, as described above. The N1s peak position did not change with the TMS concentration, showing that the type of N-containing species did not change though their concentration did change. The clean silicon wafer also exhibited a small C1s photoelectron peak due to contamination from organic compounds in the ambient, and a small N1s peak due to activation of N₂ during the O₂ atmospheric plasma treatment used to clean the wafer.[35]

Figure C-6. High-resolution XPS spectra for deposited superhydrophobic coatings at varying TMS concentrations. (a) Silicon 2p; (b) Nitrogen 1s; (c) Carbon 1s; (d) Oxygen 1s. The coating deposition conditions were the same as those used for the sample in Figure C-3.
The O1s and Si2p peaks showed some peak shifting, indicating a change in the chemical bonding of those species. The O1s peaks, Figure C-6c, behaved similarly to the N1s in that the peak intensity decreased as TMS concentration increased. The peak at 532.3 eV for a bare silicon wafer came from the native oxide always found on silicon surfaces that have been exposed to air. As the TMS precursor concentration increases in the plasma gas, the O1s peak slightly shifted toward a higher binding energy (532.8 eV at 0.04 v% TMS). The Si2p peak in Figure C-6d shows a considerable peak shift over the TMS concentration range. The clean silicon wafer has a peak at 99.3 eV due to the underlying silicon substrate, while the smaller peak at 103.5 eV is due to SiO2 in the native oxide layer. The latter peak shifted from 102.3 eV to 101.4 eV as the TMS precursor concentration increased. This peak position of Si2p is within the typical range for the Si-O-Si species found in siloxane compounds, and the shifting to lower binding energy indicates a lesser degree of oxidation, i.e. less bonding with electronegative O atoms that pull electrons from the Si atoms. This was consistent with the decrease of the O/Si ratio as the TMS concentration increased (Figure C-6b). The decrease of O content and the decrease of bonding between Si and O must be counter-balanced by the increased bonding between Si and C as the TMS concentration increases and the particles become larger.

Reflection absorption infrared spectroscopy (RAIRS) was performed to probe the molecular groups present in the superhydrophobic coatings. Figure C-7 gives the RAIRS spectrum for a sample coating deposited at the optimum conditions outlined by Figure C-1: precursor concentration of 0.03 v%, He flow rate of 2.5 L/min, and rf power of 150 W. The XPS spectra at this condition show a significant amount of oxygen in the coating, though a very low (<5%) elemental concentration of nitrogen; RAIRS was not sensitive enough to pick up any peaks from nitrogen-containing functional groups. It is noteworthy that the broad hydroxyl stretching peak between 3300–3400 cm⁻¹ is absent; there was not a significant concentration of
OH functional groups in the particles, nor was there much water adsorbed to the surface of the particles. The lack of adsorbed water implies that the outer surface of the particles was hydrophobic, so the surfaces must be terminated with hydrocarbons formed from the dissociation of the methyl groups in TMS. The O detected by XPS must then be due to siloxanes below the surface of the particles.

![RAIRS spectrum](image)

**Figure C-7.** RAIRS spectrum for a superhydrophobic coating on silicon wafer. Deposition conditions were 0.03 v% TMS in 2.5 L/min He at 150 W rf power and 10 passes.

Identifying the functional groups present in the coating can help to illuminate the reactions that took place to produce it. Considering each molecule of the TMS precursor contained four methyl groups, the presence of C-H stretching peaks from CH$_3$ at 2950 cm$^{-1}$ (asymmetric) and 2900 cm$^{-1}$ (symmetric) was to be expected.[24] The peak at 1060 cm$^{-1}$ can be attributed to the Si-O-Si stretch:[36] the existence of this bond indicates the excitation and incorporation of O$_2$ from air during the plasma deposition, and is corroborated by the XPS data. The peak at 1260 cm$^{-1}$ comes from the Si-CH$_3$ symmetric deformation.[37] It is unlikely that there was much contribution to the IR spectrum from C-O-C ether groups since XPS did not detect any significant C1s oxidized peak around 286.5 eV. The peak at 2120 cm$^{-1}$ indicates the presence of
the Si-H groups in the sample.[38, 39] The Si-O-Si and Si-H peaks indicate that some of the Si-CH₃ bonds comprising the TMS molecules were dissociated in the plasma, and their fragments reacted with each other and with dissociated oxygen from air to form these new bonds.[27] These reactions are, of course, the basis of plasma polymerization.[14, 26, 27] It is important to note that not all of the species that react in the plasma will be present in the coating; low molecular weight species that are not incorporated into a particle may just dissipate with the outflow of the carrier gas.

The environmental durability of the coatings was tested by exposing them to various liquid solutions. Samples exposed to tap water, light paraffin oil, and soapy water for two days, then rinsed with ethanol and deionized water and dried in air, showed no change in water contact angle, which compares with results from other studies.[40, 41] Samples stored in air for one year also showed no detectable change in contact angle. After exposure to ~4 kW·hr/m² of UV light to simulate degradation due to sunlight (equivalent to about the power of 16 hours of sunlight concentrated in the UV range[42]), the contact angles of the superhydrophobic coatings did not change by more than one standard deviation from the previously measured average.

Glow discharge plasma deposition is not limited to hard and smooth surfaces like the silicon wafers and glass slides used in the experiments outlined above; the particles produced in the plasma can deposit on any nearby surface. The ability to form superhydrophobic coatings on office paper, low-lint paper wipes and cotton fabrics was also tested, and these surfaces did indeed allow for coatings with contact angles around 160°. The deposition of the superhydrophobic coating in the inner surfaces of a woven fabric was confirmed from changes in the water wicking (capillary rise) rate. When a dry fabric is brought into contact with liquid water, it will start absorbing the liquid at a rate which decreases over time. If the TMS plasma-polymerized coating is deposited in the interior of the fabric, then the water contact angle of inner
region of the fiber crossing will be changed and thus the capillary rise rate of water will be reduced.[43] The water wicking rate decreased from ~4 cm/min\(^{1/2}\) for pristine cotton to ~0.3 cm/min\(^{1/2}\) after the TMS plasma treatment. This implied that the TMS plasma deposition on the twill cotton fabric significantly reduced the water wicking channel.

In contrast, the superhydrophobic coating on the office paper substrate did not change the water wicking rate. The wicking rate was ~0.3 cm/min\(^{1/2}\) for both untreated paper and paper treated on both sides with the superhydrophobic coating from TMS. The treated paper still allowed water to enter the interior through the unmodified edges. It seems that the pores in the paper were not big enough to allow the hydrophobic coating to be deposited inside the paper, so the coating affected only the external surface of the paper. Furthermore, the superhydrophobicity of the paper surface was unaffected by capillary filling in the bulk. Figure C-8 shows a piece of untreated paper (left) that has sunk to the bottom of a petri dish filled with water, while the sample coated on both sides with superhydrophobic TMS coatings (right) floats on top of the water. The superhydrophobic paper still demonstrates a high contact angle even though its bulk is completely soaked with water.

Figure C-8. A picture of a petri dish filled with water that contains (left) an untreated piece of office paper that has sunk to the bottom and (right) a piece of paper coated on both sides with a superhydrophobic coating. Deposition conditions were 0.025 v\% TMS in 2.5 L/min He at 150 W rf power and 10 passes.
The coatings produced from the TMS precursor were much better adhered to the substrate than the coatings previously produced with benzene.[24] The benzene-based particles comprising the coating could be damaged or blown off the surface with a jet of air, while the TMS-based coatings were not damaged by jets of air or even water. This increase in durability is likely due to the mild fusing/agglomeration of particulates seen for the TMS-based coatings (Figure C-2). The benzene-based coatings were comprised of individual, non-fused particles.[24] Judging from the film morphology, it looks like that the particulates produced in the benzene plasma were solid-like while the ones produced in the TMS plasma were gel-like. The particles deposited from the benzene plasma were a rounded shape with very little connections between particles,[24] but the coating deposited with the TMS plasma contains partially fused particulates (Figure C-2). Fusing the particles causes them to behave more like a continuous layer than a powder coating. The coating on the paper sample was also more difficult to destroy than that on the glass slide. Rubbing a coated glass slide with a low-lint wipe led to a contact angle drop from 160° to 90° degrees, which is the contact angle seen on a smooth surface coated with hydrocarbon or oil. The contact angle on paper after rubbing, however, decreased much less only to 120°. This increased rubbing resistance is likely due to the intrinsic roughness of the paper, though the exact mechanism will be examined in future work.
C.5 Conclusion

Superhydrophobic coatings were produced using glow-discharge atmospheric rf plasma polymerization. Tetramethylsilane precursor allowed for a single-step process to produce these coatings on a variety of substrates in ambient conditions (without a vacuum chamber) while avoiding the use of fluorinated compounds. The dust particles produced in the plasma could be coated on many different surfaces, including glass, plastic, metal, paper, and fabric, all without requiring any pre- or post-treatment. Contact angles greater than 150° could be produced on all of these surfaces, allowing for a wide range of practical uses. Characterization of the films showed that the plasma dust contained chemical groups not present in the tetramethylsilane molecule (e.g., Si-H or Si-O), indicating that the molecule was split in the plasma and the components recombined to form complex polymer particles. The inorganic-organic hybrid network created in the plasma resulted in a greater level of particle fusing than was previously seen with a pure hydrocarbon (benzene) precursor. The fused particles from TMS were more mechanically stable than the non-fused particles from benzene, and could resist various environmental factors as well.

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C.6 References

37. Baraton, M.I., W. Chang, and B.H. Kear, *Surface Chemical Species Investigation by Ft-Ir Spectrometry and Surface Modification of a Nanosized Sicn Powder Synthesized Via


VITA

David Joseph Marchand was born on June 5, 1987 to his parents Carol and Ari and lived with them in Cheltenham, Pennsylvania until his graduation from the Cheltenham High School in 2005. After enrolling at Lehigh University, his research career began in the lab of Professor Anand Jagota, where he studied the alignment of DNA-wrapped carbon nanotubes using Atomic Force Microscopy (AFM). He graduated with a BS in Chemical Engineering and a minor in Materials Science and Engineering in May of 2009. He then began his graduate research at The Pennsylvania State University with Professor Seong Kim. His research on the development of a novel AFM technique led to an MS degree in May of 2011. A grant funded by the National Science Foundation allowed him to travel to China during the summer of 2011 to study nano-scale friction and wear using AFM. After his return, he embarked on a new course of research focused on coal and petroleum coke, which is presented in this dissertation. He graduated with his PhD in Chemical Engineering in May of 2015.